Handbook of Hydroxyacetophenones

Preparation and Physical Properties

Enlarged Second Edition

Volume I

Robert Martin

Springer

Handbook of Hydroxyacetophenones: Preparation and Physical Properties

(Enlarged 2nd edition; 2-volume set)

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Volume 1

by

Robert Martin

formerly of the Institut Curie
Paris, France

Springer

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Volume 2

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DEDICATION

To my dear Angèle, my faithful and devoted wife,
and our two mothers, Alice and Caroline, whom we are missing so much.

Robert MARTIN

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MONOKETONES UNSUBSTITUTED ON THE ACETYL GROUPS

CONTENTS

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MONOKETONES SUBSTITUTED ON THE ACETYL GROUPS

DI- AND POLYKETONES

SHORT BIOGRAPHY

Robert Martin graduated as engineer from CNAM, then as doctor-engineer and doctor es sciences (Ph.D.) from Paris University. He studied with professors Léon Denivelle and Albert Kirrmann.

After having worked in the pharmaceutical industry, Robert Martin completed his career of organic chemist at a Research Laboratory of the French CNRS, located in the Curie Institute in Paris.

He has been studying the Fries reaction since 1956 without interruption. He has prepared a considerable number of aromatic hydroxyketones. A large part of these are included in the reference NMR and IR spectra collection of Sadtler (Philadelphia, USA).

His research on aromatic hydroxyketones gave rise to about forty publications between 1963 and 1992, some of them in collaboration with Mainz University (Germany) and others with Institut Curie (Paris).

In 1992, he published a review on the Fries reaction in *Organic preparations and Procedures International*. This was followed by two books dealing with aromatic hydroxyketones, published by Kluwer in 1997 and 2000.

For his various works concerning aromatic hydroxyketones he received the silver gilt medal from the Société d'Encouragement à l'Industrie Nationale in 1985.

FOREWORD

When Dr Martin asked me to write a preface to his new handbook, I was really enthusiastic. Indeed I met Dr Martin for the first time when joining the Institute Curie at the beginning of the 1990s to direct the team of medicinal chemists. At that time Dr Martin was retired from the Sanofi company but was working at the bench from early in the morning to late in the evening like a young and brillant student. He devoted all his time and energy to make complete the description of what constitutes the subject of his published handbooks. Tireless reader of a huge number of periodicals, he collected, day after day, a large amount of data about the hydroxyacetophenones and the hydroxybenzophenones.

As a continuation of the two handbooks of both classes of compounds already published, Dr Martin now takes care of substituted hydroxyacetophenones. As these new collected compounds have been added to the unsubstituted analogs, one can say that this book constitutes an enlarged second edition of the first hydroxyacetophenone handbook. No less than 3000 molecules and 3500 references can be found in this new volume. The presentation is the same as in the first two volumes with consistent data on the synthetic route or on the natural origine of each compound, its physicochemical and spectroscopic characteristic available in the literature.

I am sure that, even at the internet era, this hanbook will be helpful for the readers concerned with the use of these compounds in all the aspects of chemistry covering pharmaceutical, agrochemical, perfume, plastics and preservatives domains or elaboration of small libraries of organic compounds for biological sceening.

Besides, consulting such a handbook is greatly facilitated by the presence of three comprehensive tables including CAS number, official nomenclature and usual names.

This will be helpful to the reader and I am sure that this book will meet with the success it deserves.

Claude Monneret
Research Director at the CNRS

ACKNOWLEDGEMENTS

I wish to express my heartfelt thanks to Dr. Pierre Demerseman who accepted me in his Laboratory at Institut Curie in 1987, and kindly revised my manuscript. I am also grateful to Dr. J.-P. Buisson, always so amiable and efficient, whose knowledge of word-processing largely contributed to the final page-setting of this work.

My thanks are also directed to Prof. Claude Monneret, formerly Head of the Chemical Department at Institut Curie, who has always been so benevolent to me. The foreword of this Handbook was also written by Prof. Claude Monneret. I most appreciate this mark of kindness.

I acknowledge as well his successor to the management of the laboratory, Dr. Jean-Claude Florent, who maintains the tradition and always welcomes me with much kindness, and all his collaborators for their warm welcome at each of my visits.

I thank my son Serge Martin for friendly advice on the English edition of this book. Moreover, Mr. Serge Martin was a constant aid to me as regards data processing.

Various friends who readily agreed to translate foreign publications are also to be acknowledged here, in particular Dr. Jean Burkhard who has been of invaluable help for translating German papers over the last 30 years. The diverse abbreviations used in ancient reviews – particularly *Chemisches Zentralblatt* – had no secrets for him. Unfortunately, he left us in 2001 at the age of 91.

In this connection, thanks are due to Mrs. Feiga Weisbuch for her precious assistance as regards Rumanian and Russian texts, Mrs. Elisabeth Matarasso-Tchiroukhine as regards German and Russian texts as well as to Miss Marie-Françoise Liachenko and Dr. Daniel Dauzonne. I wish to express my thanks to Mrs. Mireille Guyonneau and Mrs. Françoise Boucheron for their keen contribution to my bibliographic research.

Before closing, I would like to remember my dear departed. My affectionate thoughts are turned towards Prof. Léon Denivelle who transmitted to me his passion for aromatic organic chemistry in 1945, and Prof. Albert Kirrmann who accepted me among his students in 1961 and was always so amiable and well-disposed whenever I went to him. I cannot mention without emotion Prof. Albert Saint-Maixen who largely communicated to me his knowledge of analytical chemistry.

I also have a personal thought towards my friends from the industry who left us too soon. I am particularly thankful to Drs. Henri Barbier, Félix Lepors and Henri Ruelleux (SPCA, Ltd.) who gave me the practical means to carry out my work on aromatic hydroxyketones. In this firm, I started my research on the Fries reaction. I also wish to acknowledge the late Dr. François Krausz who, at that time, made me benefit from his precious advice.

Robert Martin

INTRODUCTION

Acylphenols are used as starting material for an extremely large number of syntheses in organic chemistry, leading to a wide range of applications. For this reason, it seemed interesting to bring up to date the first dictionary, entitled *Handbook of Hydroxyacetophenones,* published in 1997.

All the ketones appearing in this first dictionary will also be included in the enlarged second edition entitled above. Some texts have been revised as the new informations show some interest. On top of this a large number of homologous ketones has been introduced.

However, this new (2004) version is not only an update of the former data, but 11 other ketone families have been added.

The new dictionary covers about 3000 hydroxyacetophenones, methodically classified usually under the official nomenclature of 'Ethanones' according to the International System (IUPAC) and the recommendations given in the Chemical Abstracts 'Collective Index' (CI) since 1972.

About 3500 bibliographic references are compiled in this book. Names of periodicals are abbreviated according to the Chemical Abstracts Service Source Index (CASSI). Whenever hydroxyacetophenones can be obtained from plants, sources and corresponding references are given.

For each compound described, the different protocols of synthesis are presented as well as the main physicochemical characteristics and references of spectroscopic data. Besides, the usual abbreviations are also indicated at the end of this dictionary.

For precise and quick location of an hydroxyacetophenone, you can refer either to the classification by molecular formula (*Molecular Formula Index*) or to the *Chemical Abstracts Registry Numbers* table.

A *Usual Names Index* including the current names of some hydroxyacetophenones and their precursors is also available.

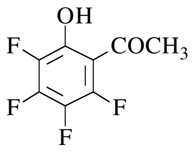
Finally, a glance through any chapter of this Dictionary will inform the reader on the diverse ways of synthesizing hydroxyacetophenones. These methods can also be used to obtain hitherto unknown analogs in the related series.

PART 1 MONOKETONES

Chapter 1. Compounds derived from acetic acid

1-(2,3,4,5-Tetrafluoro-6-hydroxyphenyl)ethanone

[182951-74-2] $C_8H_4F_4O_2$ mol.wt. 208.11



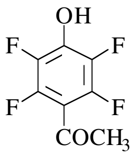
Synthesis

-Obtained by hydrolytic cleavage of 2-amino-3-(2-hydroxy-3,4,5,6-tetrafluorobenzoyl)acrylic acid (**I**) or of 3-(2-hydroxy-3,4,5,6-tetrafluorobenzoylmethylene)-piperazin-2-one (**II**) in boiling aqueous sodium hydroxide for 20 min (53% and 44% yields, respectively) [179].

m.p. 36° [179]; ^{1}H NMR [179], ^{19}F NMR [179], IR [179].

1-(2,3,5,6-Tetrafluoro-4-hydroxyphenyl)ethanone

[145797-51-9] $C_8H_4F_4O_2$ mol.wt. 208.11



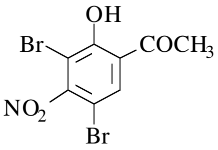
Synthesis

-Preparation by reaction of acetyl chloride on 2,3,5,6-tetrafluorophenol with aluminium chloride in carbon disulfide at 5° (10%) [720].

m.p. 109-111° [720].

1-(3,5-Dibromo-2-hydroxy-4-nitrophenyl)ethanone

$C_8H_5Br_2NO_4$ mol.wt. 338.94



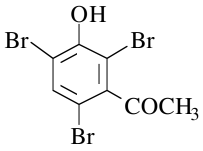
Synthesis

-Preparation by reaction of bromine on 2-hydroxy-4-nitro-acetophenone in refluxing acetic acid-sodium acetate mixture (68%) [1649].

m.p. 157° [1649].

1-(2,4,6-Tribromo-3-hydroxyphenyl)ethanone

[49605-14-3] $C_8H_5Br_3O_2$ mol.wt. 372.84



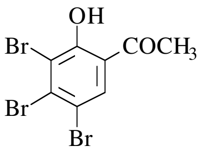
Synthesis

-Preparation by bromination of 3-hydroxyacetophenone in water at 50° (94%) [521] [650].

m.p. 127°5 [521] [650].

1-(3,4,5-Tribromo-2-hydroxyphenyl)ethanone

[145666-19-9] $C_8H_5Br_3O_2$ mol.wt. 372.84

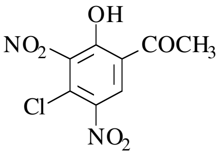


Synthesis not yet described.

-Refer to: [1205] (compound 1h).

1-(4-Chloro-2-hydroxy-3,5-dinitrophenyl)ethanone

$C_8H_5ClN_2O_6$ mol.wt. 260.59



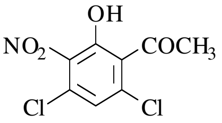
Syntheses

-Preparation by nitration of 4-chloro-2-hydroxyacetophenone (77%) [924].
-Also obtained (by-product) by nitration of 2-acetyl-5-chlorophenyl acetate in sulfuric acid solution at -10° (24%) [924].

m.p. 149-150° [924].

1-(4,6-Dichloro-2-hydroxy-3-nitrophenyl)ethanone

[81515-01-7] $C_8H_5Cl_2NO_4$ mol.wt. 250.04



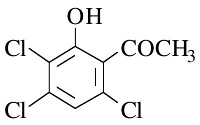
Synthesis

-Preparation by nitration of 2,4-dichloro-6-hydroxyacetophenone with potassium nitrate in concentrated sulfuric acid, first between -10° and 0°, then at r.t. [1483].

m.p. 62-64° [1483].

1-(3,4,6-Trichloro-2-hydroxyphenyl)ethanone

[126712-08-1] $C_8H_5Cl_3O_2$ mol.wt. 239.48



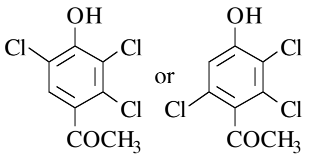
Synthesis

-Preparation by Fries rearrangement of 2,3,5-trichlorophenyl acetate with aluminium chloride without solvent at 130-140° (49%) [1778].

m.p. 103-104° [1778]; ^{1}H NMR [1778], MS [1778].

1-(Trichloro-4-hydroxyphenyl)ethanone

[94650-96-1] $C_8H_5Cl_3O_2$ mol.wt. 239.48

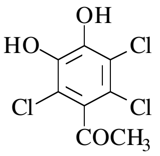


Synthesis not yet described.

- Identified in wheat and rye straw pulp bleaching and combined mill effluents [617].
- Identified during control of effluent from the manufacturing of bleached pulp and paper from sugarcane bagasse [616].

1-(2,3,6-Trichloro-4,5-dihydroxyphenyl)ethanone

[154638-87-6] $C_8H_5Cl_3O_3$ mol.wt. 255.48



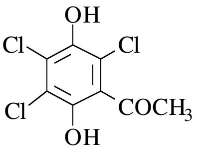
Synthesis

- Obtained (by-product) by chlorination of 4-hydroxy-3-methoxyacetophenone in dioxane-water mixture at 40° (4%) [1456].

MS [1456].

1-(2,4,5-Trichloro-3,6-dihydroxyphenyl)ethanone

[7714-14-9] $C_8H_5Cl_3O_3$ mol.wt. 255.48



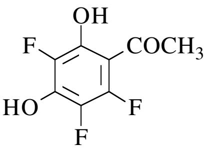
Syntheses

- Preparation by reaction of chlorine on 2,5-dihydroxyacetophenone in chloroform solution containing a drop of triethylamine, under UV light, at 0° (50%) [944].
- Preparation by reaction of excess of chlorine on acetyl-1,4-benzoquinone in chloroform, followed by treatment of the adduct obtained with hydrochloric acid in ethyl ether (60%) [180].

m.p. 127°5-129° [180], 79-81° [944]. One of the reported melting points is obviously wrong. ^{1}H NMR [180], IR [180], MS [180].

1-(2,3,5-Trifluoro-4,6-dihydroxyphenyl)ethanone

[182951-75-3] $C_8H_5F_3O_3$ mol.wt. 206.12



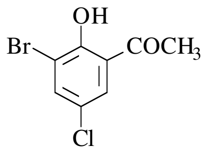
Syntheses

- Obtained by treatment of 2-amino-3-(2-hydroxy-3,4,5,6-tetrafluorobenzoyl)acrylic acid with boiling aqueous sodium hydroxide for 2 h (40%) [179].
- Also obtained by treatment of 3-(2-hydroxy-3,4,5,6-tetrafluorobenzoylmethylene)piperazin-2-one with boiling aqueous sodium hydroxide for 2 h (30%) [179].

m.p. 146-147° [179]; ^{1}H NMR [179], ^{19}F NMR [179], IR [179].

1-(3-Bromo-5-chloro-2-hydroxyphenyl)ethanone

[59443-15-1] $C_8H_6BrClO_2$ mol.wt. 249.49



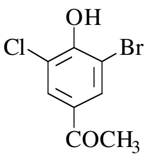
Syntheses

-Preparation by bromination of 5-chloro-2-hydroxyacetophenone in acetic acid (65%) [152].
-Preparation by Fries rearrangement of 2-bromo-4-chlorophenyl acetate with aluminium chloride without solvent at 140° [1647].
-Also refer to: [153] [1204] (compound 1b), [1205] (compound 1e) and [1547] (compound 1c).

m.p. 104-105° [152].

1-(3-Bromo-5-chloro-4-hydroxyphenyl)ethanone

$C_8H_6BrClO_2$ mol.wt. 249.49



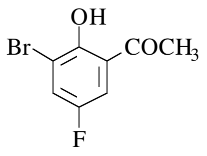
Synthesis

-Preparation by bromination of 3-chloro-4-hydroxyacetophenone [1024] [1167].

m.p. 170° [1024] [1167].

1-(3-Bromo-5-fluoro-2-hydroxyphenyl)ethanone

[393-62-4] $C_8H_6BrFO_2$ mol.wt. 233.04



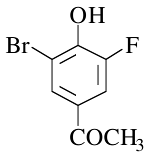
Syntheses

-Preparation by bromination of 5-fluoro-2-hydroxyacetophenone in acetic acid [334].
-Preparation by Fries rearrangement of 2-bromo-4-fluorophenyl acetate with aluminium chloride without solvent at 130° [919].

m.p. 97° [334] [919].

1-(3-Bromo-5-fluoro-4-hydroxyphenyl)ethanone

[402-84-6] $C_8H_6BrFO_2$ mol.wt. 233.04



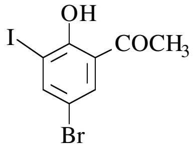
Synthesis

-Preparation by bromination of 3-fluoro-4-hydroxyacetophenone in acetic acid [335].

m.p. 173° [335].

1-(5-Bromo-2-hydroxy-3-iodophenyl)ethanone

[28467-11-0] $C_8H_6BrIO_2$ mol.wt. 340.94



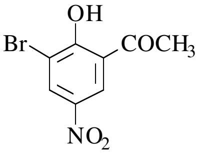
Synthesis

-Preparation by reaction of iodine-iodic acid mixture on 5-bromo-2-hydroxyacetophenone in ethanol (75-85%) [484], (68%) [341].

m.p. 116° [341], 105° [484]; ^{1}H NMR [484], IR [484].

1-(3-Bromo-2-hydroxy-5-nitrophenyl)ethanone

[90004-97-0] $C_8H_6BrNO_4$ mol.wt. 260.04



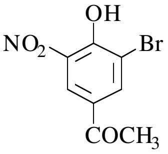
Syntheses

-Preparation by reaction of bromine on 2-hydroxy-5-nitroacetophenone in refluxing acetic acid-sodium acetate mixture (83%) [1649].
-Also obtained by treatment of 2-hydroxy-5-nitroacetophenone with NBS in acetonitrile (56%) (compound 31) [1848].

m.p. 132° [1649]; ^{1}H NMR [1848], MS [1848].

1-(3-Bromo-4-hydroxy-5-nitrophenyl)ethanone

[90004-98-1] $C_8H_6BrNO_4$ mol.wt. 260.04



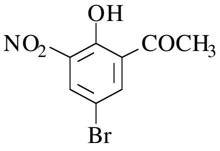
Synthesis

-Preparation by reaction of bromine on 4-hydroxy-3-nitroacetophenone in refluxing acetic acid-sodium acetate mixture (83%) [1649].

m.p. 136° [1649].

1-(5-Bromo-2-hydroxy-3-nitrophenyl)ethanone

[70978-54-0] $C_8H_6BrNO_4$ mol.wt. 260.04



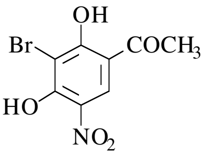
Syntheses

-Preparation by nitration of 5-bromo-2-hydroxyacetophenone in refluxing carbon tetrachloride (88%) [1866].
-Preparation by reaction of nitric acid on 5-bromo-2-hydroxyacetophenone in concentrated sulfuric acid between -2 to 0° (75%) [1646].

m.p. 99°5 [1646]; IR [1023].

1-(3-Bromo-2,4-dihydroxy-5-nitrophenyl)ethanone

[116465-22-6] $C_8H_6BrNO_5$ mol.wt. 276.04



Syntheses

-Preparation by bromination of 5-nitroresacetophenone in acetic acid at 90° [870].

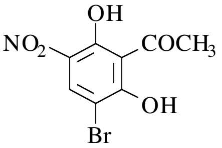
-Obtained by saponification of 8-bromo-7-hydroxy-2-methyl-6-nitrochromone with 10% aqueous sodium hydroxide [1288].

-Also obtained by reaction of nitric acid on 3,3'-diacetyl-5,5'-dibromo-4,4',6,6'-tetrahydroxy-diphenyl thioether in acetic acid at r.t. [868].

m.p. 182-183° [868] [870], 181-182° [1288].

1-(3-Bromo-2,6-dihydroxy-5-nitrophenyl)ethanone

$C_8H_6BrNO_5$ mol.wt. 276.04



Syntheses

-Preparation by bromination of 2,6-dihydroxy-3-nitroacetophenone in acetic acid [1288].

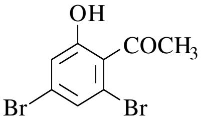
-Preparation by reaction of nitric acid on 3,5-dibromo-2,6-dihydroxyacetophenone in acetic acid at 0° [1288].

-Obtained by saponification of 6-bromo-5-hydroxy-2-methyl-8-nitrochromone or of 8-bromo-5-hydroxy-2-methyl-6-nitrochromone with 10% aqueous sodium hydroxide at reflux [1288].

m.p. 127-128° [1288].

1-(2,4-Dibromo-6-hydroxyphenyl)ethanone

$C_8H_6Br_2O_2$ mol.wt. 293.94



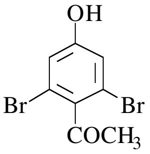
Synthesis

-Preparation by reaction of acetyl chloride on 3,5-dibromo-anisole with aluminium chloride in refluxing carbon disulfide (33%) [114].

m.p. 96-97° [114].

1-(2,6-Dibromo-4-hydroxyphenyl)ethanone

$C_8H_6Br_2O_2$ mol.wt. 293.94



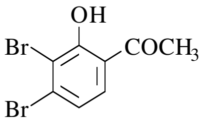
Synthesis

-Obtained by reaction of acetyl chloride on 3,5-dibromo-anisole with aluminium chloride in refluxing carbon disulfide (10%) [114].

m.p. 141-142° [114].

1-(3,4-Dibromo-2-hydroxyphenyl)ethanone

[145666-18-8] $C_8H_6Br_2O_2$ mol.wt. 293.94

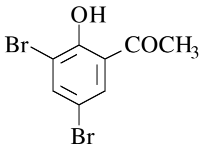


Synthesis

-Refer to: [1205] (compound 1f).

1-(3,5-Dibromo-2-hydroxyphenyl)ethanone

[22362-66-9] $C_8H_6Br_2O_2$ mol.wt. 293.94



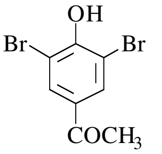
Syntheses

-Preparation by Fries rearrangement of 2,4-dibromophenyl acetate with aluminium chloride without solvent between 150° and 165° [400] [411] [1788], (46%) [411], (51%) [400].
-Preparation by reaction of acetic anhydride on 2,4-dibromophenol with aluminium chloride in nitrobenzene at 120° (41%) [411] [1788].
-Preparation by bromination of 2-hydroxyacetophenone [330] [1511], (61%) [330] or 5-bromo-2-hydroxyacetophenone in acetic acid (78%) [152].
-Preparation by reaction of bromine on 2-hydroxyacetophenone in acetic acid-potassium acetate mixture (55%) [1511].
-Also obtained (by-product) by Fries rearrangement of 2-bromophenyl acetate with aluminium chloride without solvent at 180° (2%) [540].
-Also obtained by reaction of sodium iodide on 3,5-dibromo-2-hydroxy-α,α,α-tribromoacetophenone in acetic acid-dioxane-hydrochloric acid mixture (50%) [7].
-Also obtained by action of hydriodic acid with 3,5-dibromo-2-hydroxy-α,α,α-tribromoacetophenone [7].

m.p. 111° [330], 110° [411], 109-110° [7] [152] [400], 108-109° [540] [1511], 108° [121]; ^{1}H NMR [540] [1698], ^{13}C NMR [736], UV [1161] [1698], fluorescence spectra [1698].

1-(3,5-Dibromo-4-hydroxyphenyl)ethanone

[2887-72-1] $C_8H_6Br_2O_2$ mol.wt. 293.94



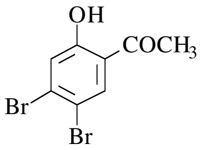
Syntheses

-Preparation by bromination of 4-hydroxyacetophenone in dilute acetic acid [1024] [1167] [1320], (94%) [1446], (80%) [1511], (75%) [89], (62%) [335].
-Preparation by reaction of bromine on 4-hydroxyacetophenone in acetic acid-potassium acetate mixture (91%) [89], (80%) [1511].
-Preparation by bromination of 4-hydroxyacetophenone [917].
-Preparation by Fries rearrangement of 2,6-dibromophenyl acetate with aluminium chloride without solvent at 120° (60%) [917].
-Also refer to: [436] (compound **9**) and [1702].

m.p. 187° [1024] [1167], 184° [917], 181° [335] [1446] [1511], 180-184° [89]; UV [1160].

1-(4,5-Dibromo-2-hydroxyphenyl)ethanone

[30186-15-3] $C_8H_6Br_2O_2$ mol.wt. 293.94



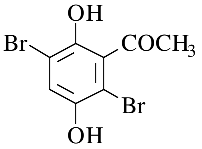
Syntheses

-Obtained (by-product) by Fries rearrangement of 2-bromophenyl acetate with aluminium chloride without solvent at 180° (1%) [540].
-Also obtained (by-product) by Fries rearrangement of 3-bromophenyl acetate with aluminium chloride without solvent at 175-180° [1786].

m.p. 136° [1786], 130-131° [540]; ^{1}H NMR [540] [1786].

1-(2,5-Dibromo-3,6-dihydroxyphenyl)ethanone

$C_8H_6Br_2O_3$ mol.wt. 309.94



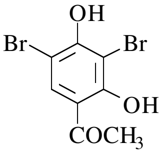
Synthesis not yet described

-Obtained by alkaline hydrolysis of 5,8-dibromo-6-hydroxy-2-methylchromone [516].
-Also obtained by bromination of quinacetophenone [516].
N.B.: The results of reference [516] were erroneous [170].

m.p. 86° [516].

1-(3,5-Dibromo-2,4-dihydroxyphenyl)ethanone

[36772-98-2] $C_8H_6Br_2O_3$ mol.wt. 309.94



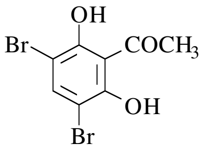
Syntheses

-Preparation by bromination of resacetophenone in acetic acid [475] [508] [686] [947] [1850] [1877].
-Preparation by saponification of 6,8-dibromo-7-hydroxy-2-methylchromone with 5% aqueous sodium hydroxide [506] [1288].
-Obtained by reaction of bromine on 3,3'-diacetyl-4,4',6,6'-tetrahydroxydiphenyl thioether in acetic acid at 50° [868].
-Preparation by saponification of 6,8-dibromo-7-hydroxyflavone with refluxing 10% aqueous sodium hydroxide [1287].
-Preparation by saponification of 3-benzoyl-6,8-dibromo-7-hydroxyflavone with 10% ethanolic potassium hydroxide in a water bath [1287].
-Also obtained (by-product) by reaction of bromine with resacetophenone in ethanol at -78° [637].

m.p. 174° [506], 173-174° [475] [508] [868] [1877], 173° [686], 172-173° [1287] [1288].

1-(3,5-Dibromo-2,6-dihydroxyphenyl)ethanone

[63411-84-7] $C_8H_6Br_2O_3$ mol.wt. 309.94



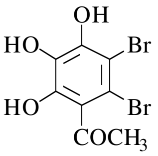
Syntheses

-Preparation by bromination of 2-acetylresorcinol in acetic acid [1288].
-Obtained by saponification of 6,8-dibromo-5-hydroxy-2-methylchromone with 10% aqueous sodium hydroxide at reflux [1288].
-Also refer to: [1287] (compound IVc).

m.p. 173° [1288].

1-(2,3-Dibromo-4,5,6-trihydroxyphenyl)ethanone

[65883-24-1] $C_8H_6Br_2O_4$ mol.wt. 325.94



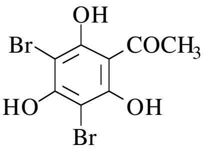
Synthesis

-Preparation by reaction of bromine on gallacetophenone in chloroform at 10° [1542] [1543].

Pale yellow crystals [1542] [1543].

1-(3,5-Dibromo-2,4,6-trihydroxyphenyl)ethanone

[63990-67-0] $C_8H_6Br_2O_4$ mol.wt. 325.94



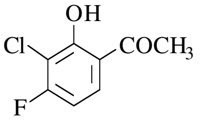
Syntheses

-Preparation by reaction of acetyl chloride or acetic anhydride on 2,4-dibromophloroglucinol with boron trifluoride (72-78%) [1915].
-Preparation by bromination of phloroacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture [391].

m.p. 202-204° [1915], 200-202° [391]; ^1H NMR [391], MS [391].

1-(3-Chloro-4-fluoro-2-hydroxyphenyl)ethanone

[703-97-9] $C_8H_6ClFO_2$ mol.wt. 188.59

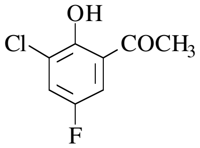


Synthesis not yet described

-There is a single reference, erroneous, concerning the 3-chloro-**5**-fluoro-2-hydroxyacetophenone [919].

1-(3-Chloro-5-fluoro-2-hydroxyphenyl)ethanone

[445-38-5] $C_8H_6ClFO_2$ mol.wt. 188.59



Syntheses

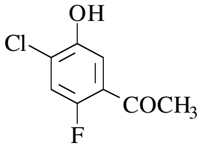
-Preparation by Fries rearrangement of 2-chloro-4-fluorophenyl acetate with aluminium chloride without solvent at 130° [919].

-Preparation by reaction of chlorine on 5-fluoro-2-hydroxyacetophenone in acetic acid solution [334].

m.p. 84° [334] [919].

1-(4-Chloro-2-fluoro-5-hydroxyphenyl)ethanone

[148254-30-2] $C_8H_6ClFO_2$ mol.wt. 188.59

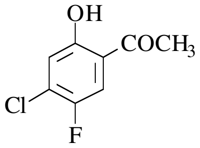


Synthesis

-Refer to: [1748] (Japanese patent).

1-(4-Chloro-5-fluoro-2-hydroxyphenyl)ethanone

[105533-69-5] $C_8H_6ClFO_2$ mol.wt. 188.59



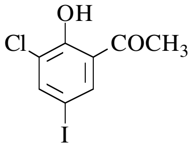
Synthesis

-Preparation by reaction of acetyl chloride on 3-chloro-4-fluorophenol with aluminium chloride at 95-100° (86%) [1191].

m.p. 72° [1191].

1-(3-Chloro-2-hydroxy-5-iodophenyl)ethanone

[292144-84-4] $C_8H_6ClIO_2$ mol.wt. 296.49



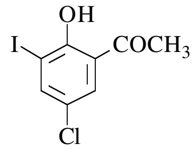
Synthesis

-Preparation by iodination of 3-chloro-2-hydroxyacetophenone with iodine (1 mol) and iodic acid (1 mol) in ethanol at 35-40° for 1.5 h (75-85%) [484].

m.p. 112° [484].

1-(5-Chloro-2-hydroxy-3-iodophenyl)ethanone

[175655-11-5] $C_8H_6ClIO_2$ mol.wt. 296.49



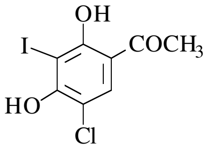
Synthesis

-Preparation by iodination of 5-chloro-2-hydroxyacetophenone with iodine (1 mol) and iodic acid (1 mol) in ethanol at 35-40° for 1.5 h (75-85%) [484].

m.p. 89° [484].

1-(5-Chloro-2,4-dihydroxy-3-iodophenyl)ethanone

[102297-89-2] $C_8H_6ClIO_3$ mol.wt. 312.49



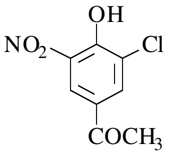
Synthesis

-Preparation by reaction of a iodine-iodic acid mixture on 5-chloro-2,4-dihydroxyacetophenone in water (73%) [569].

m.p. 173-176° [569]; ^{1}H NMR [569].

1-(3-Chloro-4-hydroxy-5-nitrophenyl)ethanone

[52129-62-1] $C_8H_6ClNO_4$ mol.wt. 215.59

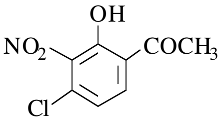


Synthesis

-Preparation by reaction of potassium nitrate on 3-chloro-4-hydroxyacetophenone in concentrated sulfuric acid between 5-10° [315] [1404].

1-(4-Chloro-2-hydroxy-3-nitrophenyl)ethanone

$C_8H_6ClNO_4$ mol.wt. 215.59



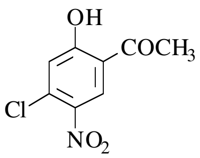
Synthesis

-Obtained (by-product) by nitration of 2-acetyl-5-chlorophenyl acetate in sulfuric acid at -20° [924].

m.p. 105-106° [924]; IR [924].

1-(4-Chloro-2-hydroxy-5-nitrophenyl)ethanone

$C_8H_6ClNO_4$ mol.wt. 215.59



Syntheses

-Obtained by Fries rearrangement of 3-chloro-4-nitrophenyl acetate with aluminium chloride in nitrobenzene at 120° (18%) [924].

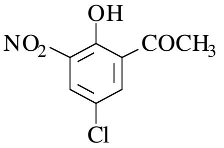
-Preparation by nitration of 2-acetyl-5-chlorophenyl acetate in sulfuric acid solution at -10° (50%) [924].

-Preparation by hydrolysis of 2-acetyl-5-chloro-4-nitrophenyl 4-methyl-3-nitrobenzenesulfonate with 2 N sodium hydroxide (86%) [924].

m.p. 104-105° [924]; IR [924].

1-(5-Chloro-2-hydroxy-3-nitrophenyl)ethanone

[84942-40-5] $C_8H_6ClNO_4$ mol.wt. 215.59



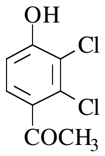
Syntheses

-Preparation by reaction of nitric acid on 5-chloro-2-hydroxyacetophenone in acetic acid at r.t. [125] [318] [774], (98%) [318], (63%) [774].
-Preparation by reaction of nitric acid on 5-chloro-2-hydroxyacetophenone in concentrated sulfuric acid between -2 to 0° (80%) [1646].
-Preparation by reaction of copper nitrate on 5-chloro-2-hydroxyacetophenone in acetic anhydride [125].
-Also refer to: [667].

m.p. 135-136° [318], 132° [1646], 131-132° [774]; IR [774].

1-(2,3-Dichloro-4-hydroxyphenyl)ethanone

[2977-53-9] $C_8H_6Cl_2O_2$ mol.wt. 205.04



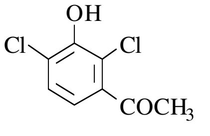
Syntheses

-Preparation by reaction of aluminium chloride on 2,3-dichloro-4-methoxyacetophenone in methylene chloride at 5° [1897].
-Preparation by reaction of aluminium chloride on 2,3-dichloro-4-methoxyacetophenone (or 2,3-dichloro-4-ethoxyacetophenone) in heptane [1221] [1222] [1679].

m.p. 153-155° [1679].

1-(2,4-Dichloro-3-hydroxyphenyl)ethanone

[92119-05-6] $C_8H_6Cl_2O_2$ mol.wt. 205.04



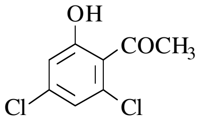
Syntheses

-Preparation from 3-hydroxyacetophenone by chlorination of its ethylene ketal using two equivalents of tert-butyl hypochlorite. Hydrolysis of the obtained dichloroketal with dilute hydrochloric acid in tetrahydrofuran gave essentially 2,4-dichloro-3-hydroxyacetophenone [344].
-Also obtained (by-product) by reaction of tert-butyl hypochlorite on 3-hydroxyacetophenone in chloroform at 15°, in subdued light (9%) [344].

oil [344].

1-(2,4-Dichloro-6-hydroxyphenyl)ethanone

[57051-50-0] $C_8H_6Cl_2O_2$ mol.wt. 205.04



Syntheses

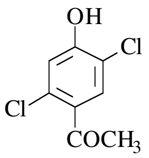
-Preparation by reaction of acetyl chloride on 3,5-dichloroanisole with aluminium chloride in boiling carbon disulfide [114] [1788], (35-40%) [114].

-Preparation by Fries rearrangement of 3,5-dichlorophenyl acetate with aluminium chloride without solvent at 120° [114] [1483].

m.p. 49-50° [114], 48-49° [1483].

1-(2,5-Dichloro-4-hydroxyphenyl)ethanone

[73239-04-0] $C_8H_6Cl_2O_2$ mol.wt. 205.04



Syntheses

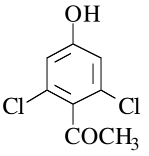
-Preparation by reaction of acetyl chloride on 2,5-dichloroanisole with aluminium chloride at 110° (36%) [1448].

-Preparation by Fries rearrangement of 2,5-dichlorophenyl acetate with aluminium chloride without solvent at 155-165° (36%) [559].

m.p. 151-152° [1448], 148-149° [559]; ^1H NMR [1448], IR [1448], UV [1448].

1-(2,6-Dichloro-4-hydroxyphenyl)ethanone

$C_8H_6Cl_2O_2$ mol.wt. 205.04



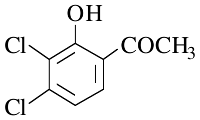
Synthesis

-Obtained by reaction of acetyl chloride on 3,5-dichloroanisole with aluminium chloride in refluxing carbon disulfide (30%) [114].

m.p. 117-119° [114]; b.p.$_{14}$ 197° [114].

1-(3,4-Dichloro-2-hydroxyphenyl)ethanone

[55736-71-5] $C_8H_6Cl_2O_2$ mol.wt. 205.04



Syntheses

-Preparation by Fries rearrangement of 2,3-dichlorophenyl acetate with aluminium chloride without solvent at 130-140° [517] [1257] [1778] [1788], (75%) [1778].

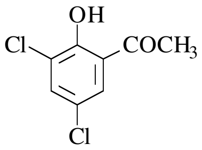
-Also obtained by reaction of 40% peracetic acid on 2-(benzyloxy)-3,4-dichloroacetophenone in acetic acid at 50° (40%) [862].

-Preparation by reaction of aqueous sodium hydroxide solution on 7,8-dichlorochromone-2-carboxylic acid at 95° (38%) [608].

m.p. 113-114° [862], 109-111° [608], 109-110° [1778];
^1H NMR [1778], IR [1778], MS [1778].

1-(3,5-Dichloro-2-hydroxyphenyl)ethanone

[3321-92-4] $C_8H_6Cl_2O_2$ mol.wt. 205.04



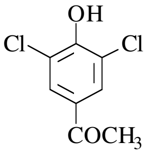
Syntheses

-Preparation by Fries rearrangement of 2,4-dichlorophenyl acetate with aluminium chloride in tetrachloroethane at 150-160° [1833] and without solvent between 115-170° (43-75%) [214] [399] [683] [896] [1581] [1773].
-Preparation by reaction of chlorine on 2-hydroxyacetophenone with ferric chloride in dilute acetic acid [315] [1404].
-Preparation by reaction of hydrated sodium sulfide (containing 7 to 9 mol of water) with 2-piperidino-4-[3,5-dichloro-2-hydroxyphenyl]-1,3-dithiolane perchlorate in ethanol (63%) [357].

m.p. 100-101° [357], 97° [896], 95-96° [315] [399] [683] [1404], 95°5 [1833], 94-96° [1773]; b.p.$_{18}$ 132-134° [214] [1581];
^{1}H NMR [357] [683] [1698], UV [1698], IR [357], MS [683], fluorescence spectra [1698].

1-(3,5-Dichloro-4-hydroxyphenyl)ethanone

[17044-70-1] $C_8H_6Cl_2O_2$ mol.wt. 205.04



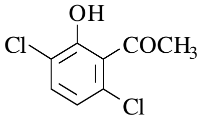
Syntheses

-Preparation by Fries rearrangement of 2,6-dichlorophenyl acetate with aluminium chloride without solvent at 140-150° [829] [1774], (69%) [1774].
-Preparation by chlorination of 4-hydroxyacetophenone in acetic acid [315] [602] [1404].

m.p. 164-165°5 [1774], 164-165° [315], 160-160°5 [602];
pK_a [602].

1-(3,6-Dichloro-2-hydroxyphenyl)ethanone

[55736-72-6] $C_8H_6Cl_2O_2$ mol.wt. 205.04



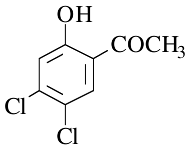
Syntheses

-Preparation by Fries rearrangement of 2,5-dichlorophenyl acetate with aluminium chloride,
*without solvent, at 155-165° (57%) [559];
*in nitrobenzene, at 130° (42%) [1628].
-Preparation by reaction of methyl 3,6-dichloro-2-methoxybenzoate with carbanion reagent (78% yield), followed by ether cleavage (95%) [727].
-Preparation by reaction of aqueous sodium hydroxide solution on 5,8-dichlorochromone-2-carboxylic acid on a steam bath (92%) [608].
-Preparation by hydrolysis of 5,8-dichlorochromone with 10% sodium hydroxide at 100° (80%) [728].
-Also refer to: [608] [1346] [1629], and [921] (compound III); [502] (compound VIIIk); [1347] (compound 11).

m.p. 55-56° [608].

1-(4,5-Dichloro-2-hydroxyphenyl)ethanone

[22526-30-3] $C_8H_6Cl_2O_2$ mol.wt. 205.04



Syntheses

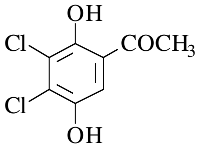
-Preparation by Fries rearrangement of 3,4-dichlorophenyl acetate with aluminium chloride without solvent between 120 to 140° [517] [1108] [1519] [1778] [1788], (72-73%) [1519] [1778], (52%) [1108] or at 200° [445].

-Also obtained by cleavage of 5,6-dichloro-2,3-dimethylbenzofuran with chromium trioxide in acetic acid at 50°, the keto ester formed was saponified with potassium hydroxide (70%) [1519].

m.p. 104-105° [1778], 102° [1519], 99-105° [1108];
b.p.$_{15}$ 151° [1519]; ^{1}H NMR [1778], IR [1778], MS [1778].

1-(3,4-Dichloro-2,5-dihydroxyphenyl)ethanone

[79755-07-8] $C_8H_6Cl_2O_3$ mol.wt. 221.04



Syntheses

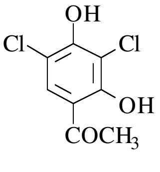
-The preparation from acetylhydroquinone required conversion into its ethylene acetal, oxidation to the quinone with silver oxide, addition of chlorine in acetic acid and enolisation and cleavage of the acetal with, at first hydrogen chloride in ethyl ether, then sulfuric acid in aqueous ethanol (overall yield of 51%) [180].

-Also obtained by Fries rearrangement of 2,3-dichlorohydroquinone diacetate with aluminium chloride without solvent at 165° (poor yield) [180].

m.p. 219-220° [180]; ^{1}H NMR [180], IR [180], MS [180].

1-(3,5-Dichloro-2,4-dihydroxyphenyl)ethanone

$C_8H_6Cl_2O_3$ mol.wt. 221.04



Syntheses

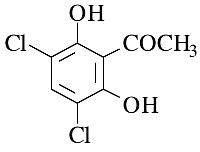
-Preparation by reaction of chlorine on resacetophenone in acetic acid solution [288] [1578].

-Also obtained by reaction of sulfuryl chloride on the 3,3'-diacetyl-4,4',6,6'-tetrahydroxydiphenyl thioether with a crystal of bismuth chloride as a catalyst [868].

m.p. 195-196° [288] [868] [1578].

1-(3,5-Dichloro-2,6-dihydroxyphenyl)ethanone

[87953-95-5] $C_8H_6Cl_2O_3$ mol.wt. 221.04



Syntheses

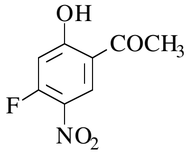
-Preparation by reaction of chlorine on 2,6-dihydroxyacetophenone in ethanol at 0° (84%) [1111].

-Also refer to: [1067] (compound 1d).

m.p. 174°5-175° [1111]; IR [1111].

1-(4-Fluoro-2-hydroxy-5-nitrophenyl)ethanone

[119994-02-4] $C_8H_6FNO_4$ mol.wt. 199.14



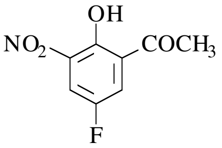
Syntheses

-Preparation by reaction of fuming nitric acid with 4-fluoro-2-hydroxyacetophenone, first between -5° and 0°, then at 0° for 30 min [572].
-Also refer to: [571] [573] [574] (Japanese patents).

m.p. 96° [572].

1-(5-Fluoro-2-hydroxy-3-nitrophenyl)ethanone

[70978-39-1] $C_8H_6FNO_4$ mol.wt. 199.14



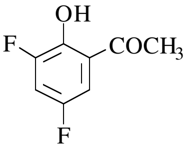
Synthesis

-Preparation by nitration of 5-fluoro-2-hydroxyacetophenone with nitric acid (d = 1.42) in concentrated sulfuric acid between -15 to -5° (46%) [620] [1463].

m.p. 87-90° [1463], 87-89° [620].

1-(3,5-Difluoro-2-hydroxyphenyl)ethanone

[140675-42-9] $C_8H_6F_2O_2$ mol.wt. 172.13



Syntheses

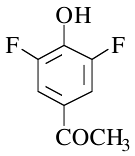
-This compound can be easily obtained by Fries rearrangement of 2,4-difluorophenyl acetate with aluminium chloride without solvent at 150°, and purified by recrystallization from ethanol (80-90%) [1168]; the 2,4-difluorophenyl acetate is prepared by reaction of acetic anhydride on 2,4-difluorophenol [1857] [1905].

-Also refer to: [276].
N.B.: This compound was purchased from Fluorochem Ltd., (Old Glossop, UK) - Catalogue 1993-1994 page 48-reference F-02826 [736].

m.p. 108-110° [736]; ^{13}C NMR [736].

1-(3,5-Difluoro-4-hydroxyphenyl)ethanone

[133186-55-7] $C_8H_6F_2O_2$ mol.wt. 172.13



Syntheses

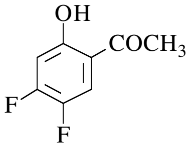
-Preparation by Fries rearrangement of 2,6-difluorophenyl acetate (b.p.$_7$ 62-63°) with aluminium chloride at 140-150° for 5 h under nitrogen atmosphere (56%) [1630].
-Also refer to: [1080].
N.B.: Refer to: [1050] (Japanese patent) and [1904]; there is one erroneous reference. It concerns the 2,6-difluorophenyl

acetate (compound 11) [1904]. This ester, by Fries rearrangement with aluminium chloride, can easily give the aforesaid ketone.

black solid [1630]; ^{1}H NMR [1630], IR [1630].

1-(4,5-Difluoro-2-hydroxyphenyl)ethanone

[199586-38-4] $C_8H_6F_2O_2$ mol.wt. 172.13

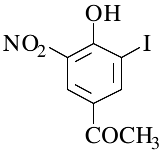


Synthesis

-Refer to: [1063].

1-(4-Hydroxy-3-iodo-5-nitrophenyl)ethanone

[76748-71-5] $C_8H_6INO_4$ mol.wt. 307.04

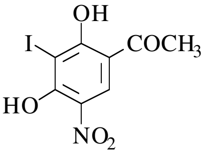


Synthesis

-Refer to: [1717] [1934] (compound NIP).

1-(2,4-Dihydroxy-3-iodo-5-nitrophenyl)ethanone

$C_8H_6INO_5$ mol.wt. 323.04



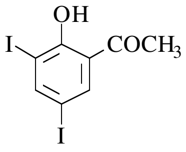
Syntheses

-Preparation by nitration of 2,4-dihydroxy-3-iodo-acetophenone [928].
-Preparation by iodination of 2,4-dihydroxy-5-nitro-acetophenone [928].

m.p. 189° [928].

1-(2-Hydroxy-3,5-diiodophenyl)ethanone

[7191-46-0] $C_8H_6I_2O_2$ mol.wt. 387.94



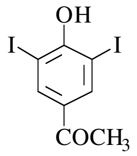
Syntheses

-Preparation by iodination of 2-hydroxyacetophenone,
*with iodine in aqueous sodium carbonate at r.t. [437] [439] [440] [443] [1425], (25%) [443], (42%) [1425];
*with iodine and iodic acid in ethanol at 35-40° for 1.5 h (75-85%) [484] or at 60° [1849] [1850], (75%) [1849].

m.p. 128° [484], 127° [1849], 126° [439], 125°5-126° [440] [443]; UV [443].

1-(4-Hydroxy-3,5-diiodophenyl)ethanone

[7191-55-1] $C_8H_6I_2O_2$ mol.wt. 387.94



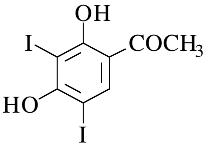
Syntheses

-Preparation by reaction of iodine on 4-hydroxyacetophenone in aqueous sodium carbonate solution at r.t. [438] [440] [441] [442] [1425], (75%) [441] [1425].
-Preparation by iodination of 4-hydroxyacetophenone with iodine-iodic acid mixture in ethanol at 35-40° for 1.5 h (75-85%) [484] or in 50% aqueous ethanol (61-69%) [370] [1849] [1850].
-Preparation by iodination of 4-hydroxyacetophenone by treatment with iodine monochloride (good yield) [535] [1562].
-Also obtained by Fries rearrangement of 2-iodophenyl acetate with aluminium chloride [370].

m.p. 174-175° [441], 172-173° [535] [1562], 171-172° [370], 162° [484], 158° [1849]; UV [441].

1-(2,4-Dihydroxy-3,5-diodophenyl)ethanone

[62069-34-5] $C_8H_6I_2O_3$ mol.wt. 403.94



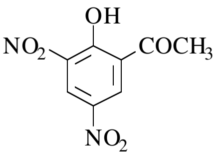
Syntheses

-Preparation by addition of an aqueous iodine and potassium iodide solution on resacetophenone in 30% ammonium hydroxide solution at r.t. (93%) [1558].
-Preparation by addition of an aqueous iodine and iodic acid solution on resacetophenone in ethanol at ambient temperature (86%) [1600] [1850].

m.p. 189-190° [1558], 180° [1600]; ^{1}H NMR [1558].

1-(2-Hydroxy-3,5-dinitrophenyl)ethanone

[69027-37-8] $C_8H_6N_2O_6$ mol.wt. 226.15



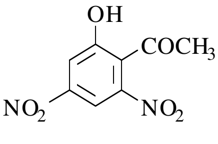
Syntheses

-Preparation by nitration of 2-hydroxyacetophenone,
*in acetic acid (27-36%) [923] [1015];
*without solvent (34%) [253].

m.p. 123°5-124°5 [1015], 123-124° [923]; IR [1125].

1-(2-Hydroxy-4,6-dinitrophenyl)ethanone

[13684-24-7] $C_8H_6N_2O_6$ mol.wt. 226.15



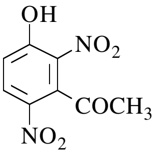
Synthesis not yet described

-Claimed to be prepared by reaction of boiling 50% nitric acid with 2-hydroxyacetophenone (34%) [253].
N.B.: No physical data is indicated in the patent for this compound. According to the rules dealing with aromatic

substitution (Holleman rules) [791] and electronic induction using the Hammett substituent constants [376], the obtained product most likely is the 2-hydroxy-3,5-dinitroacetophenone.

1-(3-Hydroxy-2,6-dinitrophenyl)ethanone

[172669-49-7] $C_8H_6N_2O_6$ mol.wt. 226.15



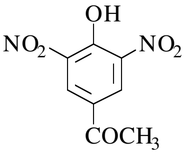
Syntheses

-Obtained by action of concentrated nitric acid (d = 1.42) with 3-hydroxyacetophenone in concentrated sulfuric acid at -20° for 15 min (25%) [455].
-Also refer to: [326].

m.p. 182-183° [455]; ^{1}H NMR [455]; Crystal data [455].

1-(4-Hydroxy-3,5-dinitrophenyl)ethanone

[52129-61-0] $C_8H_6N_2O_6$ mol.wt. 226.15



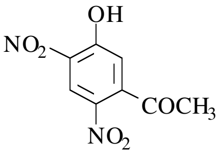
Syntheses

-Preparation by nitration of 4-hydroxyacetophenone with potassium nitrate in concentrated sulfuric acid at 5-10° [315] [1404].
-Preparation by nitration of 4-hydroxy-3-nitroacetophenone with potassium nitrate in sulfuric acid at 5-10° (64-70%) [173] [270].

m.p. 123°2-123°5 [173], 119-121° [315], 119-120°5 [270].

1-(5-Hydroxy-2,4-dinitrophenyl)ethanone

[22633-36-9] $C_8H_6N_2O_6$ mol.wt. 226.15

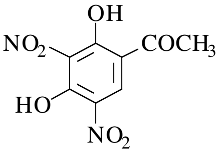


Synthesis not yet described

-There is a single reference, erroneous. It concerns the 2-hydroxy-3,5-dinitroacetophenone or 6'-hydroxy-2',4'-dinitroacetophenone [1125].

1-(2,4-Dihydroxy-3,5-dinitrophenyl)ethanone

[54917-82-7] $C_8H_7N_2O_7$ mol.wt. 242.14



Syntheses

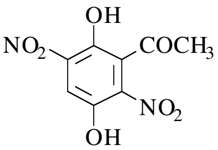
-Preparation by reaction of nitric acid on resacetophenone [7] [1217] or 4-acetoxy-2-hydroxyacetophenone in acetic acid [7].
-Also obtained by reaction of nitric acid on 3-benzoyl-2,4-dihydroxyacetophenone 4-β-glucopyranoside (35-36%) [1480].

-Also obtained by reaction of nitric acid on 3,3'-diacetyl-4,4',6,6'-tetrahydroxydiphenyl thioether in a water bath [868].
-Resacetophenone by treatment with cerium (IV) ammonium nitrate in hot acetic acid yields 2,4-dihydroxy-3,5-dinitroacetophenone (22%) [380].
-Preparation by reaction of an ammonia liquor on 7-hydroxy-4-methyl-3,6,8-trinitrocoumarin in a boiling water bath [1286].
-Also obtained by hydrolysis of 7-hydroxy-2-methyl-6,8-dinitrochromone by heating its solution in sodium hydroxide (4%) on a steam bath [1217].
-Also obtained by reaction of concentrated nitric acid (d = 1.42) or fuming nitric acid on the 7-hydroxy-2-methylchromone in acetic acid, heated on a steam bath [1217].
-Also obtained by hydrolysis of 7-hydroxy-8-nitroflavone by refluxing with 10% sodium hydroxide solution [1217].

m.p. 168-169° [1286], 168° [380], 167° [254] [1217], 166-167° [7] [868], 165-167° [1480].

1-(2,5-Dihydroxy-3,6-dinitrophenyl)ethanone

$C_8H_6N_2O_7$ mol.wt. 242.14



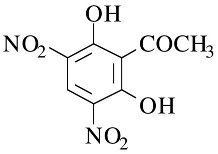
Syntheses

-Obtained by alkaline hydrolysis of 6-hydroxy-2-methyl-5,8-dinitrochromone [516].
-Also obtained by nitration of quinacetophenone [516].
N.B.: The results of reference [516] were erroneous [170].

m.p. 69-70° [516].

1-(2,6-Dihydroxy-3,5-dinitrophenyl)ethanone

$C_8H_6N_2O_7$ mol.wt. 242.14



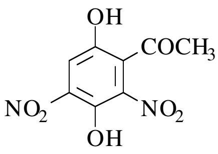
Synthesis

-Preparation by nitration of 2,6-dihydroxyacetophenone (31%) [1291].

m.p. 104° [1291].

1-(3,6-Dihydroxy-2,4-dinitrophenyl)ethanone

$C_8H_6N_2O_7$ mol.wt. 242.14



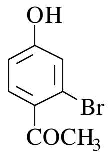
Synthesis

-Preparation by Fries rearrangement of 3,5-dinitro-4-hydroxyphenyl acetate with aluminium chloride in nitrobenzene (61%) [577].

m.p. 133-134° [577].

1-(2-Bromo-4-hydroxyphenyl)ethanone

[61791-99-9] $C_8H_7BrO_2$ mol.wt. 215.05



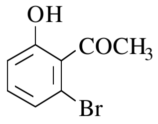
Syntheses

-Obtained (by-product) by Fries rearrangement of 3-bromophenyl acetate with aluminium chloride without solvent at 45° (10%) [385].
-Also refer to: [349] [1416] and [1711] (Japanese patent).

m.p. 85-89° [385].

1-(2-Bromo-6-hydroxyphenyl)ethanone

[55736-69-1] $C_8H_7BrO_2$ mol.wt. 215.05



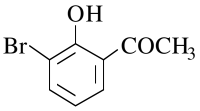
Synthesis

-Preparation by diazotization of 2-amino-6-bromoacetophenone, followed by hydrolysis of the obtained diazonium salt (50%) [608].

m.p. 106-108° [608].

1-(3-Bromo-2-hydroxyphenyl)ethanone

[1836-05-1] $C_8H_7BrO_2$ mol.wt. 215.05



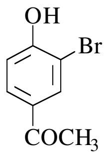
Syntheses

-Preparation by diazotization of 5-amino-3-bromo-2-hydroxyacetophenone, followed by hydrolysis of the obtained diazonium salt (49%) [540].
-Also obtained (by-product) by Fries rearrangement of 2-bromophenyl acetate with aluminium chloride without solvent at 120-140° (11-13%) [477] [479] [540].
-Also obtained by reaction of bromine on 2-hydroxyacetophenone with tert-butylamine in methylene chloride at -70° (12%) [538] or in aqueous acetic acid [736].

m.p. 33° [540], 30°5-32°5 [743] [744]; b.p.$_6$ 140-145° [477];
^{1}H NMR [540], ^{13}C NMR [736], UV [477] [479].

1-(3-Bromo-4-hydroxyphenyl)ethanone

[1836-06-2] $C_8H_7BrO_2$ mol.wt. 215.05



Syntheses

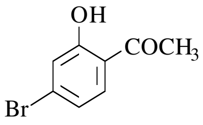
-Preparation by reaction of acetyl chloride on 2-bromophenol with aluminium chloride in refluxing carbon disulfide (86%) [1069].
-Preparation by bromination of 4-hydroxyacetophenone (70%) [1190].
-Preparation by diazotization of 3-amino-4-hydroxyacetophenone and replacement of the diazonium group by bromine (Sandmeyer reaction) (51%) [560].
-Preparation by Fries rearrangement of 2-bromophenyl acetate with aluminium chloride without solvent at 100-120° [386] [477] [479] [540], (68%) [540].

-Also obtained by reaction of ammonium tribromide on 4-hydroxyacetophenone in methylene chloride-methanol mixture [1183].
-Also refer to: [1702].

m.p. 129° [540], 125-128° [1069], 119-121° (anhydrous) [1190], 112° [560], 97-99° (hydrate) [1190], 95° [477], 93-94° [1183], 92-95° [386];
^{1}H NMR [540], UV [477] [479].

1-(4-Bromo-2-hydroxyphenyl)ethanone

[30186-18-6] $C_8H_7BrO_2$ mol.wt. 215.05



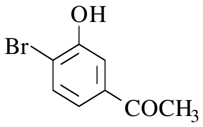
Syntheses

-Preparation by Fries rearrangement of 3-bromophenyl acetate with aluminium chloride [383] [385] [390] [410] [1789],
*without solvent, at 170-180° (85-88%) [383] [385] [390];
*in chlorobenzene, heating in a water bath [1789].
-Also obtained (by-product) by Fries rearrangement of 2-bromophenyl acetate with aluminium chloride without solvent at 180° (6%) [540] (intermolecular bromine migration).
-Also refer to: [225] [819] [1043].

m.p. 43° [1789], 42-43° [383] [385] [390]; ^{1}H NMR [540], IR [1923].

1-(4-Bromo-3-hydroxyphenyl)ethanone

[73898-22-3] $C_8H_7BrO_2$ mol.wt. 215.05



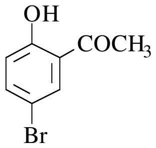
Synthesis

-Preparation by diazotization of 4-amino-3-hydroxyacetophenone and replacement of the diazonium group by bromine (Sandmeyer reaction) (36%) [1069].

m.p. 122-123° [1069].

1-(5-Bromo-2-hydroxyphenyl)ethanone

[1450-75-5] $C_8H_7BrO_2$ mol.wt. 215.05



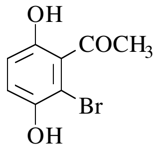
Syntheses

-Preparation by Fries rearrangement of 4-bromophenyl acetate with aluminium chloride without solvent between 110-160° [186] [372] [477] [479] [990] [1334] [1426] [1850] [1866], (84-91%) [186] [477] [1426] [1866].
-Preparation by reaction of acetic acid on 4-bromophenol with boron trifluoride in a sealed tube at 120° (44%) [979].
-Preparation by bromination of 2-hydroxyacetophenone in acetic acid [152] [330] [736] [812], (63%) [330].
-Also obtained by reaction of bromine on 2-hydroxyacetophenone with tert-butylamine in methylene chloride at -70° (17%) [538].
-Also obtained by reaction of sodium ethoxide on 6-bromo-4-phenacylideneflavene in refluxing ethanol [594] [1011].
-Also obtained (by-product) by Fries rearrangement of 2-bromophenyl acetate with aluminium chloride without solvent at 180° (6%) [540].
-Also refer to: [419] [1472].

m.p. 62-63° [477], 62° [330], 61-62° [152] [594] [1011], 59-60° [372] [387], 59° [1334], 57°4-59°2 [812], 57°3 [990], 56° [979], 55-56° [186], 43-44° [1426];
b.p.$_7$ 110-115° [1426], b.p.$_{20}$ 143° [186], b.p.$_{20}$ 145-148° [330];
^{1}H NMR [540] [914], ^{13}C NMR [736] [914], IR [186] [1923], UV [186] [477] [479] ; pK$_a$ [1697].

1-(2-Bromo-3,6-dihydroxyphenyl)ethanone

[30095-76-2] $C_8H_7BrO_3$ mol.wt. 231.05



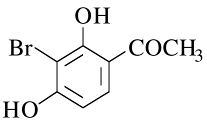
Synthesis

-Obtained from 5-bromo-6-hydroxy-2-methylchromone by alkaline degradation with 10% aqueous sodium hydroxide solution at reflux (22%) [170].

m.p. 143-144° [170];
^{1}H NMR [170], IR [170], UV [170].

1-(3-Bromo-2,4-dihydroxyphenyl)ethanone

[60990-39-8] $C_8H_7BrO_3$ mol.wt. 231.05



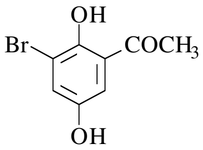
Syntheses

-Obtained by reaction of cupric bromide on resacetophenone in refluxing chloroform-ethyl acetate mixture (6%) [1137].
-Also obtained by reaction of acetic acid on 2-bromoresorcinol with zinc chloride (Nencki reaction) (26%) [1287].
-Also obtained by saponification of 8-bromo-7-hydroxyflavone with 10% aqueous sodium hydroxide on a steam bath (14%) [1287].
-Preparation by bromination of resacetophenone in acetic acid with bromine in the presence of quinoline sulfate while cooling (90%) [1515] according to the method [1509] or in ethanol at -78° (43%) [637].

m.p. 139° [1515], 134-135° [1137], 133° [1287], 118-121° [637];
^{1}H NMR [637] [1137], IR [637], MS [637].

1-(3-Bromo-2,5-dihydroxyphenyl)ethanone

[33857-20-4] $C_8H_7BrO_3$ mol.wt. 231.05



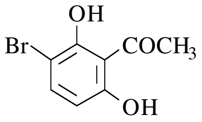
Syntheses

-Preparation from 3-bromo-2-hydroxyacetophenone by persulfate oxidation (Elbs reaction) [743].
-Also obtained by hydrolysis of 8-bromo-6-hydroxy-2-methylchromone with a 10% aqueous solution of sodium hydroxide, heated on a sand bath [516].
-Also obtained by reaction of bromine on quinacetophenone in acetic acid at r.t. [516].
-Also refer to: [667] [668].
N.B.: All the results of reference [516] were erroneous [170].

m.p. 142-144° [743], 132° [516].

1-(3-Bromo-2,6-dihydroxyphenyl)ethanone

[82320-47-6] $C_8H_7BrO_3$ mol.wt. 231.05



Syntheses

-Obtained by saponification of 8-acetyl-6-bromo-7-hydroxy-4-methylcoumarin with 10% aqueous sodium hydroxide solution at reflux (64%) [1593] [1594].

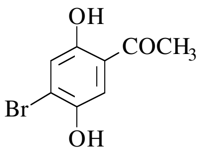
-Also obtained by decarboxylation of 3-acetyl-5-bromo-2,4-dihydroxybenzoic acid with dilute acetic acid containing few drops of concentrated hydrochloric acid, at reflux (40%) [1593] [1594].

-Preparation by reaction of 2-carboxyethyltriphenylphosphonium perbromide on 2,6-dihydroxyacetophenone in tetrahydrofuran at r.t. [1077].

m.p. 143° [1593] [1594], 140-142° [1077]; ^{1}H NMR [1077].

1-(4-Bromo-2,5-dihydroxyphenyl)ethanone

[52376-19-9] $C_8H_7BrO_3$ mol.wt. 231.05



Syntheses

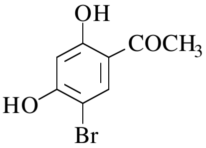
-Preparation by reaction of boron tribromide on 4-bromo-2,5-dimethoxyacetophenone in methylene chloride at -70° (90%) [176].

-Preparation by Fries rearrangement of 2-bromohydroquinone diacetate with aluminium chloride without solvent between 160 and 180° (66%) [680], (25%) [1604].

m.p. 152° [176], 148-149° [680], 132° [1604].

1-(5-Bromo-2,4-dihydroxyphenyl)ethanone

[60965-25-5] $C_8H_7BrO_3$ mol.wt. 231.05



Syntheses

-Preparation by reaction of acetic acid on 4-bromoresorcinol with zinc chloride (Nencki reaction) [366] [1578].

-Preparation by bromination of resacetophenone in acetic acid at r.t. [508].

-Preparation by bromination of resacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture (26%) [1137].

-Preparation by saponification of 4-acetoxy-5-bromo-2-hydroxyacetophenone with sodium hydroxide in dilute methanol at r.t. (76-83%) [947] [1571].

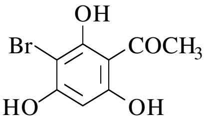
-Also obtained by saponification of 3-benzoyl-6-bromo-7-hydroxyflavone with 10% ethanolic potassium hydroxide in a water bath [1287].

-Preparation by Fries rearrangement of 4-bromoresorcinol diacetate with aluminium chloride in boiling nitrobenzene [947].

m.p. 171° [947], 170-171° [1137], 167° [366] [508] [1287], 165-170° [1571];
^{1}H NMR [1137] [1571].

1-(3-Bromo-2,4,6-trihydroxyphenyl)ethanone

[155818-27-2] $C_8H_7BrO_4$ mol.wt. 247.05



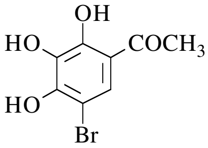
Synthesis

-Preparation by reaction of cupric bromide on phloroacetophenone in refluxing chloroform-ethyl acetate mixture [391].

^{1}H NMR [391].

1-(5-Bromo-2,3,4-trihydroxyphenyl)ethanone

$C_8H_7BrO_4$ mol.wt. 247.05



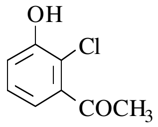
Syntheses

-Preparation by bromination of gallacetophenone in acetic acid with bromine in the presence of quinoline sulfate while cooling [337], (95%) [1515] according to the method [1509].
-Also obtained by reaction of acetyl chloride with 4-bromopyrogallol [337].

m.p. 186° [1515], 183° [337].

1-(2-Chloro-3-hydroxyphenyl)ethanone

[69240-96-6] $C_8H_7ClO_2$ mol.wt. 170.60



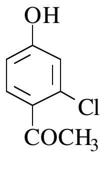
Syntheses

-Preparation by reaction of tert-butyl hypochlorite on 3-hydroxyacetophenone in chloroform at 15°, in subdued light (49%) [344].
-Also refer to: [1009] (compound XVIIa) and to [1933].

m.p. 61-63° [344]; ^{1}H NMR [344], IR [344].

1-(2-Chloro-4-hydroxyphenyl)ethanone

[68301-59-7] $C_8H_7ClO_2$ mol.wt. 170.60



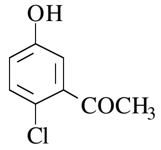
Syntheses

-Obtained (by-product) by Fries rearrangement of 3-chlorophenyl acetate with aluminium chloride [146] [410] [1603].
-Preparation by reaction of acetyl chloride on 3-chlorophenol with aluminium chloride (Friedel-Crafts reaction) [410].
-Also refer to: [1009] (compound XVIIb) and to [1933].

m.p. 110° [1603].

1-(2-Chloro-5-hydroxyphenyl)ethanone

[58020-38-5] $C_8H_7ClO_2$ mol.wt. 170.60

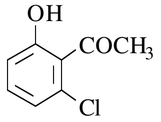


Syntheses

-Obtained by reaction of tert-butyl hypochlorite on 3-hydroxyacetophenone in chloroform at 15°, in subdued light (24%) [344].
-Also refer to: [963] (Japanese patent), [1009] (compound XVIIc) and to [1933].

1-(2-Chloro-6-hydroxyphenyl)ethanone

[55736-04-4] $C_8H_7ClO_2$ mol.wt. 170.60



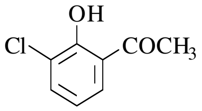
Synthesis

-Preparation by diazotization of 2-amino-6-chloro-acetophenone, followed by hydrolysis of the obtained diazonium salt (55%) [608].
-The reference [1039] is erroneous. The compound above mentioned is, in reality, the 5-chloro-2-hydroxyacetophenone.

oil [608], b.p.$_{0.5}$ 78-80° [608].

1-(3-Chloro-2-hydroxyphenyl)ethanone

[3226-34-4] $C_8H_7ClO_2$ mol.wt. 170.60



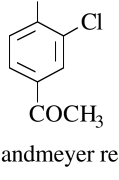
Syntheses

-Preparation by Fries rearrangement of 2-chlorophenyl acetate with aluminium chloride,
*without solvent, between 110° and 180° (40 to 21%) [479] [540] [1586] [1603] [1850];
*in tetrachloroethane at 70-80° [1833].
-Preparation in two steps: At first, by reaction of acetyl chloride on 2-chlorophenol with aluminium chloride in refluxing petroleum ether, one obtains the 2-acetoxy-3-chloroacetophenone (83%); the saponification of this keto ester leads to the 3-chloro-2-hydroxyacetophenone (93%) [214] [1581].
-Obtained by reaction of acetyl chloride on 2-chlorophenol with ferric chloride at r.t. (22%) [478].

m.p. 84° [1586], 55° [1603], 49-50° [540], 48°5 [1833]. One of the reported melting points is obviously wrong.
b.p.$_6$ 66-67° [478], b.p.$_1$ 87-89° [214] [1581], b.p.$_{20}$ 148-153° [1833]; UV [478] [479].

1-(3-Chloro-4-hydroxyphenyl)ethanone

[2892-29-7] $C_8H_7ClO_2$ mol.wt. 170.60



Syntheses

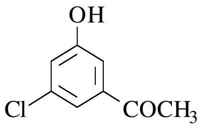
-Preparation by reaction of acetyl chloride on 2-chloro-phenol with aluminium chloride in refluxing carbon disulfide (98%) [1069].
-Preparation by diazotization of 3-amino-4-hydroxy-acetophenone and replacement of diazonium group by chlorine (Sandmeyer reaction) [560] [1810], (84%) [560].

-Preparation by Fries rearrangement of 2-chlorophenyl acetate with aluminium chloride without solvent [386] [478] [479] [540] [1024] [1603], (60-66%) [478] [540].
-Preparation by Fries rearrangement of 2-chlorophenyl acetate with aluminium chloride in nitrobenzene at 100° (30%) [1603].
-Preparation by Fries rearrangement of 2-chlorophenyl acetate with aluminium chloride in tetrachloroethane at 70-80° [1833].
-Also obtained by reaction of acetyl chloride on 2-chlorophenol with ferric chloride [478] [1320] [1321].
-Also obtained (by-product) by reaction of acetyl chloride on 2-chloroanisole or 2-chlorophenetole with aluminium chloride [788].

m.p. 107-108° [1833], 107° [788], 100-100°5 [540], 96° [1320] [1603] [1810], 95° [560], 94-95° [478], 93° [1024], 92-95° [386] [1069];
^{1}H NMR [540], IR [1833], UV [478] [479]; pK$_a$ [1697].

1-(3-Chloro-5-hydroxyphenyl)ethanone

[23164-97-8] $C_8H_7ClO_2$ mol.wt. 170.60

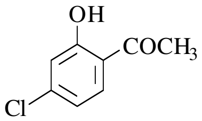


Synthesis not yet described

-The reference [479] is erroneous. In this one, the compound **4** is, in reality, the 5-chloro-2-hydroxyacetophenone.
-Also refer to: [1627].

1-(4-Chloro-2-hydroxyphenyl)ethanone

[6921-66-0] $C_8H_7ClO_2$ mol.wt. 170.60



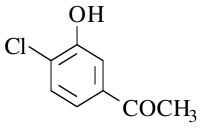
Syntheses

-Preparation by Fries rearrangement of 3-chlorophenyl acetate with aluminium chloride,
*without solvent at 130-135° (74-75%) [309] [1589], between 135 and 200° [146] [309] [383] [449] [924] [1589] [1603], and 175-200° (85-89%) [383] [924];
*with solvent, at r.t., in nitrobenzene (88%) [1589], in tetrachloroethane (50%) [1603] or in chlorobenzene [1789].
-Also obtained by treatment of 4-chloroacetophenone with sodium trifluoroacetate in nitromethane-trifluoroacetic acid-trifluoroacetic anhydride mixture in the presence of a platinum electrode followed by treatment of the intermediate trifluoroacetate ester with 10% potassium hydrogen carbonate solution (51%) [1661] (hydroxylation of aromatic compounds).
-Preparation by reaction of methyl magnesium iodide on 4-chloro-2-hydroxybenzoyl chloride in ethyl ether, at -70°, followed by hydrolysis of the complex so obtained [39].

m.p. 50-51° [146], 26° [449]. One of the reported melting points is obviously wrong.
b.p.$_2$ 96° [1589], b.p.$_{14}$ 119-122° [924], b.p.$_{10}$ 120-122° [309], b.p.$_{15}$ 121-124° [383], b.p.$_{16}$ 126° [449], b.p. 247° [1789];
IR [924] [1923], (Sadtler: standard n° 8980);
pK$_a$ [1697].

1-(4-Chloro-3-hydroxyphenyl)ethanone

[61124-56-9] $C_8H_7ClO_2$ mol.wt. 170.60



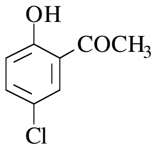
Syntheses

-Preparation by diazotization of 3-amino-4-chloroacetophenone (quantitative yield) [39], (16-18%) [1069].
-Obtained by treatment of 4-chloroacetophenone with sodium trifluoroacetate in nitromethane-trifluoroacetic acid-trifluoroacetic anhydride mixture in the presence of a platinum electrode, followed by treatment of the intermediate trifluoroacetate ester with 10% potassium hydrogen carbonate solution (33%) [1661] (hydroxylation of aromatic compound).
-Preparation by reaction of pyridinium chloride on 4-chloro-3-methoxyacetophenone between 170 to 200° (40%) [1069].
-Preparation from 3-hydroxyacetophenone by chlorination of its 2,3-butylene ketal or its ethylene ketal using tert-butyl hypochlorite. The hydrolysis of these chloroketals with concentrated hydrochloric acid in tetrahydrofuran-water mixture gave 3-hydroxy-4-chloroacetophenone (94 and 48% yields, respectively) [344].
-Also obtained by reaction of acetyl chloride on 2-chlorophenol with ferric chloride [1320].
-Also obtained (by-product) by reaction of tert-butyl hypochlorite on 3-hydroxyacetophenone in chloroform at 15° (6%) [344].

m.p. 106-107° [344], 103-104° [1069], 96° [1320]; ^{1}H NMR [344], IR [344].

1-(5-Chloro-2-hydroxyphenyl)ethanone

[1450-74-4] $C_8H_7ClO_2$ mol.wt. 170.60



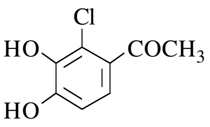
Syntheses

-Preparation by Fries rearrangement of 4-chlorophenyl acetate with aluminium chloride without solvent between 110° and 200° [107] [125] [214] [285] [372] [478] [479] [613] [812] [991] [1334] [1581] [1582] [1603] [1683] [1850] [1894], (90-100% yield) [107] [285] [478] [613] [812] [1582] [1603] [1683] [1894].
-Preparation by Fries rearrangement of 4-chlorophenyl acetate with aluminium chloride,
*in tetrachloroethane at 150-160° [1833];
*in chlorobenzene, in a sealed tube and subjected to high power microwave irradiation for 2 min only (85%) [1683].
-Preparation by Fries rearrangement of 4-chlorophenyl acetate with boron trifluoride in acetic acid at 125°, in a sealed tube (91%) [979].
-Preparation by photo-Fries rearrangement of 4-chlorophenyl acetate with potassium carbonate in hexane at r.t. (88%) [660].
-Preparation by reaction of acetyl chloride on 4-chlorophenol with ferric chloride [107] [1320] [1321].
-Preparation by reaction of acetyl chloride on 4-chlorophenol with aluminium chloride in refluxing petroleum ether, and saponification of the obtained keto ester, the 2-acetoxy-5-chloroacetophenone (90%) [1581].
-Preparation by reaction of acetic acid on 4-chlorophenol with boron trifluoride at 150°, in a sealed tube (94%) [979].
-Preparation by diazotization of 5-amino-2-hydroxyacetophenone and replacement of the diazonium group by chlorine (Sandmeyer reaction) [395].
-Also obtained (by-product) by heating 4-chlorophenyl 3,3-dimethylacrylate at 255-260°, in a sealed tube (4%) [1650].
-Also refer to: [153] (compound 1b); [1204] (compound 1a); and to [1205] (compound 1d).

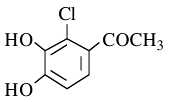
m.p. 72° [613], 57° [395], 56-57° [1603], 55° [478] [1320], 54° [979] [991], 53°5-54°5 [1894], 53-54° [372] [1582], 53° [1650] [1833], 52°5-53° [387], 52°2-53°6 [812], 52°5 [1334], 52-53° [285], 52° [125], 50-52° [660];
b.p.$_{2}$ 97-99° [991], b.p.$_{12}$ 107-109° [214] [1581], b.p.$_{14}$ 125-126° [979], b.p.$_{28}$ 126-128° [1581], b.p.$_{26\text{-}27}$ 134-136° [285];
^{1}H NMR [914] [1698], ^{13}C NMR [914], IR [613] [1923], UV [478] [479] [812] [1698], fluorescence spectra [1698]; pK$_{a}$ [1697].

1-(2-Chloro-3,4-dihydroxyphenyl)ethanone

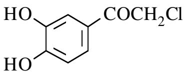
[56961-48-9] $C_8H_7ClO_3$ mol.wt. 186.59



N.B.: The titled compound seems, to our knowledge, to have never been prepared so far [1166]. However, in the various considered publications which mentioned the usage of this compound, for example [234], it is always another substance that is used as starting material, namely [99-40-1].



1-(2-Chloro-3,4-dihydroxyphenyl)ethanone
[56961-48-9] *titled compound*

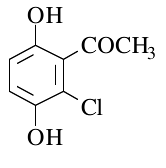


2-Chloro-1-(3,4-dihydroxyphenyl)ethanone
[99-40-1] *starting material*

As far as the titled compound is concerned, the same confusion occurs when consulting the **Chemical Abstracts Service**, **Registry Handbook**, Number Section, (1975 supplement, p. 2202RD) and **the Beilstein Institut zur Foerderung der Chemischen Wissenschaften** (Copyright 1988-2001), Beilstein Registry Number 4921697.
Both above mentioned documents use the same Registry Number [56961-48-9], though both compounds are different even if haven the same raw formula $C_8H_7ClO_3$.

1-(2-Chloro-3,6-dihydroxyphenyl)ethanone

[52095-12-2] $C_8H_7ClO_3$ mol.wt. 186.59



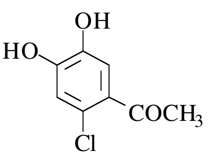
Syntheses

-Preparation by reaction of aluminium chloride on 2-acetylquinone in acetone (87%) [586].
-Preparation by reaction of hydrochloric acid on 2-acetylquinone in benzene (89%) [586].

m.p. 94-96° [586]; ^{1}H NMR [586], IR [586].

1-(2-Chloro-4,5-dihydroxyphenyl)ethanone

[69240-97-7] $C_8H_7ClO_3$ mol.wt. 186.59

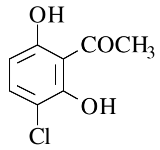


Synthesis

-Refer to: [1009] (compound XVIId).

1-(3-Chloro-2,6-dihydroxyphenyl)ethanone

[87953-93-3] $C_8H_7ClO_3$ mol.wt. 186.59



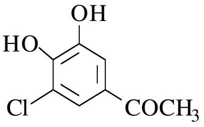
Syntheses

-Preparation by reaction of sulfuryl chloride on 2,6-dihydroxyacetophenone in refluxing ethyl ether (90%) [1112].
-Preparation by hydrolysis of 8-acetyl-6-chloro-7-hydroxy-4-methylcoumarin with 10% aqueous sodium hydroxide solution at reflux [1593] [1594].
-Obtained by decarboxylation of 3-acetyl-5-chloro-2,4-dihydroxybenzoic acid [1593] [1594].
-Preparation by reaction of thionyl chloride on 2,6-dihydroxyacetophenone in refluxing acetic acid (77%) [827] [828].

m.p. 135° [1112], 134-135° [1593] [1594].

1-(3-Chloro-4,5-dihydroxyphenyl)ethanone

[154638-86-5] $C_8H_7ClO_3$ mol.wt. 186.59



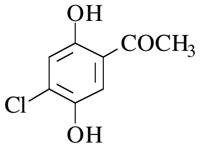
Synthesis

-Obtained (by-product) by chlorination of 4-hydroxy-3-methoxyacetophenone (acetoguaiacone) in dioxane-water mixture at 40° (8%) [1456].

MS [1456].

1-(4-Chloro-2,5-dihydroxyphenyl)ethanone

[90110-31-9] $C_8H_7ClO_3$ mol.wt. 186.59



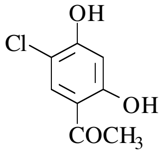
Syntheses

-Preparation by Fries rearrangement of 2-chloro-1,4-di hydroxyphenyl diacetate with aluminium chloride without solvent [514] [1604], at 160° (35%) [1604].
-Also refer to: [1927].

m.p. 145° [514] [1604].

1-(5-Chloro-2,4-dihydroxyphenyl)ethanone

[90110-32-0] $C_8H_7ClO_3$ mol.wt. 186.59



Syntheses

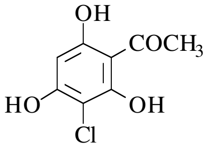
-Preparation by reaction of acetic acid on 4-chlororesorcinol with zinc chloride at 145° (Nencki reaction) (31%) [366].
-Preparation by reaction of acetic anhydride on 4-chlororesorcinol with polyphosphoric acid in the presence of one drop of concentrated sulfuric acid at reflux (12%) [1445].

-Also obtained by reaction of cuprous cyanide on 5-chloro-2,4-dihydroxy-3-iodoacetophenone in HMPT at 90° (conditions of the Rosenmund-von Braun reaction) (80%) [569].

m.p. 176-177° [1445], 174° [569], 171° [366].

1-(3-Chloro-2,4,6-trihydroxyphenyl)ethanone

[130435-29-9] $C_8H_7ClO_4$ mol.wt. 202.59



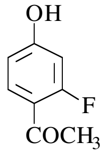
Synthesis

-Preparation by reaction of sulfuryl chloride on phloroacetophenone in ethyl ether at r.t. (86%) [1887].

m.p. 215-218° [1887];
^{1}H NMR [1887], MS [1887].

1-(2-Fluoro-4-hydroxyphenyl)ethanone

[98619-07-9] $C_8H_7FO_2$ mol.wt. 154.14



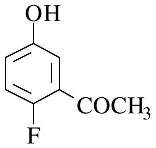
Synthesis

-Preparation by reaction of acetyl chloride on 3-fluorophenol with aluminium chloride in refluxing ethylene dichloride [968].

^{1}H NMR [968], IR [968], MS [968].

1-(2-Fluoro-5-hydroxyphenyl)ethanone

[145300-04-5] $C_8H_7FO_2$ mol.wt. 154.14



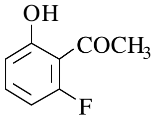
Synthesis

-Preparation by aromatization of 5-acetyl-4-fluoro-3-cyclohexenone promoted by cupric bromide-lithium bromide mixture in refluxing acetonitrile (70%) [120] [197].

m.p. 97° [120] [197]; ^{1}H NMR [197], IR [197].

1-(2-Fluoro-6-hydroxyphenyl)ethanone

[93339-98-1] $C_8H_7FO_2$ mol.wt. 154.14



Syntheses

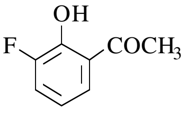
-Preparation by reaction of boron tribromide on 2-fluoro-6-methoxyacetophenone (**I**) in methylene chloride at -65 to -80° [277] [396], (56%) [396]. The precursor (**I**) was obtained by reaction of methyl magnesium iodide on 2-fluoro-6-methoxybenzonitrile in refluxing toluene (quantitative yield) [277].

-Preparation from 2-fluoro-6-methoxybenzonitrile [737] according to the procedure [739].

oil [277] [396]; b.p.$_{0.2}$ 170-172° [277];
^{1}H NMR [396] [737], ^{13}C NMR [737], ^{19}F NMR [737], MS [737].

1-(3-Fluoro-2-hydroxyphenyl)ethanone

[699-92-3] $C_8H_7FO_2$ mol.wt. 154.14



Syntheses

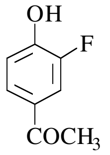
-Obtained by Fries rearrangement of 2-fluorophenyl acetate with aluminium chloride without solvent at 115° [683], 150° [277] or at 180-190° (16%) [382] [389].

-Also obtained by Fries rearrangement of 2-fluorophenyl acetate with aluminium chloride in chlorobenzene at 100° for 24 h (38%) [1837].

m.p. 75-77° [277], 75-76° [683], 72-73° [382] [389];
^1H NMR [683] [1837], MS [683].

1-(3-Fluoro-4-hydroxyphenyl)ethanone

[403-14-5] $C_8H_7FO_2$ mol.wt. 154.14



Syntheses

-Preparation by reaction of pyridinium chloride on 3-fluoro-4-methoxyacetophenone at reflux (78%) [336].

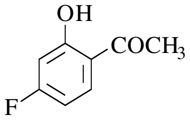
-Preparation by reaction of acetyl chloride on 2-fluorophenol with aluminium chloride in refluxing carbon disulfide (74%) [1069].

-Preparation by Fries rearrangement of 2-fluorophenyl acetate with aluminium chloride without solvent at 115° [683] or 140° (51-52%) [920] [969] [1127] [1236].

m.p. 128-128°5 [683], 127-129° [1069], 126-127° [969], 125-126°6 [1236], 125° [336];
b.p.$_2$ 125-135° [1236];
^1H NMR [683], IR [969], MS [683] [969].

1-(4-Fluoro-2-hydroxyphenyl)ethanone

[1481-27-2] $C_8H_7FO_2$ mol.wt. 154.14



Syntheses

-Preparation by Fries rearrangement of 3-fluorophenyl acetate with aluminium chloride without solvent at 160-180° [369] [773] [1678], (75%) [1678], (88-90%) [369] [773].

-Preparation by Fries rearrangement of 3-fluorophenyl acetate with alumina in methanesulfonic acid for 3 h at 160° (60%) [1613].

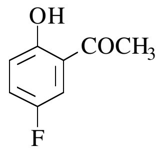
-Preparation by Friedel-Crafts acylation of 3-fluorophenol with acetic acid in the presence of alumina in methanesulfonic acid for 2 h at 120° (63%) [1613].

-Also refer to: [572] [1117] [1875].

m.p. 24° [369] [773].

1-(5-Fluoro-2-hydroxyphenyl)ethanone

[394-32-1] $C_8H_7FO_2$ mol.wt. 154.14



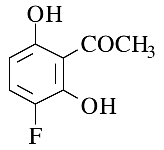
Syntheses

-Preparation by Fries rearrangement of 4-fluorophenyl acetate with aluminium chloride without solvent between 115 and 150° [372] [431] [683] [773] [918] [919] [1721], (88-89%) [372] [431] [773], (62-63%) [918] [1721].
-Preparation by reaction of acetic acid on 4-fluorophenol with boron trifluoride at 150°, in a sealed tube (89%) [979].
-Preparation by reaction of pyridinium chloride on 5-fluoro-2-methoxyacetophenone at reflux (74%) [334], (59%) [812].
-Preparation by reaction of acetyl chloride on 4-fluoroanisole with aluminium chloride in carbon tetrachloride (44%) [678] [679].
-Also obtained (by-product) by reaction of acetyl chloride on 4-fluoroanisole with aluminium chloride in carbon disulfide [334].
-Also refer to: [1927].

m.p. 57-58° [372] [387], 57° [334] [979], 56°4-57°6 [812], 56°5-57° [431], 56-57° [678] [679], 56-56°5 [1721], 56° [773], 55° [683];
b.p.$_{8}$ 65-66° [918], b.p.$_{12}$ 94-99° [1721], b.p.$_{13}$ 103-104° [334], b.p.$_{16}$ 105° [979];
^{1}H NMR [678] [683], ^{13}C NMR [736], UV [812], MS [678] [683]; pK_a [1697].

1-(3-Fluoro-2,6-dihydroxyphenyl)ethanone

[117902-14-4] $C_8H_7FO_3$ mol.wt. 170.14



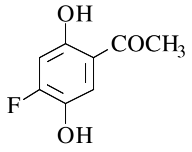
Synthesis

-Obtained (by-product) by reaction of boron tribromide on 2,6-dimethoxy-3-fluoroacetophenone in methylene chloride-methanol mixture (14%) [192].

m.p. 134-135° [192]; ^{1}H NMR [192].

1-(4-Fluoro-2,5-dihydroxyphenyl)ethanone

[88772-48-9] $C_8H_7FO_3$ mol.wt. 170.14



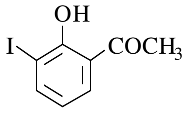
Synthesis

-Preparation by Fries rearrangement of 2-fluoro-hydroquinone diacetate with aluminium chloride in nitrobenzene at 140° (66%) [502].

m.p. 210° [502]; ^{1}H NMR [502], IR [502].

1-(2-Hydroxy-3-iodophenyl)ethanone

$C_8H_7IO_2$ mol.wt. 262.05



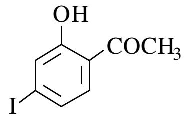
Synthesis

-Preparation by diazotization of 3-amino-2-hydroxyacetophenone with sodium nitrite in dilute sulfuric acid at 0°, and replacement of the diazonium group by iodine with potassium iodide at 65° (Sandmeyer reaction) [370] [372] [389], (50%) [372].

m.p. 59°5-60°5 [370], 58-59° [372] [389].

1-(2-Hydroxy-4-iodophenyl)ethanone

[39730-66-0] $C_8H_7IO_2$ mol.wt. 262.05



Syntheses

-Preparation by Fries rearrangement of 3-iodophenyl acetate with aluminium chloride [383] [385] [390] [410] [1001] [1789],
*in chlorobenzene, at 125-135° (64%) [383] [1789];
*in nitrobenzene, at 110-140° (40-45%) [383] [390] [1001].

-Preparation by diazotization of 4-amino-2-hydroxyacetophenone and replacement of the diazonium group by iodine (Sandmeyer reaction) (46%) [383].

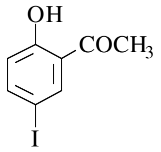
-Preparation by reaction of acetyl chloride on 3-iodoanisole with aluminium chloride in refluxing carbon disulfide (14%) [1001].

-Also refer to: [569] (compound 6).

m.p. 54° [1789], 53-54° [383] [385] [390], 52-54° [1001].

1-(2-Hydroxy-5-iodophenyl)ethanone

[7191-41-5] $C_8H_7IO_2$ mol.wt. 262.05



Syntheses

-Preparation by saponification of ethyl 4-hydroxy-6-iodocoumarin-3-carboxylate with boiling 10% aqueous potassium hydroxide solution (92%) [443] [444].

-Preparation by diazotization of 2-hydroxy-5-nitroacetophenone and replacement of the diazonium group by iodine (Sandmeyer reaction) [370] [372] [387] [1273], (75-80%) [372] [387].

-Preparation by diazotization of 4-acetamido-2-methoxyacetophenone and replacement of the diazonium group by iodine (73%) [387].

-Also obtained by reaction of iodine on 2-hydroxyacetophenone in aqueous sodium carbonate solution (37%) [1425], (14%) [440] [443].

-Also obtained by Fries rearrangement of 4-iodophenyl acetate with aluminium chloride in nitrobenzene at 25° (13%) [384].

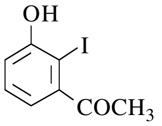
-Also refer to: [819].

m.p 91-92° [372], 90-92° [370] [387], 90° [1273], 88-89° [443] [444], 67-69° [384]. One of the reported melting points is obviously wrong.

UV [443].

1-(3-Hydroxy-2-iodophenyl)ethanone

[348616-32-0] $C_8H_7IO_2$ mol.wt. 262.05



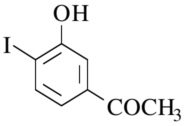
Synthesis

-Obtained by debenzylation of 3-(benzyloxy)-2-iodoacetophenone (m.p. 53-55°) with boron tribromide in methylene chloride at -70° for 50 min (93%) [784].

m.p. 93-97° [784]; ^{1}H NMR [784], ^{13}C NMR [784], IR [784], MS [784].

1-(3-Hydroxy-4-iodophenyl)ethanone

[73898-23-4] $C_8H_7IO_2$ mol.wt. 262.05



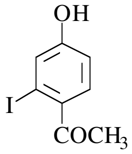
Synthesis

-Obtained by reaction of iodine-potassium iodide mixture in aqueous solution with 3-hydroxyacetophenone in concentrated aqueous ammonia at r.t. (15%) [1069].

m.p. 134-135° [1069].

1-(4-Hydroxy-2-iodophenyl)ethanone

$C_8H_7IO_2$ mol.wt. 262.05



Syntheses

-Preparation by reaction of 48% hydrobromic acid on 2-iodo-4-methoxyacetophenone in acetic acid at 100°, in a sealed tube (45%) [1001].

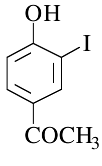
-Also obtained (by-product) by reaction of acetyl chloride on 3-iodoanisole with aluminium chloride in refluxing carbon disulfide (9%) [1001].

-Also obtained in very small quantities by Fries rearrangement of 3-iodophenyl acetate with aluminium chloride in nitrobenzene at 90-95° [385].

m.p. 131-132° [1001], 128-136° [385].

1-(4-Hydroxy-3-iodophenyl)ethanone

[62615-24-1] $C_8H_7IO_2$ mol.wt. 262.05



Syntheses

-Preparation by reaction of iodine and potassium iodide on 4-hydroxyacetophenone in aqueous ammonium hydroxide at r.t. [246] [1069] [1571], (54-57%) [1069] [1571].

-Preparation by adding an aqueous solution of potassium iodide to a solution of 4-hydroxyacetophenone in concentrated ammonium hydroxide at 35° (49%) [1065].

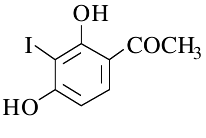
-Preparation by adding a 5% aqueous solution of sodium hypochlorite to a solution of 4-hydroxyacetophenone and sodium iodide in methanol at 15° (60%) [1665].

-Also refer to: [929].

m.p. 155-156° [1665], 154-156° [1571], 153-155° [1065], 153-154° [1069]; ^{1}H NMR [1065] [1571] [1665], IR [1065].

1-(2,4-Dihydroxy-3-iodophenyl)ethanone

[71243-12-4] $C_8H_7IO_3$ mol.wt. 278.05



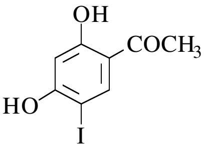
Syntheses

-Preparation by iodination of resacetophenone,
*with iodine and iodic acid in dilute ethanol at r.t. [15] [319] [655] [928] [1600] [1850], (82-84%) [319] [1600];
*with iodine in the presence of diisopropylamine in methanol at r.t. (14%) [319];
*with potassium iodate and potassium iodide in dilute acetic acid [1578].

m.p. 164° [1600], 158-162° [319], 158-159° [1578]; ^{1}H NMR [319].

1-(2,4-Dihydroxy-5-iodophenyl)ethanone

[62069-33-4] $C_8H_7IO_3$ mol.wt. 278.05



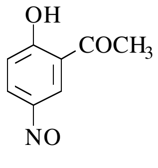
Syntheses

-Preparation by selective deiodination of 2,4-dihydroxy-3,5-diiodoacetophenone with stannous chloride in refluxing acetic acid (40%) [1558].
-Also obtained by reaction of aqueous iodine-potassium iodide solution on resacetophenone in 22% aqueous ammonia at r.t. (15%) [1600].
-Preparation by iodination of resacetophenone using iodine and iodic acid in dilute ethanol at r.t. [1850].
-Preparation by reaction of boron tribromide with 2,4-bis(benzyloxy)-5-iodoacetophenone (SM) in methylene chloride with stirring for 5 min at -70° (97%). SM was obtained from 2,4-bis-(benzyloxy)acetophenone with iodine in the presence of silver trifluoroacetate in chloroform (89%) [1665].

m.p. 185-186° [1558], 184° [1600], 180-181° [1665]; ^{1}H NMR [1558] [1665].

1-(2-Hydroxy-5-nitrosophenyl)ethanone

[15516-61-7] $C_8H_7NO_3$ mol.wt. 165.15



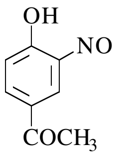
Synthesis

-Refer to: [1337] (compound XVII).

UV [1337].

1-(4-Hydroxy-3-nitrosophenyl)ethanone

[97871-70-0] $C_8H_7NO_3$ mol.wt. 165.15



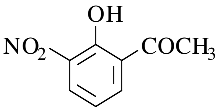
Synthesis

-Preparation by direct nitrosation [1851] of 4-hydroxyacetophenone with aqueous sodium nitrite solution in dilute hydrochloric acid between 0 to 5° [1175].

UV [1175]; pK_a [1175].

1-(2-Hydroxy-3-nitrophenyl)ethanone

[28177-69-7] $C_8H_7NO_4$ mol.wt. 181.15



Syntheses

-Preparation by reaction of boiling 5% aqueous potassium hydroxide on 8-nitrochromone (78%) [474].

-Also obtained by reaction of nitric acid on 2-hydroxyacetophenone in acetic acid [526], (30%) [827] [828], (9 to 10%) [1015] [1895], (2%) [37] [372] [923].

-Preparation by diazotization of 5-amino-2-hydroxy-3-nitroacetophenone, followed by decomposition of the obtained diazonium salt (90%) [471], (56%) [955].

-Also obtained by reaction of boiling 20% aqueous hydrochloric acid on 2-hydroxy-3-nitroacetophenone oxime [1104].

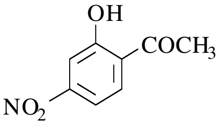
-Also obtained by nitration and hydroxylation of acetophenone with pernitrous acid (2%) [779].

-Also refer to: [957] [1278] [1457] [1473].

m.p. 103-104° [474], 99-101° [743], 98°5-99°5 [1895], 97-98° [526], 90° [779], 89-90° [1104], 84-85° [372], 82-83° [37] [471] [923] [955] [1015];
^{1}H NMR [471] [957], IR [471]; pK_a [957].

1-(2-Hydroxy-4-nitrophenyl)ethanone

[1834-91-9] $C_8H_7NO_4$ mol.wt. 181.15



Syntheses

-Obtained by Fries rearrangement of 3-nitrophenyl acetate with aluminium chloride without solvent at 125° [675] [1726] [1728], (20%) [1728], (32%) [675].

-Also obtained by reaction of acetyl chloride on 3-nitrophenol with aluminium chloride at 125° (16-18%) [1728].

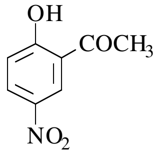
-Claimed to be prepared by reaction of boiling 50% nitric acid on 2-hydroxyacetophenone (59%) [253].

N.B.: No physical data is indicated in the patent for this compound. According to the rules dealing with aromatic substitution (Holleman rules) [791] and electronic induction using the Hammett substituent constants [376], the obtained product most likely is the 2-hydroxy-5-nitroacetophenone.

m.p. 67-68° [646] [675] [1727], 67° [1728]; ^{1}H NMR [1923], IR [1923].

1-(2-Hydroxy-5-nitrophenyl)ethanone

[1450-76-6] $C_8H_7NO_4$ mol.wt. 181.15



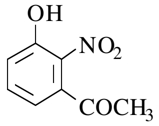
Syntheses

-Obtained by nitration of 2-hydroxyacetophenone oxime, followed by treatment of this oxime with boiling 20% hydrochloric acid (73%) [395] [1104].
-Preparation by reaction of acetyl chloride on 4-nitrophenol with aluminium chloride in nitrobenzene at 130° (44%) [923].
-Preparation by Fries rearrangement of 4-nitrophenyl acetate with aluminium chloride,
*without solvent, at 140-150° (28%) [647];
*with solvent, in nitrobenzene, at 120-130° (20-35%) [377] [646] [923] [1726] [1729].
-Preparation by nitration of 2-hydroxyacetophenone,
*in acetic acid (20-30%) [37] [372] [923] [1015] [1895];
*without solvent (59%) [253].
-Also obtained by reaction of acetic anhydride on 4-nitrophenol with aluminium chloride [377].
-Also obtained from mixture of 2-chloro-5-nitroacetophenone, sodium acetate and acetamide heated at 180-200° (49%) [1646].
-Also refer to: [1935].

m.p. 111-112° [1104], 102-103° [377] [646] [1015] [1726], 101-102° [372] [647], 99°5 [923] [1646], 98°5-99°5 [1895], 98-99° [37];
^{1}H NMR [914] [1923], ^{13}C NMR [914], IR [1923].

1-(3-Hydroxy-2-nitrophenyl)ethanone

[53967-72-9] $C_8H_7NO_4$ mol.wt. 181.15



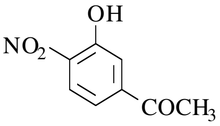
Syntheses

-Preparation by nitration of 3-hydroxyacetophenone,
*with concentrated nitric acid in concentrated sulfuric acid at -20° (35-45%) [326];
*with nitric acid (d = 1.4) in acetic acid at 70° (16%) [994];
*with cupric nitrate in acetic acid-acetic anhydride mixture between 12 to 15° (18%) [326] [552].
-Preparation by demethylation of 3-methoxy-2-nitroacetophenone with pyridinium chloride at 200° [1676].

m.p. 138° [326], 136° [1676], 135° [994]; IR [994], UV [326] [994]; pK_a [994].

1-(3-Hydroxy-4-nitrophenyl)ethanone

[89942-63-2] $C_8H_7NO_4$ mol.wt. 181.15



Syntheses

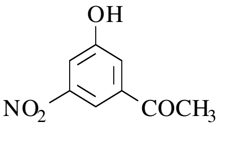
-Obtained (poor yield) by nitration of 3-hydroxyacetophenone,
*with nitric acid (d = 1.4) in acetic acid, at 70° (10%) [994];
*with cupric nitrate in acetic acid-acetic anhydride mixture, between 12 to 15° (< 1%) [326].

m.p. 131-132° [646], 71°5-72°5 [326], 69-70° [994];
IR [994], UV [326] [994]; pK_a [994].

N.B.: The melting point 131-132° [646] was erroneous. This melting point is the one of an isomer, the 3-nitro-4-hydroxyacetophenone (130-131°2) [296].

1-(3-Hydroxy-5-nitrophenyl)ethanone

[70284-07-0] $C_8H_7NO_4$ mol.wt. 181.15



Syntheses

-Obtained in two steps: First, a mixture of 3-hydroxyacetophenone and dysprosium nitrate in ethyl acetate were refluxed (85-105°) for 75 min. Then, the isolated intermediate $(C_8H_6NO_4)_3Dy$ (59%) was dissolved in 6 N hydrochloric acid (50%) [707].

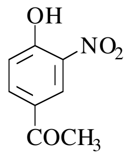
-Also refer to: [1134] (compound NP), [1245].

N.B.: Dy (III) salt [193693-92-4] [707].

m.p. 122-124° [707]; MS [707].

1-(4-Hydroxy-3-nitrophenyl)ethanone

[6322-56-1] $C_8H_7NO_4$ mol.wt. 181.15



Syntheses

-Preparation by nitration of 4-hydroxyacetophenone [154] [173] [270] [560] [649] [994] [1430] [1810], (85%) [560] [1810], (70-75%) [173] [649] [1430], (56%) [994].

-Also obtained by nitration of 4-hydroxyacetophenone,

*using properties of dinitrogen tetroxide complexes of iron — $Fe(NO_3)_3$. 1.5 N_2O_4 — and copper nitrates — $Cu(NO_3)_2$. N_2O_4 — in acetone for 5-10 min at r.t. (97-100%) [600];

*by reaction of ferric nitrate nonahydrate — $Fe(NO_3)_3$. 9 H_2O — in ethanol for 24 h at 65° (91%) [1428].

-Also obtained by reaction of peroxynitrite ($ONOO^-$) with 4-hydroxyacetophenone in aqueous phosphate buffer and acetonitrile solution [1336].

-Also obtained from aromatic nucleophilic substitution of 3,4-dichloroacetophenone with sodium nitrite in DMSO (40%) [1957].

-Preparation by reaction of acetyl chloride on 2-nitrophenol with aluminium chloride in nitrobenzene (46-47%) [296] [360] [923] [1471].

-Also obtained by reaction of acetyl chloride on 2-nitroanisole with aluminium chloride (11%) [1694].

-Preparation by Fries rearrangement of 2-nitrophenyl acetate with aluminium chloride in nitrobenzene (40-45%) [675] [923], (30%) [296] [1727].

-Also obtained by Fries rearrangement of 2-nitrophenyl acetate [1730], which occurs under mild conditions on K 10 montmorillonite using microwave radiations [931].

-Also obtained on heating 4-bromo-3-nitroacetophenone with acetamide-sodium acetate mixture between 175 to 200° (low yield) [272].

-Also obtained by mononitration of 4-hydroxyacetophenone with a combination,

*trichloroisocyanuric acid, sodium nitrite and wet silicone dioxide (50% w/w) in methylene chloride at r.t. for 20 min (97%) [1958];

*magnesium bisulfate or sodium bisulfate monohydrate, sodium nitrite and wet silicone dioxide (50% w/w) in methylene chloride at r.t. for 3 h (80-82%) [1959].

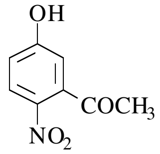
-Also refer to: [181] [624] [957] [1488] [1853] [1870] [1874] [1914].

N.B.: Na salt [42247-95-0] [1907].

m.p. 135-136° [994], 135° [1430], 133-134° [173], 133° [649], 132-132°5 [296], 132° [923], 131-132° [1471], 130°5 [1694], 130° [272] [1810], 129°5 [560], 128-130° [675], 123° [1428], 122-124° [1958] [1959];
pK_a [957] [994] [1471]; GC [1957];
^{1}H NMR [957] [1428], ^{17}O NMR [278], IR [994] [1428], UV [994] [1471], MS [1957].

1-(5-Hydroxy-2-nitrophenyl)ethanone

[30879-49-3] $C_8H_7NO_4$ mol.wt. 181.15



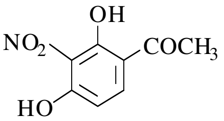
Syntheses

-Preparation by nitration of 3-hydroxyacetophenone,
*with nitric acid (d = 1.4) in acetic acid, at 70° (31%) [994], (15%) [649];
*with cupric nitrate in acetic acid-acetic anhydride mixture, between 12 to 15° (20%) [326] [552].

m.p. 148-149° [326] [649] [994]; IR [994], UV [324] [326] [994]; pK_a [994].

1-(2,4-Dihydroxy-3-nitrophenyl)ethanone

[89684-58-2] $C_8H_7NO_5$ mol.wt. 197.15



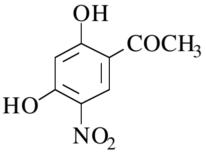
Syntheses

-Resacetophenone by treatment with cerium (IV) ammonium nitrate in acetic acid at 50-60° yields 2,4-dihydroxy-3-nitroacetophenone (good yield) [378], (23%) [380].
-Preparation by reaction of acetic anhydride on 2-nitroresorcinol with aluminium chloride in nitrobenzene at 100° [48] [1591], (53%) [48].
-Also obtained by reaction of aqueous hydrochloric acid-acetic acid mixture on 5-acetyl-2,4-dihydroxy-3-nitrobenzoic acid in a sealed tube at 140-145° [1286].
-Also refer to: [1290].

m.p. 103° [1591], 102° [48], 93° [254] [368] [1286], 90-91° [378] [380];
^{1}H NMR [378], IR [378].

1-(2,4-Dihydroxy-5-nitrophenyl)ethanone

[3328-77-6] $C_8H_7NO_5$ mol.wt. 197.15



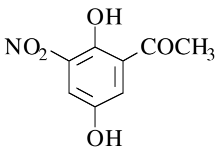
Syntheses

-Preparation by nitration of resacetophenone [138] [1319], (71%) [1362], (54-50%) [947] [1289], (44%) [471].
-Also obtained by reaction of nitric acid on 3,3'-diacetyl-4,4',6,6'-tetrahydroxydiphenyl thioether in acetic acid at r.t. [868].
-Also obtained (by-product) by reaction of acetic anhydride on 4-nitroresorcinol with aluminium chloride in nitrobenzene (6%) [1291].
-Also obtained by reaction of sodium hydroxide on 3-benzoyl-2,4-dihydroxy-5-nitroacetophenone in boiling aqueous ethanol [1480].
-Resacetophenone by treatment with cerium (IV) ammonium nitrate in hot acetic acid yields 2,4-dihydroxy-5-nitroacetophenone (31%) [380].

m.p. 145-147° [471], 145° [947], 143° [380],
142° [138] [254] [868] [1289] [1291] [1319] [1362] [1480] [1591].
^{1}H NMR [471], IR [471].

1-(2,5-Dihydroxy-3-nitrophenyl)ethanone

[30095-74-0] $C_8H_7NO_5$ mol.wt. 197.15



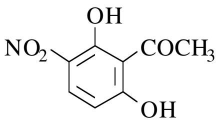
Syntheses

-Preparation by nitration of 3-acetyl-4-hydroxyphenyl acetate, followed by hydrolysis of the obtained keto ester with hydrochloric acid in refluxing methanol (61%) [170].
-Also obtained by hydrolysis of 6-hydroxy-2-methyl-8-nitrochromone with 10% aqueous sodium hydroxide [516].
-Also obtained by nitration of quinacetophenone in acetic acid [516].
-Also obtained by demethylation of 2-hydroxy-5-methoxy-3-nitroacetophenone with 48% hydrobromic acid in the presence of red phosphorous at 85-90° for 16 h under argon atmosphere (90%) [471].
N.B.: All the results of reference [516] were erroneous [170].

m.p. 141-142° [170], 136-138° [471], 58° [516]. One of the reported melting points is obviously wrong.
^{1}H NMR [170] [471], IR [170], UV [170].

1-(2,6-Dihydroxy-3-nitrophenyl)ethanone

[25205-34-9] $C_8H_7NO_5$ mol.wt. 197.15



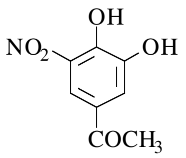
Syntheses

-Preparation by reaction of acetic anhydride on 4-nitroresorcinol with aluminium chloride in nitrobenzene [1291] [1591], (37%) [1291].
-Preparation by Fries rearrangement of 4-nitroresorcinol diacetate with aluminium chloride in nitrobenzene at 95-100° (38%) [49].
-Also obtained by nitration of 2,6-dihydroxyacetophenone (77%) [471], (27%) [1291].
-Also obtained by demethylation of 2,6-dimethoxy-3-nitroacetophenone with aluminium chloride or with boiling 10% aqueous sodium hydroxide (quantitative yield) [1291].
-Also obtained by reaction of 4-methoxy-2-methyl-8-nitrochromone or its 3-acetyl derivative with boiling 10% aqueous sodium carbonate (50% and 58% yields, respectively) [1155].
-Also refer to: [1592].

m.p. 119° [1291] [1591], 116-117° [49], 114-115° [471]; ^{1}H NMR [471], IR [471].

1-(3,4-Dihydroxy-5-nitrophenyl)ethanone

[116313-84-9] $C_8H_7NO_5$ mol.wt. 197.15



Syntheses

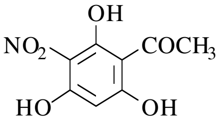
-Preparation from 4-hydroxy-3-methoxyacetophenone by nitration and subsequent demethylation of 4-hydroxy-3-methoxy-5-nitroacetophenone obtained,
*with boiling concentrated hydrobromic acid [202];
*with concentrated hydrobromic acid in acetic acid (35%) [122].

-Preparation by demethylation of 3,4-dimethoxy-5-nitroacetophenone with concentrated hydrobromic acid at 140° [202].

m.p. 161-169° [122], 159-160° [202]; pK_a [271].

1-(2,4,6-Trihydroxy-3-nitrophenyl)ethanone

[81325-88-4] $C_8H_7NO_6$ mol.wt. 213.15



Syntheses

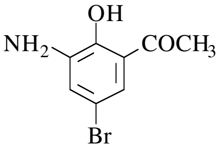
-Preparation by addition of a mixture of concentrated sulfuric acid and fuming nitric acid into a solution of phloroacetophenone in concentrated sulfuric acid and hexane mixture under cooling with an ice bath (70-80%) [1921].

-Also obtained by adding acetic anhydride to a mixture of 1,3,5-trihydroxy-2-nitrobenzene and aluminium chloride in nitrobenzene and heating on a steam bath for 7 h (20%) [2].

m.p. 133-135° [1921], 131-132° [2]; ^1H NMR [2] [1921], IR [1921], MS [1921].

1-(3-Amino-5-bromo-2-hydroxyphenyl)ethanone

[70977-85-4] $C_8H_8BrNO_2$ mol.wt. 230.06



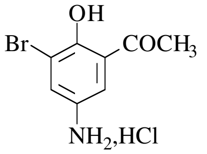
Synthesis

-Preparation by reaction of 20% aqueous titanium trichloride solution on 5-bromo-2-hydroxy-3-nitroacetophenone in toluene, at r.t., in a sealed tube [620] [1463], (31%) [620].

m.p. 99-102° [620] [1463].

1-(5-Amino-3-bromo-2-hydroxyphenyl)ethanone *(Hydrochloride)*

[30186-22-2] $C_8H_8BrNO_2$, HCl mol.wt. 266.52



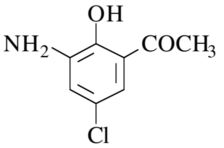
Synthesis

-Preparation by reduction of 3-bromo-2-hydroxy-5-nitroacetophenone with an excess of tin in concentrated hydrochloric acid at 100° (82%) [540].

m.p. 200°(d) [540].

1-(3-Amino-5-chloro-2-hydroxyphenyl)ethanone

[21312-85-6] $C_8H_8ClNO_2$ mol.wt. 185.61



Syntheses

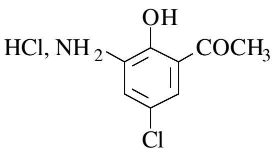
-Preparation by reaction of acetic anhydride on 2-amino-4-chlorophenol with aluminium chloride in 1,2,4-trichlorobenzene at 120° [753].

-Preparation by reaction of 75% hydrochloric acid solution on 3-acetamido-5-chloro-2-hydroxyacetophenone; the mixture was heated on a steam bath (98%) [1388].

m.p. 110-112° [1388]; UV [1388].

1-(3-Amino-5-chloro-2-hydroxyphenyl)ethanone *(Hydrochloride)*

[153404-65-0] $C_8H_8ClNO_2$, HCl mol.wt. 222.07

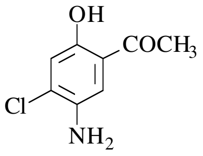


Synthesis

-Preparation by reaction of acetic anhydride on 2-amino-4-chlorophenol hydrochloride with aluminium chloride in 1,2,4-trichlorobenzene at 120° (79%) [753].

1-(5-Amino-4-chloro-2-hydroxyphenyl)ethanone

$C_8H_8ClNO_2$ mol.wt. 185.61



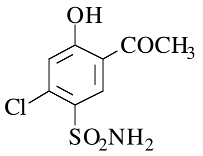
Synthesis

-Preparation by reduction of 4-chloro-2-hydroxy-5-nitroacetophenone with iron powder in dilute acetic acid at 95° (93%) [924] (Béchamp reduction).

m.p. 117-118° [924]; IR [924].

1-[5-(Aminosulfonyl)-4-chloro-2-hydroxyphenyl]ethanone

$C_8H_8ClNO_4S$ mol.wt. 249.67



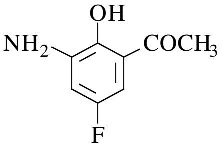
Synthesis

-Preparation by reaction of ammonia gas on 4-chloro-5-chlorosulfonyl-2-hydroxyacetophenone in tetrahydrofuran at r.t. (57%) [924].

m.p. 181-182° [924].

1-(3-Amino-5-fluoro-2-hydroxyphenyl)ethanone

[70977-84-3] $C_8H_8FNO_2$ mol.wt. 169.16



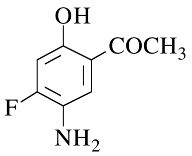
Synthesis

-Preparation by catalytic hydrogenation of 5-fluoro-2-hydroxy-3-nitroacetophenone in the presence of 5% Pd/C in ethanol at 25° [620] [1463], (99%) [620].

m.p. 113-114° [620].

1-(5-Amino-4-fluoro-2-hydroxyphenyl)ethanone

$C_8H_8FNO_2$ mol.wt. 169.16

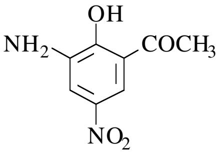


Synthesis

-Refer to: [572] (Japanese patent).

1-(3-Amino-2-hydroxy-5-nitrophenyl)ethanone

[70977-79-6] $C_8H_8N_2O_4$ mol.wt. 196.16



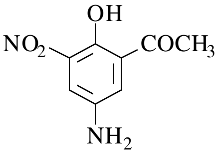
Synthesis

-Preparation by reaction of sodium sulfide on 2-hydroxy-3,5-dinitroacetophenone with ammonium chloride in refluxing methanol [620] [1463], (55%) [1463], (72%) [620].

m.p. 172-175° [1463], 172-174° [620].

1-(5-Amino-2-hydroxy-3-nitrophenyl)ethanone

[108129-55-1] $C_8H_8N_2O_4$ mol.wt. 196.16



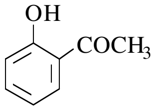
Synthesis

-Preparation by hydrolysis of 5-acetamido-2-hydroxy-3-nitroacetophenone (96%) [471], (82%) [955].

m.p. 141-142° [955], 129-130° [471];
^1H NMR [471], IR [471].

1-(2-Hydroxyphenyl)ethanone

[118-93-4] $C_8H_8O_2$ mol.wt. 136.15



Syntheses

-Preparation by Fries rearrangement of phenyl acetate,

with Lewis acids

*aluminium chloride,
with solvent:
-in petroleum ether at 25° (80%) [1724] (result not reproducible).
-in nitrobenzene [461] [1177] [1349] [1642] at 60° (26%) [1349].
-in nitroethane at 60° (12%) [1909].
-in chlorobenzene at 60-65° (23%) [1119] or in a sealed tube and subjected to high power microwave irradiation for 2 min only (30%) [1683].
without solvent:
  *between 130 to 165° (63-82%) [232] [1220] [1334] [1512] [1683] [1785] [1839].
  *between 120 to 180° (35-46%) [320] [461] [627] [1443] [1731] [1828] [1936].
  *between 90 to 200° (25-31%) [110] [113] [443] [445] [625] [632] [789] [1024] [1220] [1266].
  *at 60° (7%) [1911].
*boron trifluoride etherate, in boiling benzene (70%) [974].
*aluminium chloride-sodium chloride mixture at 240-250° (47%) [810].
*boron trifluoride at 90° (43%) [789].
*titanium tetrachloride at 110° (22%) [1925].
*scandium tris(trifluoromethanesulfonate), in nitromethane, at 50° (17%) [1000].
*zinc chloride between 125 to 160° (4-7%) [433] [789].

with Protic acids

*p-toluenesulfonic acid at 160° (25%) [789].
*methanesulfonic acid at 160° (22%) [789].
*polyphosphoric acid at 100° (20%) [1296].
*monohydrated sulfuric acid at 190° (20%) [789].
*methanetrisulfonic acid at 160° (11%) [789].
*phosphoric acid at 190° (8%) [789].

with a Cation exchange resin

*sulfonated polystyrene resin,
    *(Dowex 50 X 8) at 150° (8%) [789].
    *(Dowex 50 WX 8) at 115° (6%) [789].
*Nafion-XR 500 at 100° [1364].

with Zeolites molecular sieves

*Ga ZSM-5 at 250° (46%) [1469].
*ZSM-5 (Si/Al = 20) in sulfolane, at 180° (34%) [1852].
*H-Nu-2 (unknown structure) at 170° (6%) [468].
*H-ZSM-5 (MFI structure) at 210° (4%) [468].
*HY (Si/Al = 3) at 400° (3%) [1438].
*fluorided alumina (Al_2O_3-F; 3 % wt. F) at 400° (3%) [1438].
*H-ZSM-5 (Si/Al = 45) at 400° (1%) [1438].
-Also obtained by Fries rearrangement of 4-trimethylsilylphenyl acetate with aluminium chloride without solvent at 140° (60%) [1537].
-Also obtained by reaction of triethylamine hydrochloride on phenyl acetate at 260°, in a sealed tube [989].
-Also obtained (by-product) by Fries rearrangement of 2-bromophenyl acetate with aluminium chloride without solvent, at 180° (15%) [540].
-Also obtained by reaction of acetic acid on phenol,
*with polyphosphoric acid at 100° (20%) [1296];
*with zinc chloride (Nencki reaction) at reflux (2-5%) [433] [1266] [1398].
-Also obtained by reaction of acetyl chloride on phenol, in nitrobenzene, between 45 to 60°,
*with aluminium chloride (14-15%) [458] [1177];
*with titanium tetrachloride (11%) [458].
-Also obtained by reaction of acetyl chloride on phenyl borate with aluminium chloride in refluxing carbon disulfide (54%) [1792].
-Also obtained by reaction of acetic anhydride on phenol, using a steam bath,
*with 70% $HClO_4$ (51%) [1084];
*with aluminium chloride (38%) [1084];
*with zinc chloride at 145-150° (36%) [62].
-Also obtained by reaction of acetylacetone on phenyl benzoate with aluminium chloride in nitrobenzene, at 45° (3%) [1177].
-Preparation by diazotization of 2-aminoacetophenone and hydrolysis of the obtained diazonium salt [121] [629] [1776].
-Also obtained by demethylation of 2-methoxyacetophenone with hydrochloric acid, in a sealed tube (low yield) [629] or at 130° [1740].
-Also obtained by hydroxylation of acetophenone,
*This reaction was accomplished by oxidation of acetophenone at platinum in methylene chloride-trifluoroacetic acid mixture containing tetraethylammonium fluoborate, at r.t. (85% yield) [1662];
*This reaction was realized by treatment of acetophenone with sodium trifluoroacetate in nitromethane-trifluoroacetic acid-trifluoroacetic anhydride mixture in the presence of a platinum electrode, followed by treatment of the intermediate trifluoroester with 10% potassium hydrogen carbonate solution (50% yield) [1661];
*The 2-hydroxyacetophenone was obtained by nitration and hydroxylation of acetophenone with pernitrous acid (2% yield) [779].

-Also obtained by reaction of boiling dilute potassium hydroxide solution on flavone [1639].
-Also obtained by reaction of sodium ethoxide on chromone in refluxing ethanol [781].
-Also obtained by reaction of aqueous potassium hydroxide on 4-hydroxycoumarin (benzotetronic acid) at 180° (80%) [1398].
-Also obtained by reaction of sodium ethoxide on 4-phenacylidenflaven in refluxing ethanol [594].
-Also obtained by reaction of aqueous potassium hydroxide solution on methyl or ethyl 4-hydroxycoumarin-3-carboxylate at 180° (80%) [66].
-Also obtained by reaction of potassium hydroxide on the 2-hydroxyseneciophenone (2'-hydroxy-3,3-dimethylacrylophenone) in boiling ethanol (60%) [1650].
-Also obtained by UV light irradiation of phenyl acetate (photo-Fries rearrangement),
*in hexane, at 25° (13%) [660],
    -in the presence of potassium carbonate (78%) [660].
*in benzene (59%) [1723].
*in cyclohexane, at 25° (43%) [724].
*in methanol (28%) [1723].
*in water, at 25-30° (25-28%) [1350] [1843],
    -in the presence of β-cyclodextrin (89%) [1723], (35%) [1843], (11%) [1350].
    -in the presence of Methyl α-D-glucopyranoside (32%) [1350].
*in ethyl ether, at 25° (24%) [724].
*in ethanol [57] [58], at 30° (19%) [57].
*in isopropanol, at 25° (9%) [724].
-Also obtained by UV light irradiation of 2-methoxyphenyl acetate in benzene (14%) [280], in ethyl ether (4%) [724].
-Also obtained (by-product) on UV light irradiation of 2-hydroxy-α-chloroacetophenone in ethanol (3%) [59].

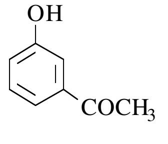
Isolation from natural sources

-From essential oil of *Chione Glabra* (Rubiaceae) [555].
-From essential oil of *Acacia farnesiana Willd* [1057].

m.p. 28° [433];
b.p.$_{0.2}$ 56° [540], b.p.$_{6}$ 73° [1724], b.p.$_{7}$ 86° [1084], b.p.$_{13}$ 91-92° [627], b.p.$_{10}$ 92-94° [1731], b.p.$_{7}$ 93-94° [1828], b.p.$_{11}$ 95-100° [1650], b.p.$_{10}$ 96-97° [66], b.p.$_{15}$ 96-98° [1731], b.p.$_{15}$ 97-98° [1024], b.p.$_{6}$ 98° [625], b.p.$_{15}$ 99-100° [1443], b.p.$_{14}$ 100° [110], b.p.$_{15}$ 101-101°5 [810], b.p.$_{17}$ 101-102° [1220], b.p.$_{20}$ 104-105° [443], b.p.$_{20}$ 106° [1936], b.p.$_{17}$ 106° [1839], b.p.$_{17}$ 106-107° [110], b.p.$_{17}$ 109° [1334], b.p.$_{32}$ 109-110° [838], b.p.$_{15}$ 110° [433], b.p.$_{33}$ 113°5-113°8 [1180], b.p.$_{30}$ 115-120° [1537], b.p.$_{22}$ 130-133° [1776] [1777], b.p.$_{34}$ 160-165° [555], b.p.$_{717}$ 213° [660] [1740], b.p. 213-214° [62] [1398], b.p. 215-218° [1119], b.p. 216-217° [1266], b.p. 218° [113] [594], b.p.$_{744}$ 220° [660];
^{1}H NMR [540] [622] [738] [765] [914] [1374] [1435] [1923],
^{13}C NMR [735] [736] [738] [914] [1486], IR [765] [839] [994] [1024] [1435] [1923],
UV [447] [570] [813] [994] [1161] [1163] [1266] [1776]; pK$_a$ [743] [994] [1697] [1899].

1-(3-Hydroxyphenyl)ethanone

[121-71-1] $C_8H_8O_2$ mol.wt. 136.15



Syntheses

-Preparation by diazotization of 3-aminoacetophenone, followed by hydrolysis of the obtained diazonium salt [220] [326] [520] [578] [650] [1349] [1419] [1530] [1776] [1838], (78-82%) [326] [650].

-Synthesis of 3-hydroxyacetophenone by means of organocadmium derivatives (77%) [1485].
-Preparation by reductive deamination of 2-amino-5-hydroxyacetophenone [682].
-Preparation by aromatization of 5-acetyl-2-cyclohexenone [197] promoted by,
    *cupric bromide and lithium bromide in refluxing acetonitrile (75%).
    *Pd/C in refluxing xylene (40%).
-Also obtained by treatment of acetophenone with sodium trifluoroacetate in nitromethane-trifluoroacetic acid-trifluoroacetic anhydride mixture in the presence of a platinum electrode, followed by treatment of the intermediate trifluoroester with 10% potassium hydrogen carbonate solution (14%) [1661], (hydroxylation of aromatic compounds).
-Also obtained (trace) by UV irradiation of phenyl acetate in ethanol at r.t. [57].
-Also obtained from 3-(allyloxy)acetophenone by cleavage of allyl group with bis(benzonitrile)-palladium (II) chloride in refluxing benzene (90%) [302].
-Also refer to: [1666].

Isolation from natural sources

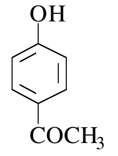
-From *Propolis* and *Populus nigra* bud exudate (compound 36) [1128].
-From commercial wood vinegar liquor (*Cryptomeria japonica*) [978].

N.B.: Toxic action of 3-hydroxyacetophenone to the ciliate *Tetrahymena pyriformis* [74] [1482].

m.p. 96° [1349] [1485] [1838], 95-96° [1419], 95° [1530], 94-96° [344], 94-95° [520] [650] [682], 94° [1776] [1777] , 92-93° [220], 92° [326], 86-88° [302];
b.p.$_{0.01}$ 82° [302], b.p.$_5$ 153° [578], b.p.$_{756}$ 296° [578];
HPLC [1128]; GC-MS [1128]; pK$_a$ [994] [1697] [1899];
^{13}C NMR [520], IR [994] [1922], UV [994] [1161] [1776] [1838], MS [978].

1-(4-Hydroxyphenyl)ethanone

[99-93-4] $C_8H_8O_2$ mol.wt. 136.15



Syntheses

-Preparation by Fries rearrangement of phenyl acetate

with Lewis acids

*aluminium chloride,

with solvent:
*in nitrobenzene at 20-25° [443] [1512] [1642] [1839] or at 50-60° [461] [1349] [1512] [1642] [1683], (75-76%) [461] [1512] [1683], (60-64%) [1349] [1642].
*in chlorobenzene between 45 to 65° [1119] [1177], (69%) [1119] or in a sealed tube and subjected to high power microwave irradiation for 2 min only (36%) [1683].
*in nitroethane at 60° (44%) [1909].
*in carbon disulfide at 45° (40%) [560].
*in petroleum ether at 50° (20%) [1724].

without solvent: [102] [119] [320] [461] [625] [632] [789] [1024] [1220] [1731] [1785] [1911] [1936], but between 130 to 175° (40-60%) [102] [320] [461] [789] [1220] [1936].
*aluminium chloride-sodium chloride mixture at 240-250° (10%) [810].
*boron trifluoride at 90° (56%) [789].
*scandium tris(trifluoromethanesulfonate), in nitromethane, at 50° (39%) [1000].
*titanium tetrachloride at 90-100° (34%) [625].
*ferric chloride at 65° (25%) [830].
*zinc chloride at 125° (8%) [433].

with Protic acids

*hydrofluoric acid [480] [482] [1641], between 20 to 100° (94%) [482], (81%) [480].
*polyphosphoric acid, between 20 to 100° (69%) [1660], (50-53%) [662] [1296], (44%) [1298].

with a Cation exchange resin

*Nafion-XR 500, sulfonic acid type at 100° [1364].

with Zeolites molecular sieves

*ZSM-5, in sulfolane, at 180° (28%) [1852].
*H-ZSM-5 at 400° [1438] or at 210° (6%) [468].
*H-Nu-2 at 170° (15%) [468].
*HY (Si/Al = 3) or fluorided alumina (Al_2O_3-F; 3 % wt. F), at 400° [1438].
-Also obtained by Fries rearrangement of 4-trimethylsilylphenyl acetate with aluminium chloride in refluxing carbon disulfide (55%) [1537].
-Also obtained (by-product) by Fries rearrangement of 2-bromophenyl acetate with aluminium chloride without solvent at 180° (8%) [540].
-Preparation by reaction of acetic acid on phenol,
*with boron trifluoride, between 30 to 80° (95%) [1146], (85%) [432], (77%) [1126].
*with polyphosphoric acid [662] [1298] [1660], between 70 to 100° (65-67%) [662] [1660].
*with hydrofluoric acid, at 100° (61%) [480].
*with zinc chloride (Nencki reaction) [433] [1230] [1398] [1776], (11%) [1398].
*with Nafion-XR 500, sulfonic acid type, at 100° [1364].
-Preparation by reaction of acetyl chloride on phenol,
*with aluminium chloride, in nitrobenzene, between 45 to 60° (70-74%) [102] [458], (50-55%) [1177] [1565].
*with titanium tetrachloride, in nitrobenzene, at 60° (70%) [458].
*with butanesulfonic acid, at 85-90° (23%) [1794].
*with ferric chloride, in carbon disulfide [1320] [1419], (21%) [1320].
*with zinc chloride [578].
-Also obtained by reaction of acetyl chloride on phenyl borate with aluminium chloride in refluxing carbon disulfide (35%) [1349].
-Preparation by reaction of acetic anhydride on phenol,
*with 70% perchloric acid (20%) [1084].
*with aluminium chloride (48%) [1210], (19%) [1084].
*with zinc chloride at 145-150° (40%) [62].
-Also obtained by reaction of phenyl 2-acetoxybenzoate on phenol with aluminium chloride at 180° (18%) [216].
-Preparation by reaction of acetonitrile on phenol with triflic acid (trifluoromethanesulfonic acid) at r.t. (74%) [268].
-Preparation by dealkylation of 4-ethoxyacetophenone [98] [751], (70%) [751] or 4-methoxyacetophenone (70%) [751] with aluminium chloride between 140 to 180°.
-Also obtained by UV light irradiation of phenyl acetate (photo-Fries rearrangement),
*in water, at 25-30° (24-25%) [1350] [1843],
    -in the presence of β-cyclodextrin [1350] [1723], (69%) [1350].
    -in the presence of methyl α-D-glucopyranoside (32%) [1350].
*in benzene or methanol, at r.t. (38-39%) [1723].
*in cyclohexane, ethyl ether, ethanol or isopropanol, at 25-30° (10-15%) [57] [58] [724].
*in hexane, at 25° (4%) [660].
    -in the presence of potassium carbonate (10%) [660].
-Also obtained by UV light irradiation of 4-methoxyphenyl acetate in ethyl ether, at 25° (7%) [724].
-Also obtained by UV light irradiation of 4-hydroxy-α-chloroacetophenone in ethanol (26%) [59].
-Also obtained by reaction of acetylacetone on phenyl benzoate with aluminium chloride in nitrobenzene at 45° (12%) [1177].
-Preparation by diazotization of 4-aminoacetophenone, followed by hydrolysis of the obtained diazonium salt [992] [1414].

-Also obtained by treatment of acetophenone with sodium trifluoroacetate in nitromethane-trifluoroacetic acid-trifluoroacetic anhydride mixture in the presence of a platinum electrode, followed by treatment of the intermediate trifluoroester with 10% potassium hydrogen carbonate solution (16%) [1661], (hydroxylation of aromatic compounds).
-Also obtained by reaction of stannous chloride on 4-hydroxyacetophenone 2,4-dinitrophenylhydrazone in refluxing aqueous acetic acid-hydrochloric acid mixture (66%) [460].

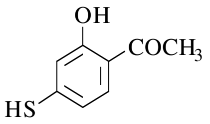
Isolation from natural sources:

-From the roots of *Paeonia broteroi* (Paeoniaceae) [490].
-The Picein or 4-hydroxyacetophenone-D-glucoside has been isolated from leaves of *Picea Glehnii Masters* (Coniferae). This compound, by hydrolysis with dilute mineral acids or with emulsin leads to 4-hydroxyacetophenone [953] [1772].
-Hinokiflavone has been isolated from *Chamaecyparis obtusa* (Coniferae) [951]. When treated with potassium hydroxide, Hinokiflavone produces 4-hydroxyacetophenone [644].
-From spruce needles (*Picea abies* L. Karst) [1369].
-Also obtained by saponification of Apiin or Apigenin with boiling 25% aqueous sodium hydroxide (87%) [1856]. Apiin or 4',5,7-trihydroxyflavone-7-apiosylglucoside was isolated from parsley or from celery [1854] [1855].

m.p. 115° [810], 112° [1856], 110-111° [1177], 110° [560] [1419] [1724], 109-110° [1024], 109° [216] [443] [1146] [1349] [1660] [1772] [1776] [1777] , 108-110° [1641], 108-109° [604] [1084] [1119] [1537], 108° [460] [461] [625] [830] [1220] [1230] [1320] [1398] [1512] [1839], 107-109° [57] [480] [662] [1731], 107°5-108° [1126], 107-108° [953] [1456], 107° [268] [420] [578] [751] [992] [1298] [1369], 106°2-107°8 [625], 106-107° [320] [433] [1565] [1722], 105-108° [432], 104-106° [62];
b.p.$_3$ 147-148° [1398], b.p.$_{20}$ 170-194° [662], b.p.$_4$ 175° [443], b.p.$_{15}$ 190° [433];
^{1}H NMR [268] [490] [540] [1369], ^{13}C NMR [520], IR [994] [1024] [1369], UV [347] [994] [1082] [1160] [1161] [1163] [1266] [1369] [1776];
pK$_a$ [994] [1697] [1899].

1-(2-Hydroxy-4-mercaptophenyl)ethanone

[35204-52-5] $C_8H_8O_2S$ mol.wt. 168.22



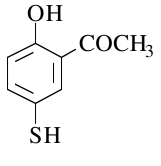
Syntheses

-Preparation by reaction of stannous chloride with 2-acetyl-5-chlorosulfonylphenol in acetic acid previously saturated with gaseous hydrochloric acid (63%) [71].
-Also refer to: [1680].

m.p. 60-62° [71].

1-(2-Hydroxy-5-mercaptophenyl)ethanone

[35204-45-6] $C_8H_8O_2S$ mol.wt. 168.22

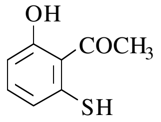


Synthesis

-Refer to: [421].

1-(2-Hydroxy-6-mercaptophenyl)ethanone

[83080-88-0] $C_8H_8O_2S$ mol.wt. 168.22

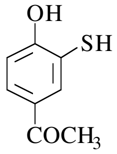


Synthesis

-Preparation by reaction of 2 N aqueous sodium hydroxide on 2-dimethylcarbamylthio-6-hydroxyacetophenone in refluxing methanol (65%) [91].

1-(4-Hydroxy-3-mercaptophenyl)ethanone

[66264-55-9] $C_8H_8O_2S$ mol.wt. 168.22



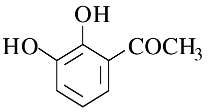
Synthesis

-Preparation by reaction of stannous chloride dihydrate on 3-(chlorosulfonyl)-4-hydroxyacetophenone with gaseous hydrochloric acid in acetic acid at 25-30° (31%) [1421] [1692].

m.p. 117-120° [1421] [1692].

1-(2,3-Dihydroxyphenyl)ethanone

[13494-10-5] $C_8H_8O_3$ mol.wt. 152.15



Syntheses

-Preparation by reaction of acetic anhydride on pyrocatechol with 70% perchloric acid on a steam bath (58%) [1084], at 100° (4%) [623].

-Preparation by demethylation of 2,3-dimethoxyacetophenone [115] [134] [988] [1020] [1437], (73%) [134], (50%) [1020], itself obtained by oxidation of 2,3-dimethoxyphenyl methyl carbinol [115] [988] [1020] [1437]. This "carbinol" was prepared either from 2,3-dimethoxybenzaldehyde by an organomagnesium synthesis [115] [988] [1020] or from 2,3-dimethoxycinnamic acid by Posner's method [1020] [1437].

-Also obtained by acid hydrolysis of 8-hydroxyflavone [1020].

-Also obtained by UV light irradiation of pyrocatechol monoacetate in ethanol at 30° (19-22%) [57] [58] [893].

-Also obtained (low yield) by degradation of an aqueous solution (pH 4.5) of D-xylose at 96° (0.5%) [1433].

-Also obtained (low yields) by degradation of aqueous solutions (pH 3.5 and 4.5) of D-glucuronic acid at 96° (0.3% and 0.2% yields, respectively) [1433].

-Also obtained from 3-acetyl-1-oxocyclohexane-2,3,6-triol, either on sublimation at 0.5 mm Hg (70% yield) or when heated in an aqueous solution (pH 4.5) and 96° (50% yield). The above triol was obtained in crystalline form (m.p. 149-150°) by reaction of D-glucuronic acid in aqueous solutions (pH 3.5 and 4.5) at 96° [1433].

-Also obtained (by product) by UV light irradiation of 3-methyl-1,2-benzisoxazole in 96% sulfuric acid (10%) [547] [673].

-Also obtained by hydrolytic rearrangement of 2-acetoacetyl-2,5-dimethoxytetrahydrofuran in refluxing 0.1 N hydrochloric acid (88%) [240], (52%) [1427].

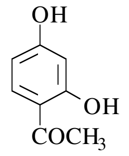
-Also obtained by hydrolysis of (2,2-dimethyl-1,3-benzodioxol-4-yl)acetone (m.p. 72-73°) with concentrated hydrochloric acid in refluxing ethanol under argon atmosphere (84%) [826].

m.p. 98-98°5 [240], 98° [57] [58] [134], 97-98° [893] [1020], 97° [1084], 96°5-97°5 [547], 96-98° [623] [1433], 96-97° [826], 95-96° [1427];

^{1}H NMR [547] [826] [893] [1427], ^{13}C NMR [826], IR [547], UV [547], MS [547] [826].

1-(2,4-Dihydroxyphenyl)ethanone *(Resacetophenone)*

[89-84-9] $C_8H_8O_3$ mol.wt. 152.15



Syntheses

-Preparation by reaction of acetic acid on resorcinol,
*with zinc chloride (Nencki reaction) [418] [453] [475] [551] [686] [906] [982] [1319] [1501] [1529] [1775] [1877], (94%) [1501], (57-65%) [551] [906] [1319];
*with boron trifluoride [1146] [1229] [1345], (85-94%) [1146] [1345];
*with Amberlite IR-120 (a cation exchange resin, sulfonic acid type) (87%) [1445];
*with polyphosphoric acid [1298] [1308], (63%) [1308];
*with 70% perchloric acid (33%) [1229].
-Preparation by reaction of acetonitrile on resorcinol,
*with triflic acid (trifluoromethanesulfonic acid) (87%) [268];
*with zinc chloride (Hoesch reaction) [782] [790] [1259] [1955] [1956], (77%) [1955], (70%) [790].
-Preparation by reaction of acetic anhydride on resorcinol,
*with boron trifluoride (91%) [975];
*with 70% perchloric acid (90%) [1084], (70%) [548];
*with Amberlite IR-120 (83%) [1445];
*with zinc chloride at 145-150° (2%) [62];
*with a trace of concentrated sulfuric acid at 130° (75%) [860].
-Preparation by reaction of acetyl chloride on resorcinol,
*with aluminium chloride in nitrobenzene at r.t. (65%) [507], (50%) [1513];
*with Amberlite IR-120 (52%) [1445];
*with zinc chloride [579] [580].
-Preparation by Fries rearrangement of resorcinol monoacetate with 70% perchloric acid in acetic anhydride at r.t. (83%) [1084].
-Preparation by Fries rearrangement of resorcinol diacetate,
*with Amberlite IR-120 (64%) [1445];
*with aluminium chloride [511] [514] [1130], (63%) [1130], (60%) [514];
*with boron trifluoride etherate in benzene at reflux (60%) [974];
*with zinc chloride [711] [1319], (52%) [711].
-Preparation by Fries rearrangement of 3-methoxyphenyl acetate with aluminium chloride without solvent at 180-185° (60%) [514].
-Also obtained by UV light irradiation of resorcinol diacetate in methanol at 25° [1389].
-Also obtained by demethylation of 2-hydroxy-4-methoxyacetophenone,
*with potassium hydroxide [1285];
*with hydriodic acid [1285].
-Also obtained by reaction of concentrated sulfuric acid on resacetophenone diacetate [511].
-Also obtained by reaction of potassium hydroxide on 4-methylumbelliferone [1399] or on 4-methylene-2-phenyl-4*H*-chromen-7-ol [317].
-Also obtained by decarboxylation of 2-acetyl-3,5-dihydroxybenzoic acid with copper powder in quinoline at 220-230° [1249].
-Also obtained by decarboxylation of 3-acetyl-2,6-dihydroxybenzoic acid with dilute hydrochloric acid at reflux [1596] [1602].
-Also obtained by decarboxylation of 5-acetyl-2,4-dihydroxybenzoic acid with dilute hydrochloric acid at 160-170°, in a sealed tube [47].

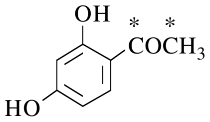
Isolation from natural sources

-From Chinese Moutan Cortex, the root of *Paeonia suffruticosa* Andrews (Paeoniaceae) [1924].
-Also obtained by thermal decomposition of the resin from *Ferula pyramidata* (Kar. et Kir.) eug. kor. [982].

m.p. 147° [475] [1146] [1345], 146° [507] [548] [860], 145-146° [982], 145° [782] [1445], 144-145° [790] [975], 144° [62], 143° [47] [1229], 142-144° [551], 142-143° [878] [1596], 142° [134] [418] [420] [453] [711] [873] [1130] [1285] [1298] [1308] [1319] [1513] [1776] [1777], 141-142° [1249] [1399], 141° [686], 140-141° [906], 138-140° [268], 133-140° [1501];
b.p. 303-305° (d) [1319];
$d^{141°1}$ = 1.18 [578]; $n_D^{141°1}$ = 1.56467 [578];
^1H NMR [43] [44] [268] [622], ^{13}C NMR [520] [736] [1396] [1400],
UV [43] [447] [448] [1775], MS [684]; pK_a [1697].

1-(2,4-Dihydroxyphenyl)ethanone-$^{13}C_2$

[74291-78-4] $C_8H_8O_3$ mol.wt. 154.13

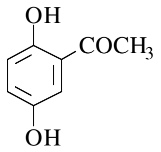


Synthesis

-Preparation by reaction of [1,2-$^{13}C_2$]acetyl chloride with resorcinol in nitrobenzene in the presence of aluminium chloride for 24 h at r.t. (65%) [34].

1-(2,5-Dihydroxyphenyl)ethanone *(Quinacetophenone)*

[490-78-8] $C_8H_8O_3$ mol.wt. 152.15



Syntheses

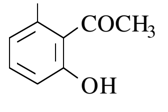
-Preparation by Fries rearrangement of hydroquinone diacetate,
*with aluminium chloride [45] [50] [510] [512] [513] [514] [812] [1240] [1510] [1572] [1608] [1895], (91%) [513], (76%) [1608] [1895], (63-77%) [45] [50] [1572], (55-60%) [512] [514] [812] [1240];
*with zinc chloride in refluxing acetic acid (quantitative yield) [1468];
*with boron trifluoride etherate in benzene at reflux (65%) [974].
-Preparation by Fries rearrangement of hydroquinone diacetate with aluminium chloride in the presence of hydroquinone (54%) [1510].
-Also obtained by UV light irradiation of hydroquinone diacetate in methanol (35%) [1614].
-Preparation by Fries rearrangement of 4-methoxyphenyl acetate with aluminium chloride without solvent at 130° (40%) [46].
-Preparation by Fries rearrangement of 4-(benzoyloxy)phenyl acetate with aluminium chloride without solvent at 125-130° (22%) [46].
-Preparation by reaction of acetic acid on hydroquinone,
*with zinc chloride (Nencki reaction) [418] [512] [1200] [1318] [1321] [1468] [1531] [1776], (25-28%) [1200] [1531];
*with boron trifluoride [723] [1051] [1052] [1146] [1345], (95%) [1052], (66-70%) [1146] [1345];
*with Amberlite IR-120 or Zeokarb 225 (22%) [1445].
-Preparation by reaction of acetyl chloride on hydroquinone with aluminium chloride [418] [512] [1510], (35-40%) [512] [1510].

-Also obtained by reaction of acetic anhydride on hydroquinone,
*with zinc chloride at 145-150° (76%) [62];
*with Amberlite IR-120 (27%) [1445].
-Also obtained (by-product) by reaction of acetic acid on 1,4-dimethoxybenzene with boron trifluoride at 70° [1345].
-Preparation by dealkylation of,
*2,5-dimethoxyacetophenone with aluminium bromide in refluxing carbon disulfide (81%) [995];
*2-hydroxy-5-methoxyacetophenone with hydriodic acid [693];
*2,5-diethoxyacetophenone or 5-ethoxy-2-hydroxyacetophenone with aluminium chloride [418].
-Preparation by diazotization of 5-amino-2-hydroxyacetophenone, connected with hydrolysis of the obtained diazonium salt [1104] [1475].
-Preparation by hydrolysis of keto esters further on,
*5-(benzoyloxy)-2-hydroxyacetophenone with concentrated sulfuric acid at r.t. [46];
*5-acetoxy-2-hydroxyacetophenone,
    -with 5% aqueous sodium hydroxide (96%) [1240],
    -with a 5% solution of hydrogen chloride in methanol (75%) [1487],
    -with aluminium chloride in refluxing carbon disulfide (55%) [1240].
-Also obtained by reduction of 2-acetyl-1,4-benzoquinone,
*with aqueous sodium hydrosulfite, in ethyl ether [995];
*with allyltrimethylstannane, in benzene (36%) [1171].
-Also obtained by reaction of acetaldehyde on 1,4-benzoquinone with sunlight, in a sealed tube (good yield) [993].
-Also obtained (by-product) from 5-bromo-6-hydroxy-2-methylchromone by alkaline degradation with 10% aqueous sodium hydroxide solution at reflux (50%) [170].
-Also obtained (poor yield) by alkaline degradation of a solution of D-xylose or D-glucose in 0.63 M sodium hydroxide at 96° under nitrogen [623].
-Also obtained by UV light irradiation of 3-methyl-1,2-benzisoxazole in 96-98% sulfuric acid (52-57%) [547] [673].
-Also obtained by heating 5'-cinnamyloxy-2'-hydroxyacetophenone at 220° (64%) [303].
-Also obtained from 5-(allyloxy)-2-hydroxyacetophenone by cleavage of allyl group with bis(benzonitrile)palladium (II) chloride in refluxing benzene (89%) [302].

m.p. 206° [512], 205-206° [623] [1487], 204°6-205°4 [812], 204° [1052], 202°6-203°6 [547], 202-204° [1445], 202-203° [50] [1240] [1572], 202° [134] [418] [513] [693] [993] [1104] [1146] [1318] [1345] [1510] [1608] [1614], 201-203° [1171], 201-202° [45] [46] [420] [995] [1200] [1468], 201° [1776] [1777], 200-201° [1531], 200° [62], 198-200° [130], 197°5-198°5 [1895], 196-198° [302] [303];
b.p.$_{0.01}$ 86° [302]; pK_a [1697];
^{1}H NMR [723] [1240], (Sadtler: standard n° 4286); ^{13}C NMR [736] [1396],
IR [547] [1171] [1240], (Sadtler: standard n° 10815);
UV [547] [720] [723] [1776], (Sadtler: standard n° 6276); MS [723] [1171].

1-(2,6-Dihydroxyphenyl)ethanone *(γ-Resacetophenone)*

[699-83-2] $C_8H_8O_3$ mol.wt. 152.15



Syntheses

-Preparation by hydrolysis of 8-acetyl-4-methylumbelliferone (8-acetyl-7-hydroxy-4-methylcoumarin) with aqueous sodium hydroxide solution at reflux (56-73%) [139] [447] [1306] [1867], (77-89%) [609] [1534] [1610] [1632] [1707] [1709], (89%-100%) [5] [1092] [1533] [1534].

-Preparation by hydrolysis of 8-acetyl-4-phenylumbelliferone with aqueous sodium hydroxide solution at reflux (33%) [1093].
-Preparation by demethylation of 2,6-dimethoxyacetophenone with aluminium chloride in toluene at 120° (24%) [1707] [1709], (59%) [1198]. The 2,6-dimethoxyacetophenone was obtained from 2,6-dimethoxybenzonitrile and methylmagnesium iodide.

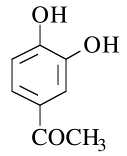
From Microorganisms

-Isolation from *Daldinia concentrica* [665].

m.p. 157-158° [1198], 157° [134] [1092] [1093], 156-157° [139] [1707] [1709] [1867], 155-156° [447], 154-157° [238], 154-156° [1533], 154-155° [1534] [1610] [1632], 154° [1306], 152-154° [5];
^{1}H NMR [238] [738], ^{13}C NMR [520] [738], UV [40] [447].

1-(3,4-Dihydroxyphenyl)ethanone

[1197-09-7] $C_8H_8O_3$ mol.wt. 152.15



Syntheses

-Preparation by Fries rearrangement of pyrocatechol diacetate with aluminium chloride in nitrobenzene between 75 to 95° [893] [1271] [1510], (80%) [1510], (64%) [893], (43%) [1271] or in chlorobenzene at 80° (83%) [1250].
-Also obtained by Fries rearrangement of guaiacol acetate with aluminium chloride in nitrobenzene at r.t. (30%) [1510] or without solvent between 20 to 50° (6%) [1939].
-Preparation by reaction of acetic acid on pyrocatechol,
*with boron trifluoride in a sealed tube at 150° (43%) [1345];
*with zinc chloride (Nencki reaction) [433] [1317], (20%) [433];
*with polyphosphoric acid (10%) [1308].
-Also obtained by reaction of acetic anhydride on pyrocatechol,
*with perchloric acid at 100° (6%) [623];
*with zinc chloride at 145-150° (51%) [62].
-Preparation by reaction of acetyl chloride with pyrocatechol with aluminium chloride at 140° [818].
-Also obtained by UV light irradiation of pyrocatechol monoacetate in ethanol at 30° (18%) [57] [58].
-Also obtained by reaction of 5% aqueous potassium hydroxide on Luteolin, at reflux [1405].
-Preparation by demethylation of acetovanillone,
*with dilute hydrochloric acid in a sealed tube at 140-150° [1317];
*using aluminium chloride and pyridine [684] [1064].
-Also obtained by reaction of zinc powder [226] [420] [558] [626] [1690] or stannous chloride [558] and hydrochloric acid on 3,4-dihydroxy-α-chloroacetophenone (quantitative yield) [420] [558], (45-49%) [626].
-Also obtained by reaction of aluminium bromide on (3,4-methylenedioxy)acetophenone (acetopiperone) in nitrobenzene at r.t. (48%) [1267].
-Also obtained from 3,4-diacetoxyacetophenone [226],
*by heating with a concentrated solution of sodium carbonate;
*by refluxing with 5% sulfuric acid;
*by treatment with porcine pancreatic lipase in diisopropyl ether and n-butanol at 42-45° (80%) [1381] [1382].
-Also obtained (by-product) by chlorination of acetoguaiacone in dioxane-water mixture at 40° (3%) [1456].
-Also obtained (poor yield) by alkaline degradation of a solution of D-xylose or D-glucose in 0.63 M sodium hydroxide at 96° under nitrogen (< 1%) [623].
-Also obtained from neutral glucose and fructose solutions heated at 120° [1718].

Isolation from natural sources

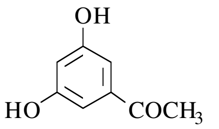
-From the needles of *Picea obovata* Ledeb. and *Picea koraiensis* Nakai (Pinaceae) [864].
-This ketone was shown to occur in natural humic acids* and fulvic acids by hydrolysis with 2 N sodium hydroxide at 170° [1569]. Allomelanins* found in soils, coals and peat, resulting from the decomposition of organic matter, particularly dead plants [1790].
-By hydrolysis of its 3-O-β-D-glucopyranoside (*poungenoside*) (m.p. 200-202°) [864].
N.B.: it was found to be an antimicrobial substance in coffee residue [1329].

m.p. 122° [57] [58], 120° [1345], 119-121° [626], 119°2-119°7 [818], 118-120° [623], 117-118° [1267], 117° [684], 116-117° [864], 116° [62] [433] [558] [1064] [1271] [1308] [1510], 115-116° [420] [893], 114-116° [1405], 114-115° [226], 114° [1690], 110-112° [1250], 96-98° [1317];
b.p.$_{11}$ 127-133° [1308]; pK_a [994]; TLC [864]; HPLC [1329];

^{1}H NMR [623] [864] [893] [1329], ^{13}C NMR [1329], IR [623] [864] [994] [1569], UV [57] [864] [893] [994], MS [623] [684] [1329] [1456] [1569].

1-(3,5-Dihydroxyphenyl)ethanone

[51863-60-6] $C_8H_8O_3$ mol.wt. 152.15



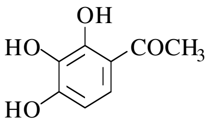
Syntheses

-Preparation from 3,5-dimethoxyacetophenone (SM) by demethylation with aluminium chloride in refluxing chlorobenzene (71%) [1193]. The starting material (SM) was prepared by a three-step procedure from 3,5-dimethoxybenzoic acid.
-Preparation from 3,5-diacetoxyacetophenone by hydrolysis with 10% sulfuric acid at reflux (41%) [832]. The starting ketone was prepared by reaction of methyl bromide on 3,5-diacetoxybenzoyl chloride in the presence of dimethyl cadmium.

m.p. 148° [832], 147-148° [1193].

1-(2,3,4-Trihydroxyphenyl)ethanone *(Gallacetophenone)*

[528-21-2] $C_8H_8O_4$ mol.wt. 168.15



Syntheses

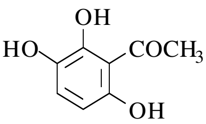
-Preparation by Fries rearrangement of pyrogallol triacetate with aluminium chloride without solvent [510] [511], (very good yield) [510].
-Preparation by reaction of acetic anhydride on pyrogallol,
*with Amberlite IR-120 or Zeokarb 225, at 160° (84%) [1445];
*with few drops sulfuric acid at 130° (65%) [860];
*with zinc chloride at 145-150° (53%) [62] or in the presence of acetic acid (58-63%) [124] [750];
*with sulfuric acid and benzene-1,3-disulfonic acid mixture at 135° (54%) [998];
*with 70% perchloric acid on a steam bath (44%) [1084].
-Preparation by reaction of acetyl chloride on pyrogallol with aluminium chloride [565] [606] [631] [1513].
-Preparation by reaction of acetic acid on pyrogallol,
*with boron trifluoride at 28-30° (90%) [1053] [1146] alone or in ethyl ether at 0° (90%) [347];
*with Amberlite IR-120 or Zeokarb 225 at 160° (75%) [1445];
*with zinc chloride at 140-150° (Nencki reaction) (good yield) [453] [605] [1319] [1776], (58%) [749];
*with 70% perchloric acid, at reflux (30%) [1229].

-Also obtained by dealkylation of 2,3-dihydroxy-4-methoxyacetophenone with aluminium chloride in refluxing chlorobenzene [1194].
-Also obtained by hydrolysis of 3,4-diacetoxy-2-hydroxyacetophenone [1614].
-By other method (90%), also refer to: [348].
-Preparation by reaction of hydrogen peroxide on 3-formylresacetophenone in 1 N aqueous sodium hydroxide (79%) [1306].
-Also obtained by cleavage of 4-methylene-2-phenyl-4*H*-chromene-7,8-diol with boiling 10% potassium hydroxide [317].

m.p. 186° [511], 173° [605] [606] [1053] [1084] [1146] [1229], 172° [1776] [1777], 171-173° [62], 171-172° [124] [750], 171° [347] [565], 170° [749], 169-171° [1445], 169-170° [860] [1614], 168° [420] [453] [631] [1194] [1306] [1319], 167° [1513];
IR [1053], UV [347] [1776].

1-(2,3,6-Trihydroxyphenyl)ethanone

[85918-30-5] $C_8H_8O_4$ mol.wt. 168.15



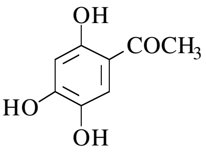
Syntheses

-Photolysis of 1,2,4-triacetoxybenzene gave a complex mixture from which 2-acetyl-3,6-diacetoxyphenol could be isolated. The triacetate of this one, by deacetylation afforded 3-acetyl-1,2,4-trihydroxybenzene [1614].
-Preparation by reaction of potassium persulfate on 2,6-dihydroxyacetophenone in aqueous sodium hydroxide solution at 15-20° (29%) [140].
-Preparation by reaction of hydrogen peroxide on 3-formyl-2,6-dihydroxyacetophenone in 1 N aqueous sodium hydroxide (71-74%) [1304] [1306].

m.p. 160° [1614], 157° [1306],
230° (d) [140], 96° [1304]. These reported melting points are obviously wrong.
(The triacetate melted to 155° [140]).

1-(2,4,5-Trihydroxyphenyl)ethanone

[1818-27-5] $C_8H_8O_4$ mol.wt. 168.15



Syntheses

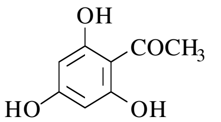
-Preparation by Fries rearrangement of 1,2,4-triacetoxybenzene,
*with aluminium chloride in nitrobenzene [147] [365] [511] [1197] [1203], (30-43%) [365] [1197] [1203];
*with zinc chloride at 135-140° [159] [168] [998] [1566], (49-53%) [159] [998];
*with p-toluenesulfonic acid in refluxing tetrachloroethane or benzene or without solvent at 135-140° (60%) [998].
-Also obtained by reaction of potassium persulfate on resacetophenone (Elbs reaction),
*in aqueous solution of potassium hydroxide at r.t. (24-30%) [1068] [1900];
*with ferrous sulfate in aqueous sodium hydroxide at r.t. (18%) [168].
-Preparation by reaction of acetonitrile on hydroxyquinol with zinc chloride (Hoesch reaction) [365] [766] [1197] [1203], (25%) [365].
-Also obtained by reaction of acetic acid-acetic anhydride mixture on hydroxyquinol with zinc chloride at 140-150° (32%) [365].
-Also obtained by reaction of acetic anhydride on hydroxyquinol with concentrated sulfuric acid at 135° (61-81%) [998].

-Preparation by reaction of acetic anhydride on p-quinone with concentrated sulfuric acid alone or with benzenesulfonic acid, p-toluenesulfonic acid, dl-camphorsulfonic acid or benzene-m-disulfonic acid at 135° (53 to 70%) [998].
-Also refer to: [687].

m.p. 208° [1566], 206-207° [365] [511] [1197] [1203], 206° [766], 202-204° [1068], 200-202° [159] [168];
^{13}C NMR [897], MS [684].

1-(2,4,6-Trihydroxyphenyl)ethanone *(Phloroacetophenone)*

[480-66-0] $C_8H_8O_4$ mol.wt. 168.15



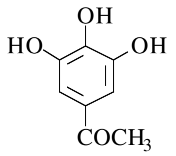
Syntheses

-Preparation by reaction of acetic anhydride on phloroglucinol,
*with concentrated sulfuric acid at 130° (70%) [860];
*with boron trifluoride at 10° (62.5-68%) [1915];
*with zinc chloride at 145-150° (50%) [62];
*with Amberlite IR-120 or Zeokarb 225 (cation exchange resins, sulfonic acid type) at 160° (39%) [1445].
-Preparation by reaction of acetonitrile on phloroglucinol,
*with zinc chloride (Hoesch reaction) [347] [416] [712] [713] [790] [817] [905] [1502], (93%) [817], (74-87%) [416] [713] [790] [905];
*with triflic acid, at r.t. (40%) [268].
-Preparation by reaction of acetyl chloride on phloroglucinol,
*with boron trifluoride, at 10° (62.5-68%) [1915];
*with aluminium chloride, in nitrobenzene [511] [1513] [1633], (25-30%) [511] [1633];
*with ferric chloride, in a boiling water bath [1321].
-Preparation by reaction of acetic acid on phloroglucinol with zinc chloride (Nencki reaction), and then saponification of 5,7-dihydroxy-4-methylene-2-(2,4,6-trihydroxyphenyl)-4*H*-benzopyran first formed (76%) [1590].
-Preparation by reaction of phenyl acetate on phloroglucinol with boron trifluoride etherate in refluxing benzene (30%) [974].
-Also obtained by Fries rearrangement of phloroglucinol triacetate with aluminium chloride in nitrobenzene at 27° (10%) [511].
-Also obtained by deacetylation of 4,6-diacetoxy-2-hydroxyacetophenone [1614].
-Also obtained (high yields) by hydrolysis of undermentioned compounds with water at 160-170° [1086],
*ethyl 5,7-dihydroxy-2,4-dioxo-chroman-8-carboxylate;
*ethyl 3-ethoxycarbonylacetyl-2,4,6-trihydroxybenzoate;
*diethyl 5-ethoxycarbonylacetyl-2,4,6-trihydroxy-isophthalate.
-Also obtained by cleavage of 4-methylene-2-phenyl-4*H*-chromen-5,7-diol with boiling 10% potassium hydroxide (low yield) [317] [769].

m.p. 284-285° [1590], 280° [317], 221-223° [1915], 220-222° [1445], 219° [712], 218°5 [817], 218-219° [713] [905], 218° [511] [790] [1086] [1513], 217-218° [416], 216-218° [268], 214-216° [62], 214-215° [879], 213-214° [860] [1633], 209-210° [769];
TLC [763]; tautomerism [1674];
^{1}H NMR [268] [738] [1493], ^{13}C NMR [520] [738] [1396] [1878], IR [1493], UV [347] [645], MS [684].

1-(3,4,5-Trihydroxyphenyl)ethanone

[33709-29-4] $C_8H_8O_4$ mol.wt. 168.15



Syntheses

-Preparation by reaction of aluminium chloride on gallacetophenone trimethyl ether in refluxing chlorobenzene (71%) [1192].
-Preparation from diethyl 3,4,5-triacetoxybenzoylmalonate by hydrolysis and decarboxylation with 10% sulfuric acid in acetic acid at 80° (92%) [652].

-Also refer to: [704] [946].

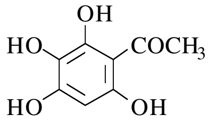
Isolation from natural sources

-This ketone was shown to occur in natural humic acids* and fulvic acids by hydrolysis with 2 N sodium hydroxide at 170° [1569]. Allomelanins* found in soils, coals and peat, resulting from the decomposition of organic matter, particularly dead plants [1790].

m.p. 187-188° [1192]; 178-180° [652]; IR [1569], MS [652] [1569].

1-(2,3,4,6-Tetrahydroxyphenyl)ethanone

[63635-39-2] $C_8H_8O_5$ mol.wt. 184.15



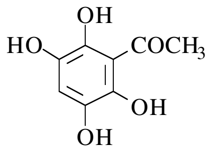
Syntheses

-Preparation by reaction of acetic acid on 1,2,3,5-tetrahydroxybenzene by heating with zinc chloride (Nencki reaction) [758] [1328], (84-85%) [1328].
-Preparation by reaction of acetonitrile on 1,2,3,5-tetrahydroxybenzene (Hoesch reaction) [1342] [1343], (65%) [1343].
-Also obtained by demethylation of 3,6-dihydroxy-2,4-dimethoxyacetophenone with aluminium chloride in boiling chlorobenzene (42%) [1199].
-Also refer to: [758] (compound I); [1344] (compound 9); [1365] (compound 2); [1366] (compound 12).

m.p. 243-244° [1199], 236-238° [1342] [1343], 204-205° [1328];
^{1}H NMR [1343], IR [1343], MS [1343].

1-(2,3,5,6-Tetrahydroxyphenyl)ethanone

$C_8H_8O_5$ mol.wt. 184.15



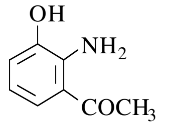
Syntheses

-Preparation by reaction of aluminium bromide on 2,3,5,6-tetramethoxyacetophenone in refluxing benzene (84%) [1560].
-Preparation by reaction of concentrated hydrochloric acid on 2,3,5,6-tetraacetoxyacetophenone in refluxing methanol (77%) [1560].

m.p. 134° [1560].

1-(2-Amino-3-hydroxyphenyl)ethanone

[4502-10-7] $C_8H_9NO_2$ mol.wt. 151.17



Syntheses

-Preparation from 3-hydroxy-2-nitroacetophenone,
*by catalytic hydrogenation in the presence of Raney nickel in ethanol (good yield) [328] or in the presence of 5% Pt/C catalyst in THF under normal pressure at r.t. for 5 h [996], (96%) [575];
*by reduction with iron filings in aqueous hydrochloric acid [1676] (Béchamp reduction).
-Preparation by reaction of hydriodic acid with 3-methoxy-2-nitroacetophenone in the presence of phosphorous. Simultaneous demethylation and reduction of the nitro group occur [1676].
-Also obtained as a side product by photolysis of 3-methylanthranil in 98% sulfuric acid (6%) [545] [546] [673].
-Also obtained from 2-azidoacetophenone, by thermal decomposition in 98% sulfuric acid (9%) [545] [546] or by photolysis in dioxane/water/sulfuric acid mixture (3%) [545] [546].
-Also refer to: [259] (compound 8b) and [321] [329].

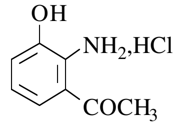
Isolation from natural sources

-By alkaline degradation,
*of *3-hydroxykynurenine* [322] [323] [325], (13%) [327], itself obtained by gentle alkaline degradation of *Xanthommatin* [325];
*of *Ommin* (SM) by heating with 2 N sodium hydroxide in a water bath for 4 h under oxygen atmosphere (53%) [323]. SM was isolated from the eyes of silkworms (*Bombyx Mori*) and prawns (*Crangon vulgaris*);
*of *Ommatin D* [322] according to the method [327];
*of *Ommochromes* (*Xanthommatin, Rhodommatin, Ommatin D* and *Bombyx Ommin*) with 2 N sodium hydroxide by heating in a water bath for 2 h [322].
-Also refer to: [1555].

m.p. 185-187° [575], 185° [1676], 184-185° [546], 183° [327];
paper chromatography [322] [323];
^{1}H NMR [546] [575], ^{13}C NMR [575], IR [327] [546], UV [322] [323] [324] [546], MS [546].

1-(2-Amino-3-hydroxyphenyl)ethanone *(Hydrochloride)*

$C_8H_9NO_2$, HCl mol.wt. 187.63



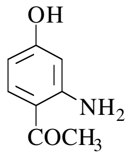
Syntheses

-Obtained by reaction of gaseous hydrochloric acid on 2-amino-3-hydroxyacetophenone in ethanol-ethyl ether mixture (93%) [328].
-Also refer to: [329].

m.p. 215° (d) [328].

1-(2-Amino-4-hydroxyphenyl)ethanone

[90033-64-0] $C_8H_9NO_2$ mol.wt. 151.17



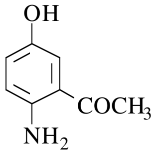
Syntheses

-Preparation by reaction of aluminium chloride with 2-amino-4-methoxyacetophenone in methylene chloride (63%) [297].
-Preparation from 3-hydroxyaniline using acetonitrile with boron trichloride as a catalyst [1710] or by classical Friedel-Crafts techniques [429].

^{1}H NMR [297].

1-(2-Amino-5-hydroxyphenyl)ethanone

[30954-71-3] $C_8H_9NO_2$ mol.wt. 151.17



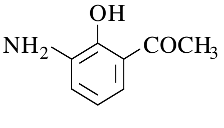
Syntheses

-Preparation by catalytic hydrogenation of 5-hydroxy-2-nitroacetophenone in the presence of platinic oxide in methanol (quantitative yield) [994].
-Also obtained by UV light irradiation of,
*3-methyl-2,1-benzisoxazole (3-methylanthranil), in 98% sulfuric acid (83%) [546], (87%) [545] [673] or in 66% sulfuric acid at 80-90° (88-95%) [682];
*3-methyl-1*H*-indazole, at 11-15°, in dilute sulfuric acid (26-28%) [672] [673] or in methanol, water and sulfuric acid mixture (19%) [673].
-Also obtained from 2-azidoacetophenone,
*by thermal decomposition in 98% sulfuric acid (67%) [545] [546];
*by UV light irradiation in dioxane, water and sulfuric acid mixture (21%) [545] [546].

m.p. 178-179° [546] [672], 176-177° [682] [994];
^{1}H NMR [546] [672], IR [546] [672], UV [546] [672], MS [546] [672].

1-(3-Amino-2-hydroxyphenyl)ethanone

[70977-72-9] $C_8H_9NO_2$ mol.wt. 151.17



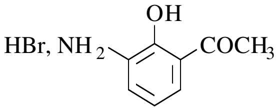
Syntheses

-Preparation by catalytic hydrogenation of 2-hydroxy-3-nitroacetophenone in the presence of Pt/C in ethanol at 25° (90%) [1463].
-Preparation by reaction of stannous chloride on 2-hydroxy-3-nitroacetophenone with hydrochloric acid [372].
-Preparation by hydrogenolysis of 3-amino-5-chloro-2-hydroxyacetophenone [753].
-Preparation by reduction of 2-hydroxy-3-nitroacetophenone (65%) [955].

m.p. 95-97° [1463], 95-96° [955], 93-94° [372] [389].

1-(3-Amino-2-hydroxyphenyl)ethanone *(Hydrobromide)*

[136450-03-8] $C_8H_9NO_2$, HBr mol.wt. 232.08

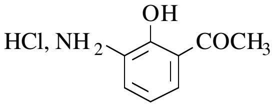


Synthesis

-Preparation by catalytic hydrogenation of 5-bromo-2-hydroxy-3-nitroacetophenone in presence of Pd/C in solution of methanol and methylene chloride mixture at r.t. (99%) [1866].

1-(3-Amino-2-hydroxyphenyl)ethanone *(Hydrochloride)*

[90005-55-3] $C_8H_9NO_2$, HCl mol.wt. 187.63

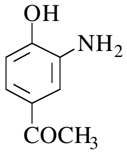


Synthesis

-Preparation by catalytic hydrogenolysis of 3-amino-5-chloro-2-hydroxyacetophenone hydrochloride at 25° in the presence of Pd/C in isopropanol (94%) [753].

1-(3-Amino-4-hydroxyphenyl)ethanone

[54255-50-4] $C_8H_9NO_2$ mol.wt. 151.17



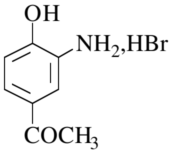
Syntheses

-Preparation by hydrolysis of 3-acetamido-4-hydroxyacetophenone with boiling aqueous hydrochloric acid at 50% HCl [925] or 10 N HCl (78%) [26].
-Preparation from 4-hydroxy-3-nitroacetophenone,
*by catalytic hydrogenation in acetone [154] [1810], (67%) [154] or in the presence of 10% Pd/C in methanol at r.t. (95%) [360];
*by reaction of tin in boiling concentrated hydrochloric acid [560].

m.p. 127-128° [26], 98-99° [360], 98° [154] [925] [1810]. One of the reported melting points is obviously wrong.
oil [560]; ^{1}H NMR [26], IR [26].

1-(3-Amino-4-hydroxyphenyl)ethanone *(Hydrobromide)*

$C_8H_9NO_2$, HBr mol.wt. 232.08



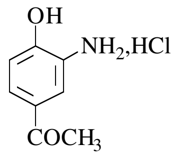
Synthesis

-Refer to: [360].

m.p. 250° (d) [360].

1-(3-Amino-4-hydroxyphenyl)ethanone *(Hydrochloride)*

[14347-14-9] $C_8H_9NO_2$, HCl mol.wt. 187.63



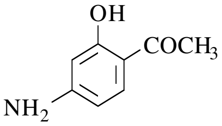
Synthesis

-Obtained on saturating with dry hydrogen chloride gas an acetone-ethyl ether solution of the amine [154].

m.p. > 250° (d) (anhydrous) [154],
232° (monohydrate) [360].

1-(4-Amino-2-hydroxyphenyl)ethanone

[2476-29-1] $C_8H_9NO_2$ mol.wt. 151.17



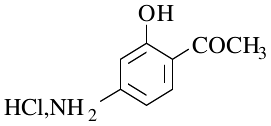
Synthesis

-Preparation by hydrolysis of 4-acetamido-2-hydroxyacetophenone with boiling aqueous hydrochloric acid at 50% HCl [925] or at 15% HCl [383] [681], (86%) [383].

m.p. 130° [925], 129-130° [383], 122-123° [681].

1-(4-Amino-2-hydroxyphenyl)ethanone *(Hydrochloride)*

[51410-07-2] $C_8H_9NO_2$, HCl mol.wt. 187.63

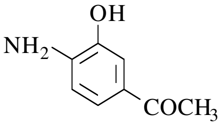


Synthesis

-Refer to: [819].

1-(4-Amino-3-hydroxyphenyl)ethanone

[54903-54-7] $C_8H_9NO_2$ mol.wt. 151.17



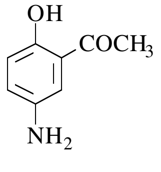
Syntheses

-Preparation from 6-acetyl-2-(3*H*)-benzoxazolinone by alkaline hydrolysis with boiling 10% aqueous sodium hydroxide solution (90 to 100%) [26] [266].
-Also refer to: [203] (compound VI) and [259], (compound 8d).

m.p. 170° [26] [266]; ^{1}H NMR [26], IR [26], UV [324].

1-(5-Amino-2-hydroxyphenyl)ethanone

[50-80-6] $C_8H_9NO_2$ mol.wt. 151.17



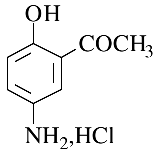
Syntheses

-Preparation by hydrolysis of 5-acetamido-2-methoxyacetophenone (80%) [387].
-Preparation by hydrolysis of 5-acetamido-2-hydroxyacetophenone with boiling aqueous hydrochloric acid solution [372] [395] [681] [925] [1047] [1048] [1273], (50%) [395] [1047], (84%) [372].
-Preparation by reduction of 2-hydroxy-5-nitroacetophenone,
*with stannous chloride [372] [395] [1104], (53%) [1104];
*by electrolytic way in concentrated sulfuric acid [666].
-The 5-amino-2-hydroxyacetophenone hydrochloride, by treatment with ammonia gave the keto-base [1475].
-Also obtained by electrolytic reduction of 3-nitroacetophenone in concentrated sulfuric acid [1694].

m.p. 121-122° [1104], 118° [1273] [1475], 112-113°5 [387],
112-113° [372], 110° [395] [666] [925] [1694], 105° [1047] [1048].

1-(5-Amino-2-hydroxyphenyl)ethanone *(Hydrochloride)*

[57471-32-6] $C_8H_9NO_2$, HCl mol.wt. 187.63



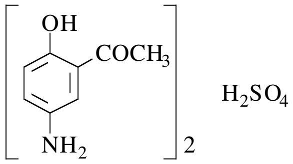
Synthesis

-Obtained by reaction of gaseous hydrochloric acid on 5-amino-2-hydroxyacetophenone in ethanol [372] [1273] or in ethyl ether [1047] [1048].

m.p. 230-240° (d) [372], 231° [1475], 155° (d) [1047] [1048].

1-(5-Amino-2-hydroxyphenyl)ethanone *(Sulfate)*

2 $C_8H_9NO_2$, H_2SO_4 mol.wt. 400.41



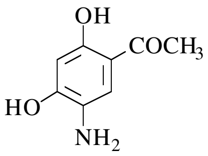
Synthesis

-Easily obtained by reaction of sulfuric acid on 5-amino-2-hydroxyacetophenone in ethyl ether [1048].

m.p. 150° [1048].

1-(5-Amino-2,4-dihydroxyphenyl)ethanone

[5528-13-2] $C_8H_9NO_3$ mol.wt. 167.16



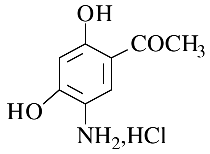
Synthesis

-Preparation from 2,4-dihydroxy-5-nitroacetophenone by reduction in acetone solution using Raney catalyst [1362].

m.p. 137-142° (d) [1362].

1-(5-Amino-2,4-dihydroxyphenyl)ethanone *(Hydrochloride)*

$C_8H_9NO_3$, HCl mol.wt. 203.61



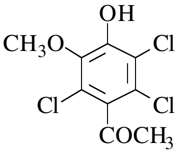
Synthesis

-Prepared by passing dry hydrochloric acid in 2,4-dihydroxy-5-aminoacetophenone in acetone solution, and adding ethyl ether when needed for precipitation [1362].

m.p. > 300° [1362].

1-(2,3,6-Trichloro-4-hydroxy-5-methoxyphenyl)ethanone

[94649-69-1] $C_9H_7Cl_3O_3$ mol.wt. 269.51



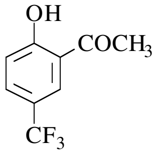
Synthesis not yet described

-Identified in wheat and rye straw pulp bleaching and combined mill effluents [617].

-Identified on control of effluent from the manufacturing of bleached pulp and paper from sugarcane bagasse [616].

1-[2-Hydroxy-5-(trifluoromethyl)phenyl]ethanone

[67589-15-5] $C_9H_7F_3O_2$ mol.wt. 204.15



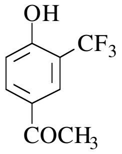
Synthesis

-Preparation by reaction of acetyl chloride with p-(trifluoromethyl)phenol in hydrofluoric acid for 6 h to 100° under 3 atmospheres (88%) [1225].

^1H NMR [1225], IR [1225].

1-[4-Hydroxy-3-(trifluoromethyl)phenyl]ethanone

[149105-11-3] $C_9H_7F_3O_2$ mol.wt. 204.15



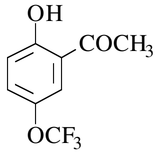
Synthesis

-Obtained by heating to 180° under nitrogen a mixture of 4-methoxy-3-(trifluoromethyl)acetophenone and pyridinium chloride (39%) [1373].

m.p. 168-170° [1373].

1-[2-Hydroxy-5-(trifluoromethoxy)phenyl]ethanone

[146575-64-6] $C_9H_7F_3O_3$ mol.wt. 220.15

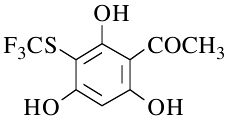


Synthesis

-Preparation by reaction of pyridinium dichromate with 4-trifluoromethoxy-2-(α-hydroxyethyl)phenol in the presence of Celite in methylene chloride at r.t. (85%) [1919] [1920].

1-[2,4,6-Trihydroxy-3-[(trifluoromethyl)thio]phenyl]ethanone

[66625-03-4] $C_9H_7F_3O_4S$ mol.wt. 268.21



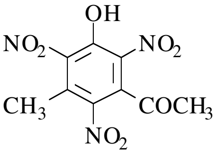
Synthesis

-Preparation by reaction of trifluoromethanesulfonyl chloride with phloroacetophenone in chloroform in the presence of a slight excess of pyridine, first at -40°, then at 60° for 3 h (33%) [456].

m.p. 139-140° [456]; ^{1}H NMR [456], IR [456].

1-(3-Hydroxy-5-methyl-2,4,6-trinitrophenyl)ethanone

$C_9H_7N_3O_8$ mol.wt. 285.17



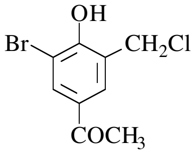
Synthesis

-Obtained by reaction of nitric acid on 3-hydroxy-5-methylacetophenone in acetic anhydride at 10° (23%) [324].

m.p. 195-196° [324].

1-[3-Bromo-5-(chloromethyl)-4-hydroxyphenyl]ethanone

[107724-60-7] $C_9H_8BrClO_2$ mol.wt. 263.52



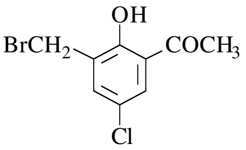
Synthesis

-Preparation by adding a methylene chloride solution of bromine to a methanol/methylene chloride solution of 3-(chloromethyl)-4-hydroxyacetophenone at 0° (85%) [273].

m.p. 120-121° [273]; ^{1}H NMR [273], IR [273], MS [273].

1-[3-(Bromomethyl)-5-chloro-2-hydroxyphenyl]ethanone

[50317-56-1] $C_9H_8BrClO_2$ mol.wt. 263.52



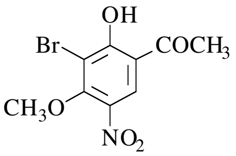
Syntheses

-Preparation by heating 3,3'-diacetyl-5,5'-dichloro-2,2'-dihydroxydibenzyl ether with an 48% aqueous hydrobromic acid solution during 8 h (61%) [284].
-Preparation by [Quelet (bromomethylation) reaction] of 5-chloro-2-hydroxyacetophenone [284] according to [1141].

m.p. 74-76° [284].

1-(3-Bromo-2-hydroxy-4-methoxy-5-nitrophenyl)ethanone

[134700-74-6] $C_9H_8BrNO_5$ mol.wt. 290.07

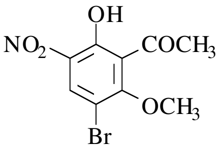


Synthesis

-Refer to: [63] (compound 1d).

1-(3-Bromo-6-hydroxy-2-methoxy-5-nitrophenyl)ethanone

[7253-20-5] $C_9H_8BrNO_5$ mol.wt. 290.07



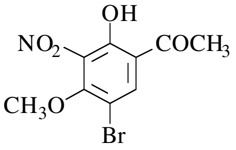
Syntheses

-Preparation by bromination of 2-hydroxy-6-methoxy-3-nitroacetophenone [476] [1023] [1094], (44%) [1023].
-Obtained by reaction of nitric acid (d = 1.4) on 2,2'-dihydroxy-3,3'-diacetyl-4,4'-dimethoxy-5,5'-dibromophenyl thioether, at 0° [476].

m.p. 160-162° [1023], 156-157° [476] [1094]; IR [1023].

1-(5-Bromo-2-hydroxy-4-methoxy-3-nitrophenyl)ethanone

$C_9H_8BrNO_5$ mol.wt. 290.07



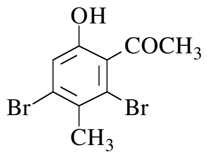
Synthesis

-Preparation by reaction of nitric acid on 5-bromo-2-hydroxy-4-methoxyacetophenone in acetic acid at r.t. [7].

m.p. 112-114° [7].

1-(2,4-Dibromo-6-hydroxy-3-methylphenyl)ethanone

[212494-38-7] $C_9H_8Br_2O_2$ mol.wt. 307.97

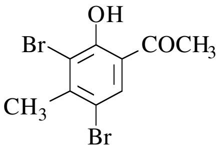


Synthesis

-Refer to: [1292].

1-(3,5-Dibromo-2-hydroxy-4-methylphenyl)ethanone

[145666-17-7] $C_9H_8Br_2O_2$ mol.wt. 307.97



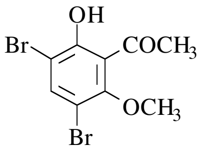
Syntheses

-Preparation by reaction of bromine with 2-hydroxy-4-methylacetophenone in aqueous acetic acid (68%) [228].
-Also refer to: [1205] (compound 1b).

m.p. 107-108° [228]; ^{1}H NMR [228], IR [228].

1-(3,5-Dibromo-2-hydroxy-6-methoxyphenyl)ethanone

[16290-04-3] $C_9H_8Br_2O_3$ mol.wt. 323.97



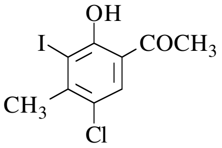
Synthesis

-Preparation by reaction of bromine with 2-hydroxy-6-methoxyacetophenone in acetic acid at 35° (62%) [403].

m.p. 90-90°5 [403]; ^{1}H NMR [403].

1-(5-Chloro-2-hydroxy-3-iodo-4-methylphenyl)ethanone

[292144-86-6] $C_9H_8ClIO_2$ mol.wt. 310.52



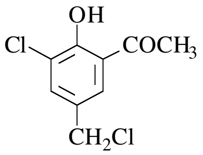
Synthesis

-Preparation by iodination of 5-chloro-2-hydroxy-4-methylacetophenone with iodine (1 mol) and iodic acid (1 mol) in ethanol at 35-40° for 1.5 h (75-85%) [484].

m.p. 76° [484].

1-[3-Chloro-5-(chloromethyl)-2-hydroxyphenyl]ethanone

[66883-87-2] $C_9H_8Cl_2O_2$ mol.wt. 219.07



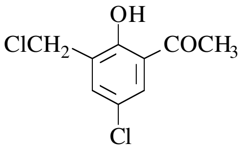
Syntheses

-Preparation from 3-chloro-2-hydroxyacetophenone in acetic acid solution by introduction of the chloromethyl group into aromatic ring by treatment with formaldehyde and hydrogen chloride in the presence of zinc chloride (44%) [719] [Blanc (Chloromethylation) reaction].
-Also refer to: [717] [718].

m.p. 145° [719].

1-[5-Chloro-3-(chloromethyl)-2-hydroxyphenyl]ethanone

[34987-36-5] $C_9H_8Cl_2O_2$ mol.wt. 219.07



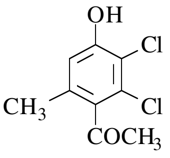
Syntheses

-Preparation from 5-chloro-2-hydroxyacetophenone in ethylene dichloride solution by introduction of the chloromethyl group into aromatic ring by treatment with 37% formalin and hydrogen chloride in the presence of zinc chloride at 60-65° (76-68%) [283] [285], [Blanc (Chloromethylation) reaction].
-Preparation by reaction of concentrated hydrochloric acid with 5-chloro-2-hydroxy-3-hydroxymethylacetophenone for 5 days at 20° (95%) [284].
-Also refer to: [289] [717] [718].

m.p. 68°5-69° [285], 67-68° [284];
b.p.$_2$ 130-135° [285], b.p.$_3$ 140-142° [284]; IR [283].

1-(2,3-Dichloro-4-hydroxy-6-methylphenyl)ethanone

[21472-87-7] $C_9H_8Cl_2O_2$ mol.wt. 219.07



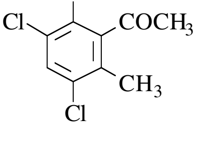
Synthesis

-Obtained as a trace during the rearrangement of 1,2,3,3-tetrachlorocyclopropane-cis-1,2-diacetone by heating with a saturated solution of sodium bisulfate in acetic acid at 100° (< 1%) [767].

m.p. 107-108° [767]; ^{1}H NMR [767], IR [767].

1-(3,5-Dichloro-2-hydroxy-6-methylphenyl)ethanone

$C_9H_8Cl_2O_2$ mol.wt. 219.07



Syntheses

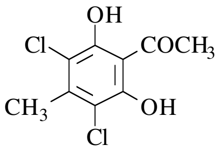
-Obtained by Fries rearrangement of 2,4-dichloro-5-methylphenyl acetate with aluminium chloride at 135° (21%) [452].
-Obtained by reaction of pyridinium chloride on 3,5-dichloro-2-methoxy-6-methylacetophenone at 210° (21%) [452].

-Also obtained by reaction of levulinic acid on 3,5-dichloro-2-hydroxy-6-methylacetophenone hydrazone in 1 N hydrochloric acid using a steam bath (15%) [452].
-Also obtained by basic hydrolysis of 6,8-dichloro-2,5-dimethylchromone with 5% aqueous sodium hydroxide in refluxing methanol (4%) [452].

m.p. 104-105°5 [452].

1-(3,5-Dichloro-2,6-dihydroxy-4-methylphenyl)ethanone

[3361-23-7] $C_9H_8Cl_2O_3$ mol.wt. 235.07



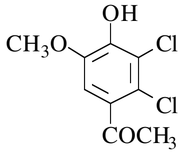
Synthesis

-Preparation by reaction of sulfuryl chloride with 2,6-dihydroxy-4-methylacetophenone in ethyl ether (71%) [612].

m.p. 164-165° [612].

1-(2,3-Dichloro-4-hydroxy-5-methoxyphenyl)ethanone

[154638-85-4] $C_9H_8Cl_2O_3$ mol.wt. 235.07



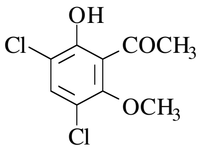
Synthesis

-Obtained by chlorination of acetoguaiacone in dioxane-water mixture at 40° (29%) [1456].

MS [1456].

1-(3,5-Dichloro-2-hydroxy-6-methoxyphenyl)ethanone

[87953-94-4] $C_9H_8Cl_2O_3$ mol.wt. 235.07



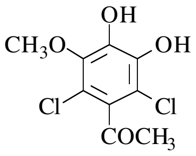
Syntheses

-Preparation by reaction of chlorine on 2-hydroxy-6-methoxyacetophenone in chloroform at r.t. (50%) [502].
-Preparation by reaction of sulfuryl chloride on 2-hydroxy-6-methoxyacetophenone in refluxing acetic acid [1112].
-Also obtained by reaction of dimethyl sulfate on 3,5-dichloro-2,6-dihydroxyacetophenone with potassium carbonate in refluxing benzene (very low yield) [1112].

m.p. 99° [502], 97-98° [1112].

1-(2,6-Dichloro-3,4-dihydroxy-5-methoxyphenyl)ethanone

[75322-34-8] $C_9H_8Cl_2O_4$ mol.wt. 251.07



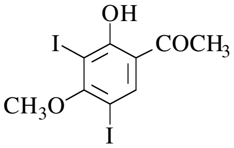
Synthesis

-Preparation by chlorination of acetosyringone (main product) [1224].

Visible light absorption spectra [1224].

1-(2-Hydroxy-3,5-diiodo-4-methoxyphenyl)ethanone

$C_9H_8I_2O_3$ mol.wt. 417.97



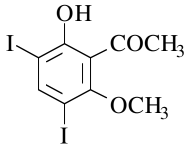
Syntheses

-Obtained by reaction of an aqueous iodine-iodic acid solution on paeonol in ethanol at r.t. (8%) [1600].
-Also obtained by hydrolysis of 6,8-diiodo-7-methoxy-2-methylchromone by boiling 10% aqueous sodium hydroxide solution [1600].

m.p. 98-99° [1600].

1-(2-Hydroxy-3,5-diiodo-6-methoxyphenyl)ethanone

$C_9H_8I_2O_3$ mol.wt. 417.97



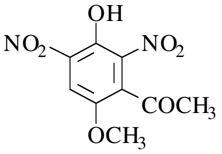
Syntheses

-Preparation by reaction of an aqueous iodine-iodic acid solution on 2-hydroxy-6-methoxyacetophenone in ethanol at r.t. (76%) [1600].
-Also obtained by hydrolysis of 6,8-diiodo-5-methoxy-2-methylchromone by boiling 10% aqueous sodium hydroxide solution [1600].

m.p. 111° [1600].

1-(3-Hydroxy-6-methoxy-2,4-dinitrophenyl)ethanone

$C_9H_8N_2O_7$ mol.wt. 256.17



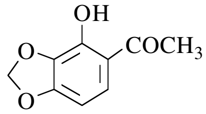
Synthesis

-Preparation by reaction of dimethyl sulfate on 3,6-dihydroxy-2,4-dinitroacetophenone with sodium hydroxide in water at 60-65° (53%) [577].

m.p. 94-96° [577]; IR [577], UV [577].

1-(4-Hydroxy-1,3-benzodioxol-5-yl)ethanone

[23780-60-1] $C_9H_8O_4$ mol.wt. 180.16



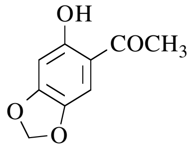
Synthesis

-Obtained (poor yield) by reaction of methylene iodide with gallacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h (9%) [1384] [1385].

m.p. 85-86° [1384] [1385]; TLC [1385]; column chromatography [1384]; ^{1}H NMR [1384] [1385], IR [1384] [1385], UV [1384] [1385].

1-(6-Hydroxy-1,3-benzodioxol-5-yl)ethanone

[66003-50-7] $C_9H_8O_4$ mol.wt. 180.16



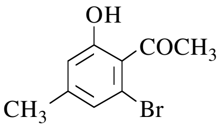
Syntheses

-Obtained by refluxing methylene iodide and 2,4,5-trihydroxyacetophenone in acetone in the presence of potassium carbonate (56%) [1670], (51%) [687].
-Also obtained by Fries rearrangement of 5-acetoxy-1,3-benzodioxole with aluminium chloride in nitrobenzene at -10 to 7°, then 3 days at r.t. (5%) [1506].
-Also obtained by Friedel-Crafts acylation of 5-hydroxy-1,3-benzodioxole *(Sesamol)* with acetic anhydride in the presence of boron trifluoride etherate for 1 h at 80-90° (75%) [1892].
-Also obtained by reaction of acetonitrile with 5-hydroxy-1,3-benzodioxole (Hoesch reaction) [1670], (35%) [641], (31%) [401].
-Also obtained by reaction of acetyl chloride with sesamol methyl ether (b.p.$_{18}$ 110-114°) in the presence of aluminium chloride in ethyl ether at r.t. overnight (36%) [641].
-Also obtained (poor yield) by reaction of acetic acid with sesamol in the presence of boron trifluoride for 3 h, then heating at 80-90° for 1.5 h (5%) [641].
-Also refer to: [401] [641].

m.p. 114° [1506], 113-114° [641], 112° [1670], 111-112° [401] [1892];
^{1}H NMR [401] [1670], IR [401] [641] [1670], UV [401], MS [401].

1-(2-Bromo-6-hydroxy-4-methylphenyl)ethanone

$C_9H_9BrO_2$ mol.wt. 229.07



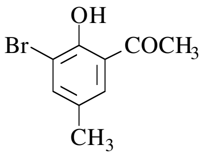
Synthesis

-Obtained by reaction of acetyl chloride with 3-bromo-5-methylanisole in the presence of aluminium chloride in refluxing carbon disulfide [111].

m.p. 50-52° [111].

1-(3-Bromo-2-hydroxy-5-methylphenyl)ethanone

[56609-15-5] $C_9H_9BrO_2$ mol.wt. 229.07



Syntheses

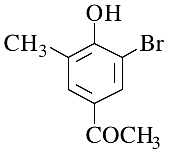
-Preparation by Fries rearrangement of 2-bromo-4-methylphenyl acetate,
*with aluminium chloride without solvent at 110° or in refluxing nitrobenzene (90%) [1798];
*with zinc chloride or boron trifluoride in nitrobenzene at 100° (80-85%) [1798];
*with ferric chloride or stannic chloride in nitrobenzene at 100° (55-70%) [1798].
-Preparation by reaction of bromine on 2-hydroxy-5-methylacetophenone in acetic acid at r.t. (quantitative yield) [1893], (65-70%) [152] [330] [1152] [1206].
-Also refer to: [1204] [1205] [1207] [1208].
-Preparation by reaction of N-bromosuccinimide with 2-hydroxy-5-methylacetophenone in DMF at r.t. (93-96%) [527] [528].
N.B.: It is mentioned in the patent [1149] (page 26) that this hydroxyketone, the 1-(3-bromo-2-hydroxy-5-methylphenyl)ethanone (**I**) has been prepared by Fries rearrangement ($AlCl_3$/165°) of

4-bromo-3-methylphenyl acetate, itself obtained from the 4-bromo-3-methylphenol. This is impossible. The Fries rearrangement of the above ester always leads to 1-(5-bromo-2-hydroxy-4-methylphenyl)ethanone (**II**). There are two possibilities:
*either the ester used for Fries rearrangement was the 2-bromo-4-methylphenyl acetate and provides (**I**).
*or the obtained hydroxyketone should be (**II**). This appears confirmed later on by obtaining 6-bromo-3,4-dihydro-2,2,7-trimethyl-2*H*-1-benzopyran-4-one with this hydroxyketone [1149].

m.p. 95° [1152], 94-95° [152], 89° [330], 88°5-89°5 [1893], 88-89° [527] [528].
b.p.$_2$ 126-127° [1798]; pK$_a$ [1387]; ^{1}H NMR [527], MS [527].

1-(3-Bromo-4-hydroxy-5-methylphenyl)ethanone

[127923-55-1] $C_9H_9BrO_2$ mol.wt. 229.07



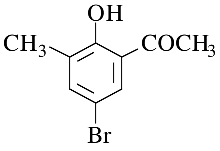
Synthesis

-Preparation by reaction of bromine with 4-hydroxy-3-methylacetophenone in aqueous acetic acid, first at 5°, then at r.t. (89%) [89].

m.p. 145-146° [89].

1-(5-Bromo-2-hydroxy-3-methylphenyl)ethanone

[72422-80-1] $C_9H_9BrO_2$ mol.wt. 229.07



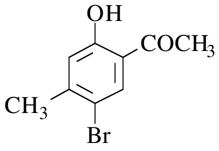
Syntheses

-Preparation by reaction of bromine with 2-hydroxy-3-methylacetophenone in acetic acid at r.t. (80%) [227] (66%) [152].
-Also refer to: [1204] (compound 1e) and [1205] (compound 1a).

m.p. 78-79° [227], 77-78° [152]; ^{1}H NMR [227], IR [227].

1-(5-Bromo-2-hydroxy-4-methylphenyl)ethanone

[50342-17-1] $C_9H_9BrO_2$ mol.wt. 229.07



Syntheses

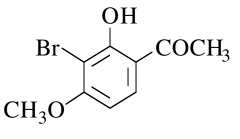
-Preparation by reaction of bromine on 2-hydroxy-4-methylacetophenone in chloroform at < -10° (74%) [653] or in acetic acid at r.t. (38%) [152].
-Preparation by Fries rearrangement of 4-bromo-3-methylphenyl acetate with aluminium chloride without solvent at 165-180° [653] [1149], (80%) [653].

-Also refer to: [1205].

m.p. 86° [152], 81-82° [1149], 80° [653]; ^{1}H NMR [653].

1-(3-Bromo-2-hydroxy-4-methoxyphenyl)ethanone

[39503-62-3] $C_9H_9BrO_3$ mol.wt. 245.07



Syntheses

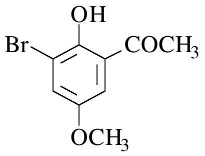
-Preparation by reaction of bromine on 2-hydroxy-4-methoxyacetophenone with titanium tetrachloride in methylene chloride at r.t. (65%) [454].

-Also obtained (by-product) by reaction of cupric bromide with 2-hydroxy-4-methoxyacetophenone in refluxing dioxane (3%) [1137].

m.p. 130-131° [454], 120-122° [1137]; ^{1}H NMR [454] [1137].

1-(3-Bromo-2-hydroxy-5-methoxyphenyl)ethanone

[37113-61-4] $C_9H_9BrO_3$ mol.wt. 245.07



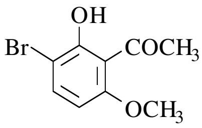
Syntheses

-Preparation by reaction of bromine on 2-hydroxy-5-methoxyacetophenone with aluminium chloride,
*in chloroform at 10° (80%) [850];
*in carbon disulfide at r.t. (65%) [374].

m.p. 78-79° [850], 76-76°5 [374]; ^{1}H NMR [850], IR [850].

1-(3-Bromo-2-hydroxy-6-methoxyphenyl)ethanone

[37113-62-5] $C_9H_9BrO_3$ mol.wt. 245.07



Syntheses

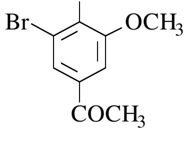
-Preparation by diazotization of 3-amino-2-hydroxy-6-methoxyacetophenone and replacement of the diazonium group by bromine (Sandmeyer reaction) (28%) [371], (19%) [1213].

-Preparation by bromination of 2-hydroxy-6-methoxyacetophenone, with bromine [371], in methylene chloride (76%) [1873], in chloroform [543] [850] [1213], (68%) [1213] or in acetic anhydride (44%) [190] or with N-bromosuccinimide (41%) [371].

m.p. 102-103° [543], 101-102° [190], 101° [1873], 100-101° [371] [850], 99-100° [1213]; ^{1}H NMR [190] [543] [850], IR [850].

1-(3-Bromo-4-hydroxy-5-methoxyphenyl)ethanone

[103653-14-1] $C_9H_9BrO_3$ mol.wt. 245.07



Syntheses

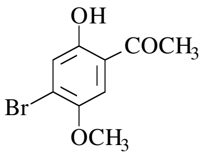
-Preparation by reaction of bromine with acetovanillone in aqueous acetic acid at 0°, then at r.t. (54%) [1937].

-Preparation by adding bromine to a solution of acetovanillone, sodium acetate and potassium bromide in aqueous methanol cooled to -60° [549].

m.p. 156-157° [1937], 155-157° [549].

1-(4-Bromo-2-hydroxy-5-methoxyphenyl)ethanone

[90971-91-8] $C_9H_9BrO_3$ mol.wt. 245.07



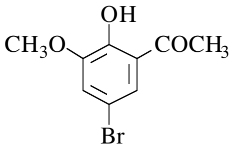
Synthesis

-Preparation by reaction of methyl iodide on 4-bromo-2,5-dihydroxyacetophenone with potassium carbonate in refluxing methyl ethyl ketone [1604].

m.p. 115° [1604].

1-(5-Bromo-2-hydroxy-3-methoxyphenyl)ethanone

$C_9H_9BrO_3$ mol.wt. 245.07



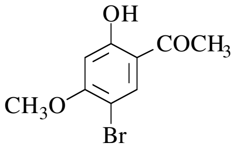
Syntheses

-Preparation by reaction of bromine on 2-hydroxy-3-methoxyacetophenone in the presence of sodium bromide in 1:1 aqueous ethanol at 25° (48%) [813].
-Preparation by reaction of hydrobromic acid on 5-bromo-2,3-dimethoxyacetophenone in acetic acid (36%) [813].

m.p. 108-109° [813]; UV [813].

1-(5-Bromo-2-hydroxy-4-methoxyphenyl)ethanone

[39503-61-2] $C_9H_9BrO_3$ mol.wt. 245.07



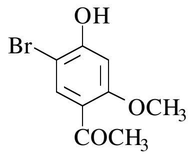
Syntheses

-Preparation by reaction of bromine on paeonol (2-hydroxy-4-methoxyacetophenone),
*in methylene chloride at r.t. (quantitative yield) [454];
*in acetic acid at r.t. [7] [943] [947] [982] [1626], (60%) [947];
*in acetic anhydride (48%) [190].
-Preparation by diazotization of 5-amino-2-hydroxy-4-methoxyacetophenone and replacement of the diazonium group by bromine (Sandmeyer reaction) [947].
-Also obtained by reaction of dimethyl sulfate on 5-bromoresacetophenone in sodium hydroxide [947].
-Also obtained as one of the products of bromination of paeonol acetate in carbon disulfide [306].
-Also obtained as one of the products of reaction of cupric bromide on paeonol in refluxing dioxane (17%) [1137].
-Also obtained (by-product) by reaction of acetic anhydride on 4-bromoresorcinol dimethyl ether with aluminium chloride in refluxing carbon disulfide [1644].
-Also obtained (by-product) by reaction of N-bromosuccinimide on 2,4-dimethoxyacetophenone with benzoyl peroxide in refluxing carbon tetrachloride [1644].
-Also refer to: [1248].

m.p. 172-174° [1626], 172-172°5 [454], 172° [947], 171-172° [1644], 171° [306], 170-172° [190], 169-170° [1137], 169° [7], 168-170° [982];
^{1}H NMR [190] [454] [1137].

1-(5-Bromo-4-hydroxy-2-methoxyphenyl)ethanone

$C_9H_9BrO_3$ mol.wt. 245.07



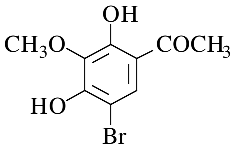
Synthesis

-Preparation by bromination of isopaeonol (4-hydroxy-2-methoxyacetophenone) in chloroform [947].

m.p. 198° [947].

1-(5-Bromo-2,4-dihydroxy-3-methoxyphenyl)ethanone

[62615-25-2] $C_9H_9BrO_4$ mol.wt. 261.07



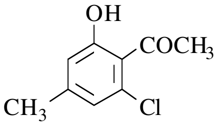
Synthesis

-Preparation by bromination of 2,4-dihydroxy-3-methoxyacetophenone with bromine in 80% acetic acid at r.t. (64%) [1571].

m.p. 110°5-112°5 [1571]; ^{1}H NMR [1571].

1-(2-Chloro-6-hydroxy-4-methylphenyl)ethanone

[24490-25-3] $C_9H_9ClO_2$ mol.wt. 184.62

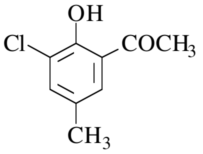


Synthesis not yet described

-Refer to: [1813]; this sole reference mentioned for this compound (Chem. Abstr., **71**, 86368b (1969)) is erroneous. Actually, the ketone described as being the 2'-chloro-6'-hydroxy-4'-methylacetophenone is in fact the 5'-chloro-2'-hydroxy-4'-methylacetophenone in original publication.

1-(3-Chloro-2-hydroxy-5-methylphenyl)ethanone

[7507-88-2] $C_9H_9ClO_2$ mol.wt. 184.62



Syntheses

-Preparation by Fries rearrangement of 2-chloro-4-methylphenyl acetate with aluminium chloride without solvent at 120° (quantitative yield) [1512].

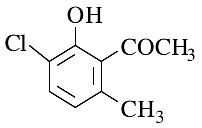
-Obtained by reaction of aluminium chloride on a mixture of 2-chloro-4-methylphenyl acetate and 4-methylphenyl benzoate without solvent at 150° (33-37%) [103].

-Obtained by reaction of aluminium chloride on a mixture of 2,4,6-trimethylphenyl acetate or 4-methylphenyl acetate and 2-chloro-4-methylphenyl benzoate without solvent at 150° (67% yield and small amounts, respectively) [103].

m.p. 91° [103] [1512]; pK_a [1387].

1-(3-Chloro-2-hydroxy-6-methylphenyl)ethanone

[85128-50-3] $C_9H_9ClO_2$ mol.wt. 184.62

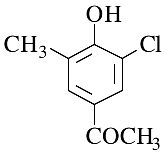


Synthesis

-Refer to: [1346] and [1347] (ketone **13**).

1-(3-Chloro-4-hydroxy-5-methylphenyl)ethanone

[54556-95-5] $C_9H_9ClO_2$ mol.wt. 184.62



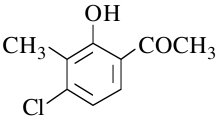
Syntheses

-Preparation by Fries rearrangement of 2-chloro-6-methylphenyl acetate in the presence of aluminium chloride without solvent at 140° (74%) [1574].
-Preparation by chlorination of 4-hydroxy-3-methylacetophenone [1574].
-Also refer to: [1573].

m.p. 123°5-124° [1574]; IR [1574].

1-(4-Chloro-2-hydroxy-3-methylphenyl)ethanone

[198344-86-4] $C_9H_9ClO_2$ mol.wt. 184.62

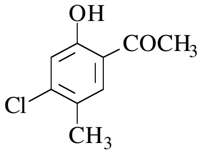


Synthesis

-Refer to: [3].

1-(4-Chloro-2-hydroxy-5-methylphenyl)ethanone

[57051-51-1] $C_9H_9ClO_2$ mol.wt. 184.62

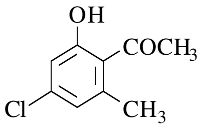


Synthesis

-Preparation by Fries rearrangement of 3-chloro-4-methylphenyl acetate with aluminium chloride without solvent at 125° [1788].

1-(4-Chloro-2-hydroxy-6-methylphenyl)ethanone

[87239-37-0] $C_9H_9ClO_2$ mol.wt. 184.62

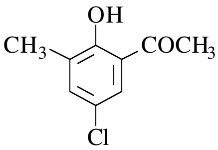


Synthesis

-Refer to: [1042].

1-(5-Chloro-2-hydroxy-3-methylphenyl)ethanone

[50343-12-9] $C_9H_9ClO_2$ mol.wt. 184.62



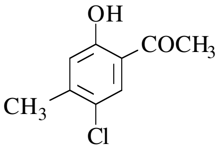
Syntheses

-Preparation by Fries rearrangement of 4-chloro-2-methylphenyl acetate with aluminium chloride without solvent at 120° (97%) [284], (75%) [367].
-Preparation by adding zinc dust to an acetic acid solution of 5-chloro-3-(chloromethyl)-2-hydroxyacetophenone at 100° (82%) [284].
-Also obtained (by-product) by chloromethylation of 5-chloro-2-hydroxyacetophenone (5%) [283].
-Also obtained (poor yield) by treatment of 5-chloro-3-(chloromethyl)-2-hydroxyacetophenone with zinc chloride in methylene chloride in the presence of water for 45 h at 60° (5%) [283].

m.p. 70° [367], 65-66° [284], 63-64° [283]; b.p.$_{16}$ 141° [284].

1-(5-Chloro-2-hydroxy-4-methylphenyl)ethanone

[28480-70-8] $C_9H_9ClO_2$ mol.wt. 184.62



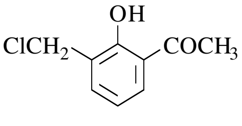
Syntheses

-Preparation by reaction of acetic acid on 4-chloro-3-methylphenol with boron trifluoride at 70-100° (80-85%) [979].
-Preparation by Fries rearrangement of 4-chloro-3-methylphenyl acetate with aluminium chloride without solvent between 110 to 155° [214] [895] [991] [1512] [1538] [1581] [1894], (quantitative yield) [1538] [1894], (64%) [214] [1581].
-Also obtained by reaction of acetyl chloride on 4-chlorothymol methyl ether with aluminium chloride in carbon disulfide at r.t. (8%) [1524].
-Also refer to: [895] (compound CHMA).

m.p 75°5 [1538], 71-72° [1512], 71° [991], 70°5 [979], 70° [1524], 69-70° [1894];
b.p.$_{15}$ 137° [1512], b.p.$_{21}$ 140-142° [214] [1581];
^{1}H NMR [1698], UV [1698], fluorescence spectra [1698] [1813].

1-[3-(Chloromethyl)-2-hydroxyphenyl]ethanone

[87165-49-9] $C_9H_9ClO_2$ mol.wt. 184.62



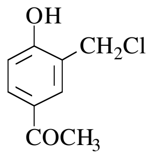
Synthesis

-Preparation by reaction of polyoxymethylene with 2-hydroxyacetophenone in the presence of concentrated hydrochloric acid at 50-60° [289].

m.p. 45° [289]; ^{1}H NMR [289], IR [289].

1-[3-(Chloromethyl)-4-hydroxyphenyl]ethanone

[24085-05-0] $C_9H_9ClO_2$ mol.wt. 184.62



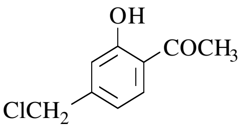
Syntheses

-Preparation by introduction of the chloromethyl group into 4-hydroxyacetophenone by treatment with formaldehyde and hydrochloric acid [775] [935] [1667] [1812], in the presence of zinc chloride [182], [Blanc (Chloromethylation) reaction], (85-92%) [775] [1667] [1812].
-Also refer to: [576] [1122].

m.p. 160° (d) [775] [1812].

1-[4-(Chloromethyl)-2-hydroxyphenyl]ethanone

[107223-42-7] $C_9H_9ClO_2$ mol.wt. 184.62



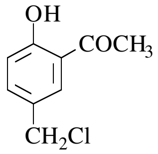
Synthesis

-Preparation by reaction of ethyl chloroformate with 4-(dimethylaminomethyl)-2-hydroxyacetophenone in toluene (22%) [530].

m.p. 34-37° [530].

1-[5-(Chloromethyl)-2-hydroxyphenyl]ethanone

[30787-43-0] $C_9H_9ClO_2$ mol.wt. 184.62



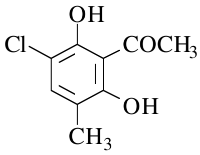
Syntheses

-Preparation by reaction of formaldehyde solution with hydrochloric acid on 2-hydroxyacetophenone at 25-30° (57-61%) [1811].
-Preparation by reaction of polyoxymethylene with 2-hydroxyacetophenone in the presence of hydrochloric acid at 50-60° [289].

m.p. 94-95° [1811].

1-(3-Chloro-2,6-dihydroxy-5-methylphenyl)ethanone

[56581-46-5] $C_9H_9ClO_3$ mol.wt. 200.62



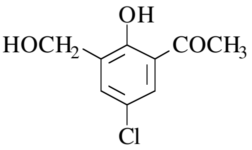
Synthesis

-Preparation by reaction of chlorine on 2,6-dihydroxy-3-methylacetophenone in acetic acid at r.t. [1746].

m.p. 152° [1746];
^{1}H NMR [1746], IR [1746], MS [1746].

1-[5-Chloro-2-hydroxy-3-(hydroxymethyl)phenyl]ethanone

[50317-52-7] $C_9H_9ClO_3$ mol.wt. 200.62



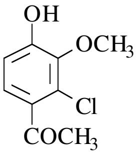
Syntheses

-Preparation by boiling an aqueous solution of 5-chloro-3-(chloromethyl)-2-hydroxyacetophenone for 6 h (73%) [284].
-Also obtained as a labile intermediate product during the chloromethylation of 5-chloro-2-hydroxyacetophenone (< 5%) [283].

m.p. 82°5-84° [284]; b.p.$_1$ 155° [284].

1-(2-Chloro-4-hydroxy-3-methoxyphenyl)ethanone

[151340-06-6] $C_9H_9ClO_3$ mol.wt. 200.62



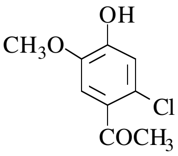
Synthesis

-Preparation from the acetate of 2-chlorovanillin by reaction with diazomethane and subsequent hydrolysis [1657] [1659] .

m.p. 97-98° [1657] [1659];
^1H NMR [1657], ^{13}C NMR [1657], MS [1657].

1-(2-Chloro-4-hydroxy-5-methoxyphenyl)ethanone

[69240-98-8] $C_9H_9ClO_3$ mol.wt. 200.62



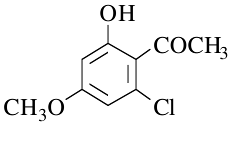
Syntheses

-Obtained from the acetate of 6-chlorovanillin by reaction with diazomethane and subsequent hydrolysis [1657] [1659], (11-17%) [892] [1657].
-Also refer to: [1009] (compound XVIIe).

m.p. 109-110° [892], 107-108° [1657];
^1H NMR [1657], ^{13}C NMR [1657], MS [1657].

1-(2-Chloro-6-hydroxy-4-methoxyphenyl)ethanone

[112954-19-5] $C_9H_9ClO_3$ mol.wt. 200.62



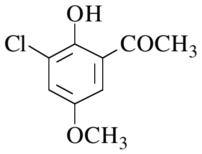
Syntheses

-Preparation by reaction of acetyl chloride with 3,5-dimethoxy-1-chlorobenzene in the presence of aluminium chloride (Friedel-Crafts reaction) (38%) [985].
-Also refer to: [741] [984].

^1H NMR [985].

1-(3-Chloro-2-hydroxy-5-methoxyphenyl)ethanone

[286931-53-1] $C_9H_9ClO_3$ mol.wt. 200.62



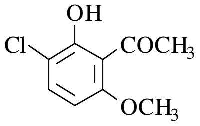
Synthesis

-Preparation by chlorination of 2-hydroxy-5-methoxyacetophenone with N-chlorosuccinimide in acetic acid containing magnesium acetate at r.t. for 24 h under nitrogen atmosphere (80%) [221] [1830].

m.p. 78-79° [1830]; ^{1}H NMR [1830], MS [1830].

1-(3-Chloro-2-hydroxy-6-methoxyphenyl)ethanone

[87953-91-1] $C_9H_9ClO_3$ mol.wt. 200.62



Syntheses

-Preparation by reaction of dimethyl sulfate on 3-chloro-2,6-dihydroxyacetophenone with potassium carbonate in refluxing benzene (38%) [1112].

-Preparation by diazotization of 3-amino-2-hydroxy-6-methoxyacetophenone with sodium nitrite in dilute sulfuric acid at 0°, and replacement of the diazonium group by chlorine with a solution of cuprous chloride in 2 N hydrochloric acid at 100° (Sandmeyer reaction) (37%) [502].

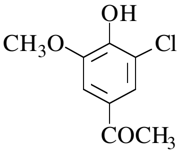
-Also obtained (by-product) by reaction of sulfuryl chloride on 2-hydroxy-6-methoxyacetophenone in refluxing acetic acid [1112].

-Also obtained (crude product) by a one-pot acylation-deprotection of 4-methoxy-2-methoxymethoxychlorobenzene (about 93%). No physical data available [1757].

m.p. 88°5-89° [1112], 82° [502].

1-(3-Chloro-4-hydroxy-5-methoxyphenyl)ethanone

[116296-35-6] $C_9H_9ClO_3$ mol.wt. 200.62



Syntheses

-Preparation from the acetate of 5-chlorovanillin by reaction with diazomethane and subsequent hydrolysis [892] [1657] [1659], (35%) [1657], (23%) [892].

-Also obtained by chlorination of acetoguaiacone in dioxane-water mixture at 40° (21%) [1456].

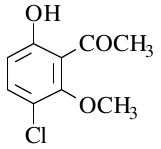
-Preparation by adding sodium hypochlorite solution to a solution of acetovanillone and sodium acetate in methanol cooled to -60° [549].

-Also obtained (by-product) by chlorination of apocynol in dioxane-ethyl ether mixture at 40° (3%) [1456].

m.p. 124-126° [549], 124-125° [892], 123-124° [1657]; MS [1456] [1657].

1-(3-Chloro-6-hydroxy-2-methoxyphenyl)ethanone

[87953-86-4] $C_9H_9ClO_3$ mol.wt. 200.62



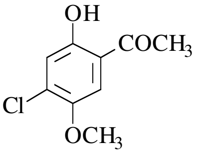
Syntheses

-Preparation by reaction of sulfuryl chloride on 2-hydroxy-6-methoxyacetophenone in refluxing ethyl ether (93%) or in refluxing acetic acid (66%) [1112].
-Preparation by reaction of chlorine on 2-hydroxy-6-methoxyacetophenone in carbon tetrachloride at -20° (62%) [502].

m.p. 31° [1112], 30-35° [502]; b.p.$_{0.001}$ 40° [1112], b.p.$_2$ 120° [502].

1-(4-Chloro-2-hydroxy-5-methoxyphenyl)ethanone

$C_9H_9ClO_3$ mol.wt. 200.62



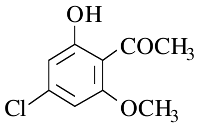
Synthesis

-Preparation by reaction of methyl iodide on 4-chloro-2,5-dihydroxyacetophenone with potassium carbonate in refluxing acetone [1604].

m.p. 130° [1604].

1-(4-Chloro-2-hydroxy-6-methoxyphenyl)ethanone

[140155-06-2] $C_9H_9ClO_3$ mol.wt. 200.62



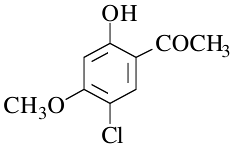
Syntheses

-Preparation by reaction of acetyl chloride with 3,5-dimethoxy-1-chlorobenzene in the presence of aluminium chloride (Friedel-Crafts reaction) (38%) [985].
-Also refer to: [741] [984].

^1H NMR [985].

1-(5-Chloro-2-hydroxy-4-methoxyphenyl)ethanone

[116265-99-7] $C_9H_9ClO_3$ mol.wt. 200.62



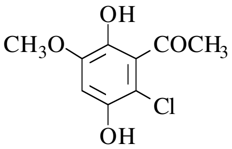
Syntheses

-Preparation by diazotization of 5-amino-2-hydroxy-4-methoxyacetophenone and replacement of diazonium group by chlorine (Sandmeyer reaction) [1626].
-Preparation by reaction of acetyl chloride with 4-chlororesorcinol dimethyl ether in the presence of aluminium chloride in ethylene dichloride (79%) [1553].
-Also refer to: [1477].

m.p. 154-155° [1553], 153-155° [1626].

1-(2-Chloro-3,6-dihydroxy-5-methoxyphenyl)ethanone

[34603-08-2] $C_9H_9ClO_4$ mol.wt. 216.62



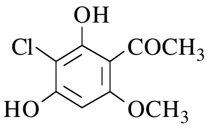
Synthesis

-Preparation by metallation of 2-chloro-5-methoxyhydroquinone-bis-[tetrahydropyranyl-(2)-ether], followed by treatment of the intermediate aryllithium compound with acetic anhydride in tetrahydrofuran at r.t. (56%) [1561].

m.p. 100° [1561].

1-(3-Chloro-2,4-dihydroxy-6-methoxyphenyl)ethanone

[200878-65-5] $C_9H_9ClO_4$ mol.wt. 216.62

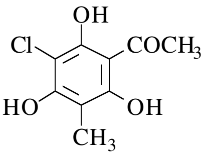


Synthesis

-Refer to: [76].

1-(3-Chloro-2,4,6-trihydroxy-5-methylphenyl)ethanone

[23053-47-6] $C_9H_9ClO_4$ mol.wt. 216.62



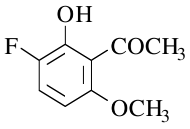
Synthesis

-Preparation by reaction of sulfuryl chloride with methylphloroacetophenone in ethyl ether, first at 0°, then at r.t. (58%) [836].

m.p. 223-224° [836].

1-(3-Fluoro-2-hydroxy-6-methoxyphenyl)ethanone

[117902-13-3] $C_9H_9FO_3$ mol.wt. 184.17



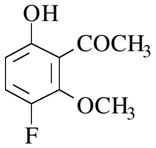
Synthesis

-Preparation by demethylation of 2,6-dimethoxy-3-fluoroacetophenone with boron tribromide (62%) [192].

m.p. 87-88° [192]; ^{1}H NMR [192].

1-(3-Fluoro-6-hydroxy-2-methoxyphenyl)ethanone

[117902-12-2] $C_9H_9FO_3$ mol.wt. 184.17



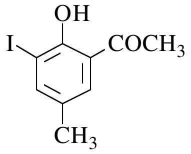
Synthesis

-Obtained (by-product) by demethylation of 2,6-dimethoxy-3-fluoroacetophenone with boron tribromide (6%) [192].

^{1}H NMR [192].

1-(2-Hydroxy-3-iodo-5-methylphenyl)ethanone

[175655-10-4] $C_9H_9IO_2$ mol.wt. 276.07



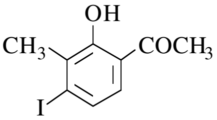
Syntheses

-Preparation by iodination of 2-hydroxy-5-methylacetophenone with iodine (1 mol) and iodic acid (1 mol) in ethanol at 35-40° for 1.5 h (75-85%) [484].
-Also refer to: [1376] [1579].

m.p. 80° [484]; ^1H NMR [484].

1-(2-Hydroxy-4-iodo-3-methylphenyl)ethanone

[40591-02-4] $C_9H_9IO_2$ mol.wt. 276.07



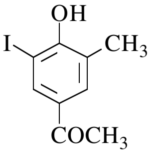
Synthesis

-Obtained (by-product) by Fries rearrangement of 3-iodo-4-methylphenyl acetate with aluminium chloride without solvent at 120° [1786].

m.p. 80° [1786]; ^1H NMR [1786].

1-(4-Hydroxy-3-iodo-5-methylphenyl)ethanone

[292144-89-9] $C_9H_9IO_2$ mol.wt. 276.07



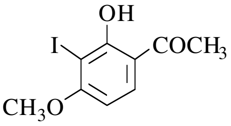
Synthesis

-Preparation by iodination of 4-hydroxy-3-methylacetophenone with iodine (1 mol) and iodic acid (1 mol) in ethanol at 35-40° for 1.5 h (75-85%) [484].

m.p. 149° [484]; ^1H NMR [484].

1-(2-Hydroxy-3-iodo-4-methoxyphenyl)ethanone

$C_9H_9IO_3$ mol.wt. 292.07



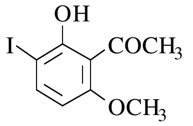
Syntheses

-Obtained from 8-iodo-7-methoxy-2-methylchromone by boiling 10% aqueous sodium hydroxide solution [1600].
-Preparation by adding an aqueous solution of iodine and iodic acid to an ethanolic solution of 2-hydroxy-4-methoxyacetophenone (15%) [1600].

m.p. 152° [1600].

1-(2-Hydroxy-3-iodo-6-methoxyphenyl)ethanone

[103440-57-9] C9H9IO3 mol.wt. 292.07



Syntheses

-Preparation by reaction of iodine monochloride with 2-hydroxy-6-methoxyacetophenone in acetic acid at 17° (88%) [1873].

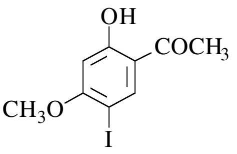
-Also obtained from 8-iodo-5-methoxy-2-methylchromone by boiling 10% aqueous sodium hydroxide solution [1600].

-Preparation by adding an aqueous solution of iodic acid and iodine to an ethanolic solution of 2-hydroxy-6-methoxyacetophenone (85%) [794].

m.p. 115° [794] [1873], 57° [1600]; ^{13}C NMR [1873], IR [1873].

1-(2-Hydroxy-5-iodo-4-methoxyphenyl)ethanone

C9H9IO3 mol.wt. 292.07



Syntheses

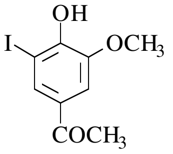
-Obtained by reaction of an aqueous iodine-potassium iodide solution on paeonol in 22% aqueous ammonia; then, the mixture was poured into excess of dilute ice-cold sulfuric acid (13%) [1600].

-Also obtained by hydrolysis of 6-iodo-7-methoxy-2-methylchromone by boiling 10% aqueous sodium hydroxide solution [1600].

m.p. 161° [1600].

1-(4-Hydroxy-3-iodo-5-methoxyphenyl)ethanone

[103440-59-1] C9H9IO3 mol.wt. 292.07



Syntheses

-Preparation by reaction of iodine with acetovanillone in 0.8 N aqueous sodium hydroxide (94%) [1937].

-Preparation by adding an aqueous solution of iodine and potassium iodide to and aqueous solution of acetovanillone and sodium bicarbonate at 80° (82%) [451].

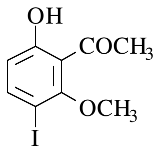
-Preparation by adding potassium iodide and iodine to an aqueous solution of acetovanillone and sodium acetate at 90° [549].

-Preparation by adding 0.1 M hydrogen peroxide to a solution of acetovanillone and potassium iodide in 0.025 M phosphate buffer (pH 3) (75%) [1074].

m.p. 179° [1937], 178-179° [451] [1938], 174-176° [549];
^{1}H NMR [1074], MS [1074].

1-(6-Hydroxy-3-iodo-2-methoxyphenyl)ethanone

$C_9H_9IO_3$ mol.wt. 292.07



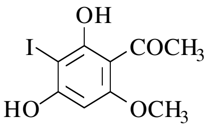
Synthesis

-Preparation by iodination of 2-hydroxy-6-methoxyacetophenone with an aqueous iodine-iodic acid solution in ethanol at r.t. (68%) [1600].

m.p. 116° [1600].

1-(2,4-Dihydroxy-3-iodo-6-methoxyphenyl)ethanone

[74047-32-8] $C_9H_9IO_4$ mol.wt. 308.07



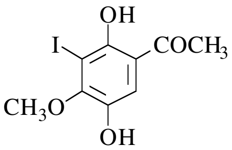
Synthesis

-Preparation by adding an aqueous solution of iodine and periodic acid to an ethanolic solution of 2,4-dihydroxy-6-methoxyacetophenone at 60-70° [15] [18] [537], (86%) [537], (74%) [18].

m.p. 198-200° [537], 193-195° [18];
^1H NMR [537], ^{13}C NMR [537], IR [537], MS [537].

1-(2,5-Dihydroxy-3-iodo-4-methoxyphenyl)ethanone

$C_9H_9IO_4$ mol.wt. 308.07



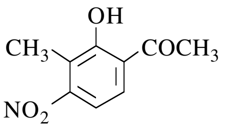
Synthesis

-Obtained from 2-hydroxy-3-iodo-4-methoxyacetophenone oxidised with potassium persulfate in aqueous sodium hydroxide solution (21%) [1600] (Elbs persulfate oxidation).

m.p. 174° (d) [1600].

1-(2-Hydroxy-3-methyl-4-nitrophenyl)ethanone

[190730-40-6] $C_9H_9NO_4$ mol.wt. 195.17



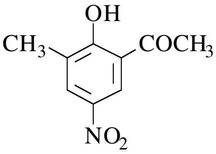
Syntheses

-Preparation by reaction of acetyl chloride (1.3 mol) with 2-methyl-3-nitrophenol (1 mol) in nitrobenzene under nitrogen. The reaction mixture was warmed at 45°, a small amount of aluminium chloride was added and the reaction mixture was stirred at 45° for 1 h. After the addition of another portion of aluminium chloride (1 mol), the temperature rose to 60° and the reaction mixture was slowly heated at 120° and allowed to stirring for another 16 h (72%) [1227].
-Also refer to: [1226] [1685].

m.p. 40-41° [1227]; ^1H NMR [1227], IR [1227], MS [1227].

1-(2-Hydroxy-3-methyl-5-nitrophenyl)ethanone

$C_9H_9NO_4$ mol.wt. 195.17



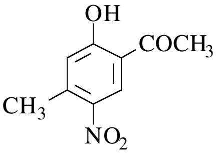
Synthesis

-Preparation by reaction of nitric acid on 2-hydroxy-3-methylacetophenone in acetic acid at 0° (58%) [397]; first at 0°, then 30° (72%) [923].

m.p. 115-116° [397], 114-114°5 [923].

1-(2-Hydroxy-4-methyl-5-nitrophenyl)ethanone

$C_9H_9NO_4$ mol.wt. 195.17



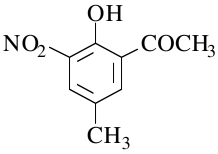
Synthesis

-Preparation by reaction of nitric acid on 2-hydroxy-4-methylacetophenone in acetic acid first at 0°, then 30° (72%) [923].

m.p. 99°5 [923].

1-(2-Hydroxy-5-methyl-3-nitrophenyl)ethanone

[66108-30-3] $C_9H_9NO_4$ mol.wt. 195.17



Syntheses

-Preparation by reaction of nitric acid on 2-hydroxy-5-methylacetophenone in acetic acid [125] [287] [318] [923], (90%) [318], (64%) [923].

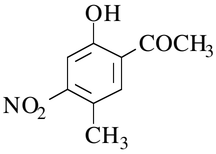
-Preparation by reaction of potassium nitrate on 2-hydroxy-5-methylacetophenone in dilute sulfuric acid (77%) [1895].

-Also obtained by reaction of copper nitrate on 2-hydroxy-5-methylacetophenone in ice-cooled acetic anhydride solution (80%) [125].

m.p. 135-136° [318], 135° [125], 132° [287] [923], 130-130°5 [1895]; pK_a [1387].

1-(2-Hydroxy-5-methyl-4-nitrophenyl)ethanone

[56609-14-4] $C_9H_9NO_4$ mol.wt. 195.17

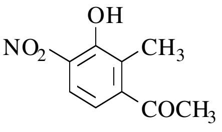


Synthesis not yet described

-There is a single reference, erroneous. It concerns the 2-hydroxy-5-methyl-3-nitroacetophenone [1387]; (see above).

1-(3-Hydroxy-2-methyl-4-nitrophenyl)ethanone

[89877-53-2] $C_9H_9NO_4$ mol.wt. 195.17

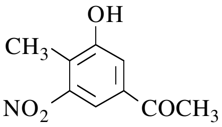


Synthesis

-Refer to: [1671].

1-(3-Hydroxy-4-methyl-5-nitrophenyl)ethanone

$C_9H_9NO_4$ mol.wt. 195.17



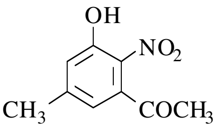
Synthesis

-Preparation by diazotization of 3-amino-4-methyl-5-nitroacetophenone (m.p. 158-159°), followed by hydrolysis of the diazonium salt so obtained (62%) [633].

m.p. 152°5-153°5 [633].

1-(3-Hydroxy-5-methyl-2-nitrophenyl)ethanone

$C_9H_9NO_4$ mol.wt. 195.17



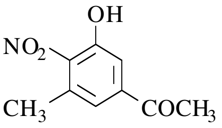
Synthesis

-Obtained (by-product) by reaction of fuming nitric acid on 3-hydroxy-5-methylacetophenone in ethyl ether between -20 to -10° (4%) [324].

m.p. 66-67° [324].

1-(3-Hydroxy-5-methyl-4-nitrophenyl)ethanone

$C_9H_9NO_4$ mol.wt. 195.17



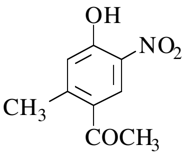
Synthesis

-Preparation by reaction of fuming nitric acid on 3-hydroxy-5-methylacetophenone in ethyl ether between -20 to -10° (23%) [324].

m.p. 148-150° [324].

1-(4-Hydroxy-2-methyl-5-nitrophenyl)ethanone

$C_9H_9NO_4$ mol.wt. 195.17



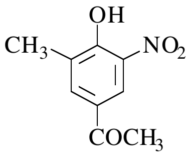
Synthesis

-Preparation by reaction of nitric acid on 4-hydroxy-2-methylacetophenone in acetic acid first at 0°, then 30° (61%) [923].

m.p. 125-126° [923].

1-(4-Hydroxy-3-methyl-5-nitrophenyl)ethanone

$C_9H_9NO_4$ mol.wt. 195.17



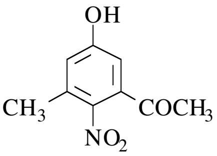
Syntheses

-Preparation by reaction of nitric acid on 4-hydroxy-3-methylacetophenone in acetic acid first at 0°, then 30° (67%) [923].
-Preparation by reaction of acetyl chloride on 2-methyl-6-nitrophenol with aluminium chloride in nitrobenzene at 130° (50%) [923].

m.p. 131°5 [923].

1-(5-Hydroxy-3-methyl-2-nitrophenyl)ethanone

$C_9H_9NO_4$ mol.wt. 195.17



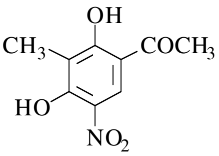
Synthesis

-Preparation by reaction of fuming nitric acid on 3-hydroxy-5-methylacetophenone in ethyl ether between -20 to -10° (29%) [324].

m.p. 148-150° [324]; UV [324].

1-(2,4-Dihydroxy-3-methyl-5-nitrophenyl)ethanone

[118824-94-5] $C_9H_9NO_5$ mol.wt. 211.17



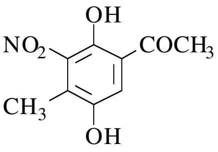
Synthesis

-Preparation by reaction of acetic anhydride on 2-methyl-4-nitroresorcinol with aluminium chloride in nitrobenzene at 80° (73%) [1470].

m.p. 178-179° [1470]; ^{1}H NMR [1470], IR [1470].

1-(2,5-Dihydroxy-4-methyl-3-nitrophenyl)ethanone

[43140-83-6] $C_9H_9NO_5$ mol.wt. 211.17



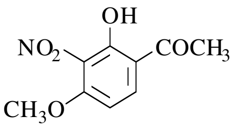
Synthesis

-Preparation by demethylation of 2-hydroxy-5-methoxy-4-methyl-3-nitroacetophenone with aluminium bromide in carbon disulfide at r.t. (96%) [1741].

m.p. 179° [1741]; ^{1}H NMR [1741], IR [1741].

1-(2-Hydroxy-4-methoxy-3-nitrophenyl)ethanone

$C_9H_9NO_5$ mol.wt. 211.17



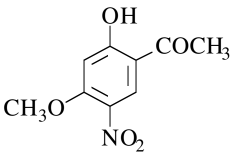
Syntheses

-Preparation by reaction of dimethyl sulfate on 2,4-dihydroxy-3-nitroacetophenone with potassium carbonate in refluxing acetone [1591].
-Also refer to: [1290].

m.p. 211-212° [1591].

1-(2-Hydroxy-4-methoxy-5-nitrophenyl)ethanone

[102877-53-2] $C_9H_9NO_5$ mol.wt. 211.17



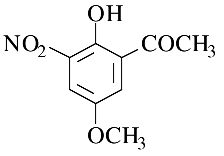
Syntheses

-Preparation by nitration of 2-hydroxy-4-methoxyacetophenone (paeonol) with nitric acid (d = 1.42) in acetic acid [7] [947] [1484] [1626], (47%) [947].
-Also obtained by reaction of concentrated nitric acid with 3,3'-diacetyl-4,4'-dihydroxy-6,6'-dimethoxydiphenyl thioether at r.t. overnight [869].
-Also refer to: [63] (compound 1b).

m.p. 157-158° [1626], 155° [7] [869], 154° [947], 153° [1484].

1-(2-Hydroxy-5-methoxy-3-nitrophenyl)ethanone

[90564-25-3] $C_9H_9NO_5$ mol.wt. 211.17



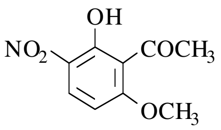
Syntheses

-Preparation from 2-hydroxy-5-methoxyacetophenone by reaction,
*with nitric acid (d = 1.2) in acetic acid at < 15° (83%) [956];
*with nitric acid (d = 1.5) in ice-cooled acetic acid and acetic anhydride mixture [170] [467] [698] [1340], (57%) [698].

m.p. 113-114° [956], 112° [698], 110-112° [467] [1340]; IR [774] [1023].

1-(2-Hydroxy-6-methoxy-3-nitrophenyl)ethanone

[38226-01-6] $C_9H_9NO_5$ mol.wt. 211.17



Syntheses

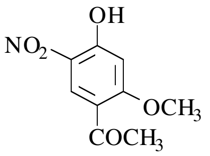
-Obtained by reaction of acetic anhydride on 5-methoxy-2-nitrophenol with aluminium chloride in nitrobenzene at 135° [1291].
-Obtained by reaction of nitric acid (d = 1.42) on 2-hydroxy-6-methoxyacetophenone in acetic acid at r.t. [371] [1023] [1213] [1291], (43%) [371], (26%) [1023].

-Also obtained by reaction of fuming nitric acid with 2-hydroxy-6-methoxyacetophenone in acetic acid, first at r.t. for 40 min, then at 45-50° for 16 h (30%) [471].
-Also obtained (small quantity) by partial methylation of 2,6-dihydroxy-3-nitroacetophenone with dimethyl sulfate in the presence of potassium carbonate in boiling acetone [1291].
-Also obtained by partial demethylation of 2,6-dimethoxy-3-nitroacetophenone,
*with aluminium chloride in nitrobenzene, heated on a steam bath (by-product) [1291];
*with concentrated hydrochloric acid in boiling acetic acid [1291];
*with boiling concentrated hydrochloric acid [1291];
*with concentrated sulfuric acid at 30° [1291];
*with potassium hydroxide in boiling ethanol [1291].
-Also obtained by reaction of nitric acid (d = 1.4) on 2,2'-dihydroxy-3,3'-diacetyl-4,4'-dimethoxyphenyl thioether at 0° [476].

m.p. 104-105° [371], 102-103° [476] [1291], 100°5-101°5 [1023], 98-100° [471];
^{1}H NMR [471], ^{13}C NMR [734], IR [471] [1023].

1-(4-Hydroxy-2-methoxy-5-nitrophenyl)ethanone

$C_9H_9NO_5$ mol.wt. 211.17



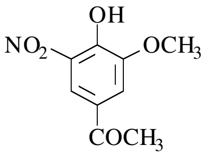
Synthesis

-Obtained by reaction of fuming nitric acid on 4-hydroxy-2-methoxyacetophenone (isopaeonol) at 10° (24%) [947].

m.p. 95° [947].

1-(4-Hydroxy-3-methoxy-5-nitrophenyl)ethanone

[20716-41-0] $C_9H_9NO_5$ mol.wt. 211.17



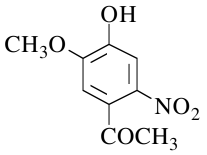
Synthesis

-Preparation by nitration of 4-hydroxy-3-methoxyacetophenone with 70% nitric acid in acetic acid, first at 10°, then at 25° (95%) [813].

m.p. 148°1-149°5 [813].

1-(4-Hydroxy-5-methoxy-2-nitrophenyl)ethanone

[418759-58-7] $C_9H_9NO_5$ mol.wt. 211.17



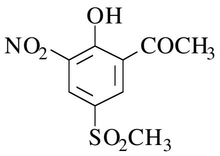
Syntheses

-Preparation by treatment of 4-benzyloxy-5-methoxy-2-nitroacetophenone (m.p. 142-143°) with trifluoroacetic acid at r.t. for 14 h (89%) [1247].
-Also refer to: [1779].

m.p. 151°5-152°5 [1247]; Crystal data [1247];
^{1}H NMR [1247], ^{13}C NMR [1247].

1-[2-Hydroxy-5-(methylsulfonyl)-3-nitrophenyl]ethanone

[70978-46-0] $C_9H_9NO_6S$ mol.wt. 259.24



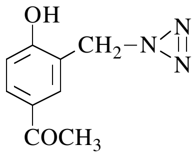
Syntheses

-Preparation by nitration of 2-hydroxy-5-(methylsulfonyl)-acetophenone in concentrated sulfuric acid,
*with 100% nitric acid at r.t. (89%) [318];
*with nitric acid (d = 1.42) between -15 to -5° [620] [1463], (50%) [620].

m.p. 192-193° [318], 189-191° [620] [1463].

1-[3-(Azidomethyl)-4-hydroxyphenyl]ethanone

[154603-69-7] $C_9H_9N_3O_2$ mol.wt. 191.19

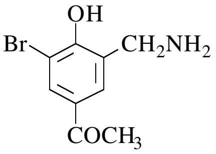


Synthesis

-Preparation by action of sodium azide with 3-chloromethyl-4-hydroxyacetophenone in DMF at 30° for 4 h (60%) [413].

1-[3-(Aminomethyl)-5-bromo-4-hydroxyphenyl]ethanone

[109314-52-5] $C_9H_{10}BrNO_2$ mol.wt. 244.09

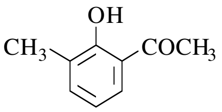


Synthesis

-Refer to: [1912] (Japanese patent).

1-(2-Hydroxy-3-methylphenyl)ethanone

[699-91-2] $C_9H_{10}O_2$ mol.wt. 150.18



Syntheses

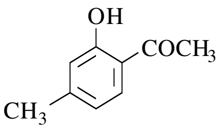
-Preparation by reaction of acetic acid on o-cresol with zinc chloride at reflux (Nencki reaction) (20%) [200].
-Preparation by Fries rearrangement of o-tolyl acetate with aluminium chloride without solvent between 130° and 180° [112] [113] [461] [827] [828] [959] [1180] [1512], (45-55%) [112] [959] [1512], (18-26%) [113] [461] [827] [828].
-Also obtained (by-product) by Fries rearrangement of o-tolyl acetate with aluminium chloride, ferric chloride or titanium tetrachloride in nitrobenzene as solvent between 20° and 60° (3-5%) [461] [463] [464] [465].
-Preparation by reaction of acetic anhydride on o-cresol without solvent, at 120°,
*with 70% perchloric acid (56%) [1084];
*with aluminium chloride (27%) [397].

-Also obtained (by-product) by reaction of acetyl chloride on o-cresol with aluminium chloride or titanium tetrachloride in nitrobenzene at 30-60° (3-6%) [458] [465].
-Preparation by treatment of methyl 4-hydroxy-8-methylcoumarin-3-carboxylate with potassium hydroxide (69%) [66].
-Also obtained by reaction of stannous chloride on 2-hydroxy-3-methylacetophenone 2,4-dinitrophenylhydrazone in refluxing aqueous acetone-hydrochloric acid mixture (81%) [460].
-Also obtained by UV light irradiation of o-tolyl acetate at 25° (photo-Fries rearrangement), in the presence of potassium carbonate in hexane (74%) [660] or without potassium carbonate in hexane (32%) [660] or in ethyl ether (16%) [724].
-Also refer to: [289].

b.p.$_1$ 62-63° [397], b.p.$_5$ 91°7-91°9 [1180], b.p.$_9$ 103-104° [113], b.p.$_9$ 103-105° [959], b.p.$_{10}$ 105° [1084], b.p.$_{10-10.5}$ 106-107° [66] [200], b.p.$_{12}$ 107° [460], b.p.$_{11}$ 108° [660], b.p.$_{15}$ 111-112° [813], b.p. 235-237° [113]; ^{1}H NMR [1180], UV [813] [1180].

1-(2-Hydroxy-4-methylphenyl)ethanone

[6921-64-8] $C_9H_{10}O_2$ mol.wt. 150.18



Syntheses

-Preparation by treatment of methyl 4-hydroxy-7-methylcoumarin-3-carboxylate with potassium hydroxide at 200° (87%) [66].
-Preparation by Fries rearrangement of m-tolyl acetate [112] [550] [1165] [1276],

with solvent:

*with aluminium chloride,
-in tetrachloroethane at 130-135° (99%) [1714];
-in nitrobenzene at 25-30° or at 165° (44-45%) [151] [461].
*with titanium tetrachloride in nitrobenzene at 165° (73%) [461].

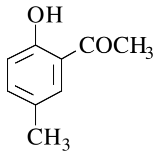
without solvent:
*with aluminium chloride,
-at 165-170° (88-95%) [461] [1512] [1926];
-between 120 to 165° (70-90%) [113] [690] [827] [828] [926] [1785];
-between 60 to 165° (38-65%) [959] [1237] [1512].
*with titanium tetrachloride at 95° (83%) [1926];
*with hydrofluoric acid at 100° (80%) [480];
*with zinc chloride at 140-160° (20%) [66] [1651].
-Preparation by reaction of acetic acid on m-cresol,
*with boron trifluoride at 70° (65%) [980];
*with zinc chloride (Nencki reaction) (25%) [200].
-Preparation by reaction of acetic anhydride on m-cresol with 70% perchloric acid,
-at r.t. (63%) [1084];
-at 125-135° (30%) [548].
-Preparation by reaction of acetyl chloride on m-cresol,
*with titanium tetrachloride,
-in nitrobenzene at 60° (75%) [458];
-in ethylene dichloride at 25° (40%) [458].
*with aluminium chloride,
-in nitrobenzene at 60° (48%) [458];
-in ethylene dichloride at 25° (42%) [458].
*with zinc chloride at r.t. (11%) [1651] or at 140-160° [580].

-Preparation by dehydrogenation of 6-acetyl-3-methyl-2-cyclohexen-1-one,
*with a 5% palladium-barium sulfate catalyst at reflux (47%) [1059];
*with refluxing 16% solution of bromine in acetic acid [1059].
-Also obtained by treatment of 4-methylacetophenone with sodium trifluoroacetate in nitromethane-trifluoroacetic acid-trifluoroacetic anhydride mixture in the presence of a platinum electrode, followed by treatment of the intermediate trifluoroester with 10% aqueous potassium carbonate solution (33%) [1661], (hydroxylation of aromatic compound).
-Preparation by UV light irradiation of m-tolyl acetate, at r.t. (photo-Fries rearrangement) [1723], in ethanol (37%), with aqueous β-cyclodextrin solution (54%) or with β-cyclodextrin (solid) (95%).

colourless oil [690]; m.p. 21° [66] [548] [580] [1512], 20-21° [480];
b.p.$_{0.6}$ 82-84° [926], b.p.$_{0.22}$ 87° [690], b.p.$_{8}$ 101° [113] [959],
b.p.$_{7.5}$ 102-104° [550], b.p.$_{7}$ 103° [66] [580] [1084], b.p.$_{9}$ 105-106° [66],
b.p.$_{7}$ 107° [548], b.p.$_{15}$ 115° [480], b.p.$_{14}$ 116-119° [980],
b.p.$_{17}$ 123-125° [1237], b.p.$_{20}$ 126° [66] [200] [580], b.p.$_{20}$ 126-127° [1276],
b.p.$_{760}$ 245° [66] [200] [580] [1651] [1926];
^{1}H NMR [690] [1923], IR [690] [1923], MS [690].

1-(2-Hydroxy-5-methylphenyl)ethanone

[1450-72-2] $C_9H_{10}O_2$ mol.wt. 150.18



Syntheses

-Obtained by treatment of methyl 4-hydroxy-6-methylcoumarin-3-carboxylate with potassium hydroxide at 200° (82%) [66].
-Preparation by Fries rearrangement of p-tolyl acetate [125] [137],

with solvent:

*with titanium tetrachloride in nitrobenzene at 50° (92%) [462] [466];
*with alumina in methanesulfonic acid for 5 min at 160° (92%) [1613];
*with zirconium chloride in nitrobenzene at 60° (86%) [466];
*with zirconium chloride in methylene chloride at r.t. for 24 h (83%). The same reaction performed in a simple ultrasound cleaning bath at r.t. for 24 h also leads to 83% yield [748];
*with stannic chloride in nitrobenzene at 60° (78%) [466];
*with aluminium chloride, (90%) [1668], (86%) [526], at 130° (90%) [1669] or at 160° (70%) [1363];
  -in nitrobenzene at 60° (92%) [463], (68%) [466], at 25° (84%) [461];
  -in diphenyl ether at 160° (30%) [446];
  -in chlorobenzene, in a sealed tube and subjected to high power microwave irradiation for 2 min only (85%) [1683];
  -in the presence of 4-ethyl-2,6-dimethylphenyl chloroacetate at 150° (72%) [103];
  -in the presence of 2-chloro-4-methylphenyl benzoate at 150° (50%) [103];
*on K 10 montmorillonite using microwave radiations (640 w, 5 min) (86%) or in refluxing DMF during 4 h (75%) [931].

without solvent:

*with aluminium chloride,
  -between 110 to 170° (85-99%) [318] [461] [793] [1512] [1582] [1894] [1926];
  -between 120 to 150° (60-74%) [1220] [1334] [1541];
  -at 120° (36-45%) [675] [959], (90%) [1683];
*with titanium tetrachloride at 120° (70%) [1926];
*with hydrofluoric acid at 120-125° (63%) [480];
*with beryllium chloride at 150° (63%) [286] [287].

-Preparation by reaction of acetyl chloride on p-cresol,
*with titanium tetrachloride in nitrobenzene at 60° (93%) [458];
*with aluminium chloride,
    -in nitrobenzene at 60° (75-80%) [458] [1143];
    -in ethylene dichloride at 110-120° (56%) [1033];
    -without solvent at 180° (64-72%) [1016].
-Preparation by reaction of acetyl chloride with p-cresol in the presence of aluminium chloride during 30 min at 180°, *via* a Fries rearrangement (98%) [976].
-Preparation by acylation of p-cresol with acetic acid in the presence of alumina in methanesulfonic acid for 5 min at 120° (90%) [1613].
-Preparation by reaction of acetyl chloride on 4-methylanisole with aluminium chloride [104] [110] [113].
-Also obtained by reaction of acetyl chloride on p-tolyl borate with aluminium chloride in refluxing carbon disulfide (15%) [1792].
-Preparation by reaction of acetic anhydride on p-cresol with 70% perchloric acid at 100° (53%) [1084], at 125-135° (30%) [548].
-Preparation by reaction of acetic acid on p-cresol,
*with boron trifluoride at 70° (95%) [980];
*with zinc chloride at reflux (14%) [200] (Nencki reaction).
-Preparation by dealkylation of,
*2-methoxy-5-methylacetophenone,
    -with pyridinium chloride at reflux (56%) [1237];
    -with hydrobromic acid in acetic acid (7%) [813];
*2-ethoxy-5-methylacetophenone with aluminium chloride [98].
-Also obtained from 2-hydroxy-5-methyl-α-chloroacetophenone by treatment with zinc powder in acetic acid [104].
-Also obtained by treatment of 2-hydroxy-5-methyl-α,α,α-trifluoroacetoacetophenone with 2 N sodium hydroxide at r.t. (100%) [1885].
-Also obtained by reaction of stannous chloride on 2-hydroxy-5-methylacetophenone 2,4-dinitrophenylhydrazone in refluxing aqueous acetic acid-hydrochloric acid mixture (80%) [460].
-Also obtained by reaction of mesityl acetate on p-cresol with aluminium chloride at 150° (72%) [103].
-Also obtained by reaction of various aryl acetates on p-tolyl benzoate with aluminium chloride at 150°, which produce the acetyl cation [103],
*with mesityl acetate (77%);
*with 2-chloro-4-methylphenyl acetate (57%);
*with 2,6-dimethylphenyl acetate (33%).
-Also obtained by degradation of 3-bromo-6-methylchromanone with alkali in boiling water [1031].
-Also obtained by hydrogenation of 2,4-dimethylindoxazen in acetic acid in the presence of $Pd/BaSO_4$ during 4 to 6 h [1103].
-Also obtained by hydrolysis of 2-(2-hydroxy-5-methylphenyl)-2-methyl-1,3-dioxolane by a catalytic amount of carbon tetrabromide (20%) in acetonitrile/water solvent mixture under sonication in a commercial ultrasonic cleaning bath for 2 h at 45° (98%) [1070].
-Also obtained by UV light irradiation of p-tolyl acetate at 25°,
*in hexane,
    -in the presence of potassium carbonate (86%) [660];
    -without potassium carbonate (35%) [660], (6%) [280];
*in ethyl ether (32%) [724], in ethanol [280] [867], (8%) [280], in benzene (6%) [280] or in methanol [867].
-Also refer to: [153] (compound 1a), [811] [1109] [1204] (compound 1c), [1376].

Isolation from natural sources

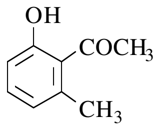
-From the coriander seed essential oil [583].
-Detected in the sorghum malt beverage [1061].
-Identified in powdered turmeric (curcuminoids) [785].

N.B.: Na salt [52166-70-8] [217] [1668].

m.p. 50° [66] [104] [110] [113] [125] [200] [460] [461] [462] [463] [480] [548] [811] [959] [1143] [1363] [1512] [1582] [1926], 49°5 [675], 49-50° [931] [980], 48-49° [446] [1033], 48° [1103], 47-48° [287] [318], 47° [1541], 46°5 [1334], 46-48° [103], 46-47°5 [813], 45-46° [660] [1894], 45° [526];
b.p.$_{0.2}$ 60-62° [1541], b.p.$_{7}$ 101-103° [1084], b.p.$_{15}$ 112° [113], b.p.$_{13}$ 118° [980], b.p.$_{15}$ 118-121° [1237], b.p.$_{7}$ 120-130° [446], b.p.$_{16}$ 124° [480], b.p.$_{740}$ 209° [526];
GC-MS [583] [785] [1061]; pK_a [1387] [1697];
^{1}H NMR [265] [867] [914] [931] [976] [1541] [1923], ^{13}C NMR [914],
IR [931] [1541] [1923], UV [265] [813] [1541].

1-(2-Hydroxy-6-methylphenyl)ethanone

[41085-27-2] $C_9H_{10}O_2$ mol.wt. 150.18



Syntheses

-Preparation from 2-hydroxy-6-methylbenzonitrile and methylmagnesium bromide in ethyl ether-tetrahydrofuran mixture at 50° (67%) [913].
-Preparation by adding a solution of methyl lithium in ethyl ether to 6-methylsalicylic acid in tetrahydrofuran and maintain a gentle reflux for 8 h. Then, the solution was cooled and acidified with hydrochloric acid (62%) [1876].
-Preparation by demethylation of 2-methoxy-6-methylacetophenone,
*with pyridinium chloride at 200-215° (44%) [452], (31%) [1930];
*with boron tribromide in methylene chloride at r.t. [356] [435], (70%) [356].
-Preparation by diazotization of 2-amino-6-methylacetophenone, connected with hydrolysis of the diazonium salt obtained [619].
-Also obtained by a potassium fluoride catalyzed self-condensation of 2,4-pentanedione in DMF solution [415] [1753].
-Also obtained by UV light irradiation of 3-methylphenyl acetate, in ethanol (36%) [1723] or in ethanol in the presence of β-cyclodextrin (42%) [1723].
-Also obtained (poor yield) by irradiation of dehydroacetic acid and vinyl acetate in an ethyl acetate solution [1753] [1754], (4%) [1754].

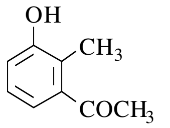
Isolation from natural sources

-The 2-hydroxy-6-methylacetophenone was isolated as exocrine compound in several neotropical species of ants in the dolichoderine genus Hypoclinea *(Hypoclinea analis, Hypoclinea abrupta, Hypoclinea bidens A)*. The ants were collected in Belem, Para, Brazil [235] [913]. It was also isolated from the bodies of *Rhytidoponera aciculata* (Australian ponerine ant) [293] [1780].
-The hydrolytic cleavage of Peripentadenine gave the 2-hydroxy-6-methylacetophenone. The Peripentadenine was obtained from dried milled bark of *Peripentadenia mearsii* (Elaeocarpaceae), collected at Boonjie (North Queensland) [1062].
-From the essential oil of *Cistus ladanifer L.* (Cistaceae) [1447].
-From the aerial parts of *Gerbera ambigua* (Compositae), collected in Transvaal [248].

oil [248] [356] [619] [913] [1754] [1780] [1876] [1930];
after two recrystallizations from water and two sublimations (130°/0.09 mm) gave a white powder, m.p. 93-98° [1930];
b.p.$_{7}$ 100° [1876], b.p.$_{18}$ 138-142° [356];
n_D^{20} = 1.5612 [619], n_D^{23} = 1.5600 [1876];
^{1}H NMR [235] [248] [356] [913] [1447] [1753] [1754] [1876], ^{13}C NMR [1062],
IR [248] [356] [452] [913] [1062] [1876], MS [235] [248] [293] [913] [1447].

1-(3-Hydroxy-2-methylphenyl)ethanone

[69976-81-4] $C_9H_{10}O_2$ mol.wt. 150.18



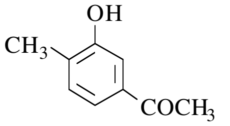
Syntheses

-Preparation by diazotization of 6-amino-3-hydroxy-2-methylacetophenone, followed by hydrolysis of the obtained diazonium salt in the presence of hypophosphorous acid at 0° (42%) [546].
-Preparation by passing a solution of 3-hydroxy-2-methylbenzoic acid in hot acetic acid over a pelleted thoria catalyst at 470-480° during 4 h (32%) [499].

m.p. 121° [499], 120°8-121°7 [546]; ^{1}H NMR [546].

1-(3-Hydroxy-4-methylphenyl)ethanone

[33414-49-2] $C_9H_{10}O_2$ mol.wt. 150.18



Syntheses

-Preparation by diazotization of 3-amino-4-methylacetophenone, followed by hydrolysis of the obtained diazonium salt [904] [1069] [1501], (75%) [1501], (40%) [1069].
-Obtained by treatment of 4-methylacetophenone with sodium trifluoroacetate in nitromethane-trifluoroacetic acid-trifluoroacetic anhydride mixture in the presence of a platinum electrode followed by treatment of the intermediate trifluoroacetate ester with 10% potassium hydrogen carbonate solution (40%) [1661], (of aromatic compounds).

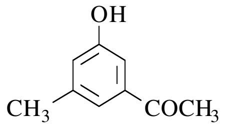
Isolation from natural sources

-From *Laurencia chilensis* De Toni, Forte and Howe (Rhodomelaceae) [1835].

m.p. 119-120° [1069] [1501], 105-107° [1835];
^{1}H NMR [1835], UV [1835], IR [1835], (Sadtler: standard n° 8331), MS [1835].

1-(3-Hydroxy-5-methylphenyl)ethanone

[43113-93-5] $C_9H_{10}O_2$ mol.wt. 150.18



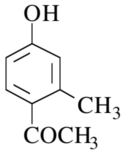
Syntheses

-Preparation by diazotization of 3-amino-5-methylacetophenone, followed by hydrolysis of the obtained diazonium salt (70%) [324].
-Preparation by hydrolysis of diethyl 3-acetoxy-5-methylbenzoylmalonate with concentrated sulfuric acid in boiling aqueous acetic acid (70%) [324].
-Also obtained by solvolysis of 3-acetyl-5-methylphenol tetrahydropyranyl ether with p-toluenesulfonic acid in methanol at r.t. (73%) [144].
-Preparation by aromatization of 5-acetyl-3-methyl-2-cyclohexen-1-one with cupric bromide and lithium bromide in boiling acetonitrile (46%) [324].
-Also obtained by alkaline transformation of methyl, tert-butyl or benzyl esters of 4-acetonyl-5-hydroxy-2,5-dimethyl-3-furoic acid with 2 N sodium hydroxide in ethanol at r.t. (35-50%) [358].
-Preparation by oxidation of 5-acetyl-3-methyl-2-cyclohexen-1-one with air in alkaline medium or by catalytic hydrogenation of the latter in the presence of Pd/C in p-cymene [358].
-Also obtained (poor yield) by alkaline degradation of a solution of D-xylose or D-glucose in 0.63 M sodium hydroxide at 96° under nitrogen [623].

m.p. 122-123° [324] [623], 118-121° [358], 118-120°5 [144];
^{1}H NMR [144] [358], IR [144] [358], UV [358], MS [144] [358].

1-(4-Hydroxy-2-methylphenyl)ethanone

[875-59-2] $C_9H_{10}O_2$ mol.wt. 150.18



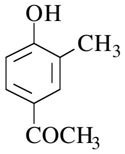
Syntheses

-Preparation by dealkylation of 4-hydroxy-2-methyl-5-isopropylacetophenone with aluminium chloride in chlorobenzene at 50° (80%) [901].
-Also obtained by reaction of aluminium chloride on 4-acetoxy-2-methylacetophenone at 130° (51%) or on 4-(benzoyloxy)-2-methylacetophenone at 170° [1512].
-Preparation by Fries rearrangement of m-tolyl acetate,
*with aluminium chloride in nitrobenzene at r.t. (80-85%) [1512], (60-66%) [103] [151] [459] [461] [1422], (54%) [674];
*with aluminium chloride without solvent [113] [461] [1237] [1785] [1926], at 65° (88%) [1926], at 60-70° (28%) [1237], at 130° (16%) [1785] and at 165° (7%) [461];
*with zinc chloride and hydrochloric acid at r.t. (30%) [1651];
*with hydrofluoric acid at 20° (17%) [480];
*with titanium tetrachloride at 95° (7%) [1926].
-Also obtained by reaction of acetyl chloride on m-cresol,
*with aluminium chloride in nitrobenzene at 25° (63%) [458];
*with titanium tetrachloride in nitrobenzene at 25° (25%) [458];
*with zinc chloride [579] [580] [1651], (14%) [1651];
*with ferric chloride in carbon disulfide [1320].
-Also obtained by reaction of acetic acid on m-cresol,
*with boron trifluoride at 70° (16%) [980];
*by heating the mixture with phosphorous oxychloride (by-product) [112].
-Also obtained by reaction of acetic anhydride on m-cresol with 70% perchloric acid at r.t. (6%) [1084].
-Also obtained by UV light irradiation on p-tolyl acetate in methanol at 25° (26%) [1389]. (There is a 1,2-migration of the methyl group).
-Also obtained by UV light irradiation of m-tolyl acetate in ethanol (13%) [1723].
-Also obtained by reduction of 4-hydroxy-2-methyl-α-chloroacetophenone with zinc dust in aqueous ethanolic acetic acid [359].

m.p. 131° [980], 129° [901], 128-130° [1389], 128-129° [1422],
128° [113] [359] [580] [674] [1084] [1237] [1926], 127° [459] [461] [1512] [1651],
126° [1320], 125° [480];
b.p.$_{17}$ 158-160° [1237], b.p. 313° [580];
^{1}H NMR [1389] [1422], IR [1389], UV [151].

1-(4-Hydroxy-3-methylphenyl)ethanone

[876-02-8] $C_9H_{10}O_2$ mol.wt. 150.18



Syntheses

-Preparation by dealkylation of 4-hydroxy-5-methyl-2-isopropylacetophenone with aluminium chloride in chlorobenzene at 50° (53%) [901].
-Preparation by Fries rearrangement of o-tolyl acetate [113] [433],

with solvent:

*with aluminium chloride in nitrobenzene at r.t. (83-85%) [463] [1512], (41-49%) [89] [150] [465] [472] or at 60° (82%) [461];
*with aluminium chloride in diphenyl ether at 175° (54%) [446];
*with titanium tetrachloride in nitrobenzene at 30° (78%) [464] [465];
*with ferric chloride in nitrobenzene at 50° (60%) [465].

without solvent:

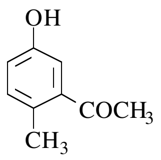
*with aluminium chloride at 160-180° (61%) [461], (27%) [959];
*with ferric chloride (42%) [465].

-Preparation by reaction of acetyl chloride on o-cresol,
*with hydrofluoric acid at 50° (98%) [263];
*with aluminium chloride,
  -in refluxing carbon disulfide (96%) [1069];
  -in nitrobenzene at 60° (86%) [458];
*with titanium tetrachloride in nitrobenzene at 30° (66%) [465] or at 60° (78%) [458];
*with ferric chloride in carbon disulfide [1320].
-Preparation by reaction of acetonitrile on o-cresol with triflic acid at r.t. (67%) [268].
-Also obtained by reaction of acetic anhydride with o-cresol in anhydrous hydrofluoric acid at 50° (quantitative yield) [89] or in 70% perchloric acid at 120° (31%) [1084].
-Also obtained by reaction of acetic acid on o-cresol with zinc chloride (Nencki reaction) (10%) [200].
-Preparation by diazotization of 4-amino-3-methylacetophenone with sodium nitrite in dilute hydrochloric acid and replacement of the diazonium group by hydroxyl group [992].
-Also obtained by UV light irradiation of o-tolyl acetate, at 25°,
*in ethyl ether (10%) [724];
*in hexane, in the presence of potassium carbonate (12%) [660] or without potassium carbonate (3%) [660].
-Also refer to: [1702].

m.p. 110° [446] [901], 108-109° [89], 108° [463], 107-109° [1069], 106-108° [150], 105°5-106°5 [268], 104-105° [420], 104° [113] [200] [461] [464] [465] [992] [1320];
b.p.$_{7.5}$ 166-167° [959], b.p.$_{5}$ 170-175° [446]; pK$_a$ [1697];
^{1}H NMR [268], IR [268], MS [268].

1-(5-Hydroxy-2-methylphenyl)ethanone

[40180-70-9] $C_9H_{10}O_2$ mol.wt. 150.18



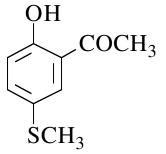
Syntheses

-Preparation from 5-acetyl-4-methyl-3-cyclohexenone by aromatization promoted,
*by cupric bromide with lithium bromide in refluxing acetonitrile (80%) [197];
*by 10% Pd/C in refluxing xylene (50%) [197].

m.p. 128° [197]; ^{1}H NMR [197], IR [197].

1-[2-Hydroxy-5-(methylthio)phenyl]ethanone

[135936-88-8] $C_9H_{10}O_2S$ mol.wt. 182.24

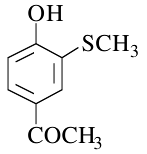


Synthesis

-Refer to: [421].

1-[4-Hydroxy-3-(methylthio)phenyl]ethanone

[66264-56-0] $C_9H_{10}O_2S$ mol.wt. 182.24



Syntheses

-Preparation by reaction of methyl iodide on 4-hydroxy-3-mercaptoacetophenone with potassium carbonate in acetone at r.t. (83%) [1421] [1692].

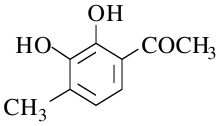
-Preparation by reaction of acetyl chloride on 2-(methylthio)phenol with aluminium chloride in nitrobenzene at 65° (34%) [1421] [1692].

-Also refer to: [1702].

m.p. 117-120° [1421] [1692].

1-(2,3-Dihydroxy-4-methylphenyl)ethanone

[69751-81-1] $C_9H_{10}O_3$ mol.wt. 166.18



Syntheses

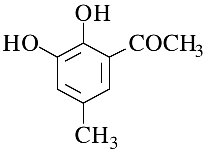
-Preparation by Fries rearrangement of 3-methylpyrocatechol diacetate with a molten mixture of aluminium chloride and sodium chloride at 200° (15%) [1116].

-Also obtained by UV light irradiation of 3,6-dimethyl-1,2-benzisoxazole in 96% sulfuric acid (5%) [547] [673].

m.p. 70° [1116], 67-68° [547]; ^1H NMR [547], IR [547] [1116], UV [547], MS [547].

1-(2,3-Dihydroxy-5-methylphenyl)ethanone

[69751-80-0] $C_9H_{10}O_3$ mol.wt. 166.18



Syntheses

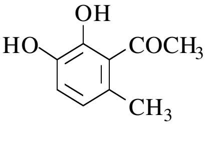
-Preparation by reaction of acetic acid on creosol with boron trifluoride at 160° (78%) [473].

-Also obtained by UV light irradiation of 3,5-dimethyl-1,2-benzisoxazole in 96% sulfuric acid (6%) [547].

m.p. 87°5-88° [547], 86-88° [473];
^1H NMR [547], IR [547], UV [547], MS [547].

1-(2,3-Dihydroxy-6-methylphenyl)ethanone

[59862-07-6] $C_9H_{10}O_3$ mol.wt. 166.18



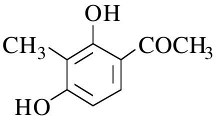
Synthesis

-Obtained (poor yield) by alkaline degradation of a solution of D-xylose or D-glucose in 0.63 M sodium hydroxide at 96° under nitrogen [623].

m.p. 82-83° [623]; ^{1}H NMR [623], IR [623], MS [623].

1-(2,4-Dihydroxy-3-methylphenyl)ethanone

[10139-84-1] $C_9H_{10}O_3$ mol.wt. 166.18



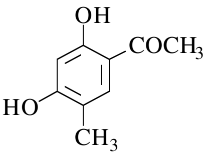
Syntheses

-Preparation by reaction of acetic anhydride on 2-methylresorcinol with boron trifluoride-ethyl ether complex at 70-80° (78%) [1470].
-Preparation by reaction of acetic acid on 2-methylresorcinol with zinc chloride (Nencki reaction) (59%) [777].
-Preparation by reaction of acetonitrile on 2-methylresorcinol (Hoesch reaction) [447] [1464].
-Preparation by demethylation of 2-hydroxy-4-methoxy-3-methylacetophenone with hydriodic acid in a boiling mixture of phenol and acetic anhydride [447] [1464].
-Also obtained by catalytic reduction of 2',4'-dihydroxy-3'-(1-piperidylmethyl)acetophenone in the presence of Pd/C [937] [939], (65%) [939]. The starting material was obtained by treatment of resacetophenone in ethanol with methylene-bis-piperidine.
-Also refer to: [1264].

m.p. 157-158° [937] [939] [1470], 156-157° [1464], 155-156° [447];
^{1}H NMR [939] [1470], ^{13}C NMR [736], IR [939] [1470], UV [447], MS [1470].

1-(2,4-Dihydroxy-5-methylphenyl)ethanone

[93578-16-6] $C_9H_{10}O_3$ mol.wt. 166.18



Syntheses

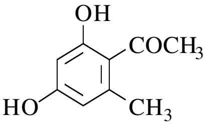
-Preparation by reaction of acetonitrile on 4-methylresorcinol (Hoesch reaction) (75%) [1277], (50-59%) [1215] [1259].
-Preparation from 2,4-dimethoxy-5-methylacetophenone by reaction with boron tribromide in methylene chloride at r.t. (48%) [256] [257].
-Preparation by reaction of acetic acid on 4-methylresorcinol with zinc chloride (Nencki reaction) (46-60%) [339] [448] [1499] [1913].
-Preparation by Fries rearrangement of 4-methylresorcinol diacetate with aluminium chloride in nitrobenzene (63%) [339].

m.p. 170-171° [448], 170° [1277] [1913], 169° [1215], 168-169° [339];
^{1}H NMR [339], IR [339], UV [447].

1-(2,4-Dihydroxy-6-methylphenyl)ethanone

(Orcacetophenone; Orsacetophenone; β-Orcacetophenone)

[703-29-7] $C_9H_{10}O_3$ mol.wt. 166.18



Syntheses

-Preparation by reaction of acetonitrile on orcinol (Hoesch reaction) [790] [860] [1597] [1598], (75%) [448], (62%) [790].
-Preparation by reaction of acetyl chloride on orcinol with aluminium chloride in nitrobenzene (56%) [507].
-Preparation by reaction of acetic acid with orcinol in the presence of boron trifluoride etherate at 102-115°, then hydrolysis of complex obtained with boiling dilute ethanol (65%) [1686].
-Preparation from 3,3'-dimethyl-5,5'-diisoxazolyl-methane by performing hydrogenolysis and subsequent hydrolysis with hydrochloric acid (80%) [97] or with 50% sulfuric acid [96].
-Preparation by reaction of 50% sulfuric acid with nonan-2,4,6,8-tetraone diethylene ketal for 10 min (77%) [1693].
-Preparation by hydrolysis of 2,8-di-(1-pyrrolidinyl)-2,7-nonanediene-4,6-dione (SM) $C_{17}H_{26}N_2O_2$ **4** (m.p. 196-199°) with refluxing 2 N sulfuric acid for 30 min (69%) [1691]. SM was obtained by reaction of 3-acetoacetyl-4-hydroxy-6-methyl-2-pyrone with an excess of pyrrolidine.
-Preparation by hydrolysis of an ionic complex $C_{22}H_{27}NO_5$ **10** (m.p. 161-162°) with refluxing 2 N sulfuric acid for 1 h (87%) [1691].
-Also obtained from 7-hydroxy-4,5-dimethylcoumarin by heating in a boiling water bath with 10% aqueous sodium hydroxide [1597].
-Also obtained by degradation of 3,8-diacetyl-4,5-dihydroxy-7-methylcoumarin by heating with aqueous sodium hydroxide solution [1640].
-Also obtained by decarboxylation of 3-acetyl-p-orsellinic acid (3-acetyl-2,6-dihydroxy-4-methylbenzoic acid) with copper in boiling quinoline [1546].
-Also obtained (by-product) by reaction of trifluoroacetic anhydride on 2-acetoxy-4-methoxy-6-methylbenzoic in the presence of orcinol at 25° (8%) [9].
-Also obtained (by-product) by Fries rearrangement of orcinol diacetate in the presence of aluminium chloride in nitrobenzene at 75-80° (5%) [1351].
-Also obtained (by-product) by reaction of acetyl chloride on orcinol dimethyl ether with aluminium chloride in carbon disulfide (3%) [1705].

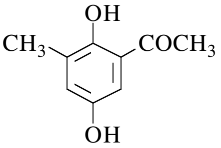
Isolation from natural sources

-From *Scolecotrichum graminis* Fuckel [1734].

m.p. 160-161° [1705], 159-160° [507], 159° [790] [860] [1640] [1693], 158-160° [9], 158-159° [448] [1691], 158° [97] [1546], 157-159° [1597], 140° [1686];
^1H NMR [97] [1734], IR [1686] [1734], UV [447] [1686] [1734], MS [97] [1734].

1-(2,5-Dihydroxy-3-methylphenyl)ethanone

[274259-41-5] $C_9H_{10}O_3$ mol.wt. 166.18



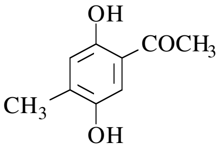
Synthesis

-Preparation by demethylation of 2-hydroxy-5-methoxy-3-methylacetophenone with boron tribromide in methylene chloride at r.t. for 5 h (71%) [20].

m.p. 111-113° [20];
^1H NMR [20], IR [20], MS [20].

1-(2,5-Dihydroxy-4-methylphenyl)ethanone

[54698-17-8] $C_9H_{10}O_3$ mol.wt. 166.18



Syntheses

-Preparation by Fries rearrangement of 2-methylhydroquinone diacetate with aluminium chloride without solvent [148] [338] [514] [1392], between 120 to 160° (53-54%) [338] [1392].
-Preparation by reaction of acetic acid on 2-methylhydroquinone with boron trifluoride [1051] [1052] [1145], (85%) [1052].
-Also obtained by saponification of 2,5-diacetoxy-4-methylacetophenone with aqueous sodium hydroxide [1051].
-Also obtained by demethylation of 2-hydroxy-5-methoxy-4-methylacetophenone and 2,5-dimethoxy-4-methylacetophenone with boiling pyridinium chloride [1524].
-Also obtained by UV light irradiation of 3,6-dimethyl-1,2-benzisoxazole in 96-98% sulfuric acid (44%) [547] [673].
-Also refer to: [33] [64] [1081].

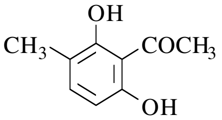
Isolation from natural sources

-From Chinese Moutan Cortex, the root of *Paeonia suffruticosa* Andrews (Paeoniaceae) [1924].

m.p. 148-149° [1392], 147-147°5 [547], 147° [1524], 145-146° [338], 145° [1051], 141° [514] [1052];
^{1}H NMR [547], IR [547] [1392], UV [547], MS [547].

1-(2,6-Dihydroxy-3-methylphenyl)ethanone

[29183-78-6] $C_9H_{10}O_3$ mol.wt. 166.18



Syntheses

-Obtained from 8-acetyl-4,6-dimethyl-7-hydroxycoumarin by alkaline degradation with 20% aqueous sodium hydroxide solution at reflux (42%) [447] [1913].
-Obtained from 4-acetoxy-3-acetyl-2-hydroxy-5-methylbenzoic acid by hydrolysis with 10% ethanolic potassium hydroxide, followed by decarboxylation [1745].

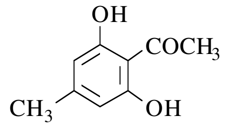
Isolation from natural sources

-From dihydrousnic acid [84] [1746] or from tetrahydrodeoxyusnic acid [84] (from Lichens substances) by potassium permanganate oxidation in 10% aqueous potassium hydroxide at r.t., followed by distillation (5%) [1746].
-From methyldihydrousnic acid [1745], either by potassium permanganate oxidation, followed by vacuum distillation [1743], or by vacuum distillation, followed by ozone oxidation [1743].

m.p. 138-139° [447], 138° [84] [1746] [1913], 136-137° [1743], 134-136° [1745];
^{1}H NMR [1745], UV [447] [1743] [1745].

1-(2,6-Dihydroxy-4-methylphenyl)ethanone *(γ- or p-orcacetophenone)*

[1634-34-0] $C_9H_{10}O_3$ mol.wt. 166.18



Syntheses

-Preparation by reaction of acetic anhydride on orcinol,
*with concentrated sulfuric acid at 130° (65%) [860].
*with Amberlite IR-120 or Zeokarb-225, cation exchange resins (sulfonic acid type) at 160° (20%) [1445].
-Preparation by reaction of acetyl chloride on orcinol with aluminium chloride in boiling nitrobenzene (50%) [447] [515].
-Preparation by reaction of acetic acid on orcinol,
*with zinc chloride (Nencki reaction) [1121];
*with phosphorous oxychloride at 100-110° [505] [790] [1474].
-Also obtained by reaction of acetyl chloride on 2,5-dimethoxytoluene (?) with aluminium chloride in carbon disulfide (26%) [723].
-Also obtained by partial deacylation of 2,4-diacetylorcinol with 85% sulfuric acid at r.t. [510] [513] [1546], (39%) [513] or with boiling solution of 1 N sodium hydroxide [1546].
-Also obtained by decarboxylation of methyl 3-acetyl-2,4-dihydroxy-6-methylbenzoate,
*by reaction of boiling solution of 1 N sodium hydroxide [1546];
*by heating at 180°, followed by distillation [1744].
-Also obtained by reaction of boiling solution of 1 N sodium hydroxide on methyl 3,5-diacetyl-2,4-dihydroxy-6-methylbenzoate, decarbonylation and decarboxylation occurring simultaneously [1546].
-Also obtained by reaction of 2-acetoxy-4-methoxy-6-methylbenzoic acid on orcinol with trifluoroacetic anhydride at 25° (5%) [9].
-Also obtained by degradation of 3,8-diacetyl-4,7-dihydroxy-5-methylcoumarin by heating with aqueous sodium hydroxide solution [1640].
-Also obtained by reaction of potassium hydroxide with 2-acetyl-3-dimethylamino-5-hydroxy-5-methyl-2-cyclohexenone in ethanol at 40° (48%) [562].
-Also refer to: [1760].

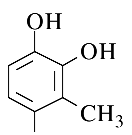
Isolation from natural sources

-From *Rumex patientia* (Polygonaceae) [1058].
-The occurrence of 2-acetylorcinol and its monoglucoside was established in Tissue Cultures from *Rumex alpinus* (Polygonaceae) [1841].

m.p. 147-149° [1445], 146-147° [447] [723], 146° [513] [790] [860] [1121] [1474] [1546] [1744], 144-146° [562], 142-144° [515], 142-143° [9] [1640];
^{1}H NMR [562] [723] [738] [1745], ^{13}C NMR [738], IR [562] [723] [1640] [1744], UV [447] [1744], MS [562] [723].

1-(3,4-Dihydroxy-2-methylphenyl)ethanone

[66296-84-2] $C_9H_{10}O_3$ mol.wt. 166.18



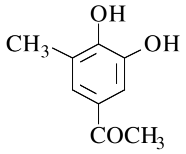
Syntheses

-Obtained (poor yield) by treatment of dihydroxyacetone in aqueous solution (pH 4.5) at 96° (2%) [1434].
-Also obtained (poor yield) by reaction of acetic anhydride on 3-methyl-1,2-benzenediol with perchloric acid [1110].
-Also obtained (poor yield) by Fries rearrangement of 3-methylpyrocatechol diacetate with aluminium chloride in nitrobenzene at 75-80° (< 19%) [1271].

m.p. 149-152° [1434]; ^{1}H NMR [1434], MS [1434].

1-(3,4-Dihydroxy-5-methylphenyl)ethanone

[80547-86-0] $C_9H_{10}O_3$ mol.wt. 166.18



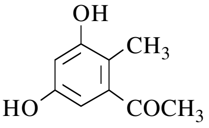
Syntheses

-Preparation by heating 3-methylpyrocatechol in boron trifluoride-acetic acid at 60-70° (62%) [1116].
-Preparation by Fries rearrangement of 3-methylpyrocatechol diacetate,
*with aluminium chloride in chlorobenzene at 110° (71%) [269] or in nitrobenzene at 75-80° (< 19%) [1271];
*with a molten mixture of aluminium chloride and sodium chloride at 200° (40%) [1116].
-Also obtained from neutral glucose and fructose solutions heated at 120° [1718].

m.p. 197-199° [1116], 139-140° [269]; ^{1}H NMR [269], IR [269] [1116].

1-(3,5-Dihydroxy-2-methylphenyl)ethanone

$C_9H_{10}O_3$ mol.wt. 166.18



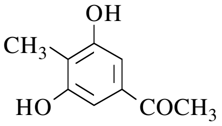
Synthesis

-Preparation by diazotization of (3 or 5)-amino-(5 or 3)-hydroxy-2-methylacetophenone hydrochloride (m.p. 110°5-111°), followed by hydrolysis of the diazonium salt so obtained (51%) [633].

m.p. 160°5-161°2 [633].

1-(3,5-Dihydroxy-4-methylphenyl)ethanone

$C_9H_{10}O_3$ mol.wt. 166.18



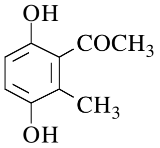
Synthesis

-Preparation by diazotization of 3-amino-5-hydroxy-4-methylacetophenone hydrochloride, followed by hydrolysis of the diazonium salt so obtained (43%) [633].

m.p. 190-191° [633].

1-(3,6-Dihydroxy-2-methylphenyl)ethanone

[176177-16-5] $C_9H_{10}O_3$ mol.wt. 166.18



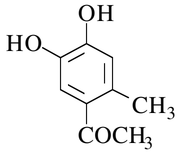
Synthesis

-Preparation by total demethylation of 2,5-dimethoxy-6-methylacetophenone (SM) with aluminium chloride in refluxing chlorobenzene for 4 h (74%) [21]. SM was obtained in three steps from 2,5-dimethoxy-6-methylaniline *via* the sequence: first, 6-bromo-2,5-dimethoxytoluene (m.p. 97-98°5), then 6-(1-hydroxyethyl)-2,5-dimethoxytoluene (m.p. 40°5-42°5) and finally SM (m.p. 59-59°5).

m.p. 122°5-123°5 [21]; sublimation at 86-90°/0.1 mm [21];
^{1}H NMR [21], IR [21], MS [21].

1-(4,5-Dihydroxy-2-methylphenyl)ethanone

[18087-17-7] $C_9H_{10}O_3$ mol.wt. 166.18



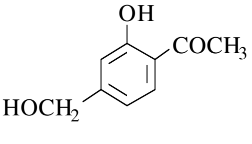
Syntheses

-Preparation by reaction of zinc powder on 4,5-dihydroxy-2-methyl-α-chloroacetophenone in dilute acetic acid between 40 to 70° [1020] [1690], (good yield) [1020].
-Preparation by Fries rearrangement of 4-methylpyrocatechol diacetate with aluminium chloride in nitrobenzene at 75-85° (87-97%) [1271] [1391], (34%) [304].
-Also obtained (poor yield) by reaction of acetic anhydride with 3,4-dihydroxytoluene in the presence of 70% perchloric acid on a steam bath for 3 h (10%) [1432].
-Also obtained (by-product) by Fries rearrangement of creosol acetate with aluminium chloride in nitrobenzene at 80° for 1 h (6%) [1150].
-Also refer to: [398].

m.p. 170°5-171° [1432], 169° [1150], 168-170° [304],
168-169° [1020] [1391], 164° [1690], 160° [1271];
^{1}H NMR [1432], MS [1432].

1-[2-Hydroxy-4-(hydroxymethyl)phenyl]ethanone

[22518-00-9] $C_9H_{10}O_3$ mol.wt. 166.18



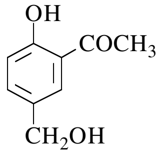
Isolation from natural sources

-By acidic hydrolysis of two esters isolated from *Gaillardia aristata*, the 7-isobutyryloxy-8,9-epoxythymol and 7-(2-methylbutyryloxy)-8,9-epoxythymol isobutyrates [250].
-From the aerial parts of *Calea nelsonii* Robinson and Greenman (Asteraceae) [1170].

m.p. 61°5-62° [250]; ^{1}H NMR [250], IR [250], UV [250].

1-[2-Hydroxy-5-(hydroxymethyl)phenyl]ethanone

[31611-90-2] $C_9H_{10}O_3$ mol.wt. 166.18

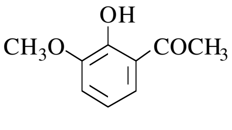


Synthesis

-Obtained by hydrolysis of 2-hydroxy-5-chloromethyl-acetophenone [316].

1-(2-Hydroxy-3-methoxyphenyl)ethanone *(ortho-Acetovanillone)*

[703-98-0] $C_9H_{10}O_3$ mol.wt. 166.18



Syntheses

-Preparation from 2,3-dimethoxybenzonitrile and methyl-magnesium iodide in refluxing ethyl ether (Grignard reaction) [51] [736], (75%) [51].
-Preparation by reaction of aluminium chloride on

the 2,3-dimethoxyacetophenone, in boiling ethyl ether (96%) [140] or in boiling toluene (67%) [1481].

-Also obtained by reaction of hydrobromic acid on 2,3-dimethoxyacetophenone in acetic acid at 25° [813].

-The usual method of synthesis involves the successive conversion of o-veratraldehyde to the 2,3-dimethoxyphenyl methyl carbinol, 2,3-dimethoxyacetophenone and demethylation [51].

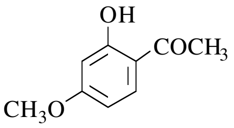
-Preparation by UV light irradiation of guaiacol acetate, in benzene (48%) [280] or in ethyl ether (20%) [724].

-Also obtained (by-product) by Fries rearrangement of guaiacol acetate with zinc chloride at reflux [1481] or with aluminium chloride without solvent between 20 to 50° (9-11%) [1939].

m.p. 54° [140], 53-54° [1481], 52-53° [813], 50-53°1 [51];
b.p.$_{0.5}$ 110-120° [1481];
^{1}H NMR [280], ^{13}C NMR [736], IR [280], UV [813].

1-(2-Hydroxy-4-methoxyphenyl)ethanone *(Paeonol)*

[552-41-0] $C_9H_{10}O_3$ mol.wt. 166.18



Syntheses

-Preparation by reaction of methyl iodide [578] [702] [1738], or dimethyl sulfate [7] [69] [156] [157] [790] [943] [1105] [1201] [1666] [1809] on resacetophenone in sodium hydroxide or potassium hydroxide solution (quantitative yield) [790], (70-75%) [7], (good yield) [1738], (60%) [1105], (52%) [69].

-Preparation by reaction of methyl iodide on resacetophenone,
*with potassium carbonate in boiling acetone (92%) [1066], (73%) [5], (55-64%) [907];
*with lithium carbonate in DMF at 55° (81%) [1899].

-Preparation by reaction of dimethyl sulfate with resacetophenone in the presence of potassium carbonate in refluxing acetone (81%) [971].

-Also obtained by reaction of methyl iodide on resacetophenone silver salt in boiling acetone [982].

-Preparation by reaction of diazomethane with resacetophenone in ethyl ether/methanol solution (90%) [1259].

-Preparation by reaction of acetic acid,
*on the resorcinol monomethyl ether, in the presence of polyphosphoric acid (25%) [1308] or zinc chloride at reflux (Nencki reaction) (29%) [433];
*on the resorcinol dimethyl ether with boron trifluoride at 125° (42%) [1345].

-Preparation by reaction of acetonitrile on resorcinol monomethyl ether (Hoesch reaction) (27%) [790].

-Preparation by reaction of bromoacetyl bromide on resorcinol dimethyl ether with aluminium chloride [233].

-Preparation by Fries rearrangement of 3-methoxyphenyl acetate with zirconium chloride in methylene chloride for 48 h at r.t. (85%) [748].

-Also obtained by Fries rearrangement of 3-methoxyphenyl acetate with aluminium chloride in nitrobenzene at r.t. (13%) [1196] [1202].

-Also obtained by reaction of zinc powder on 2,4-dimethoxy-α-bromoacetophenone in acetic acid in a water bath [105].

-Also obtained (by-product) by reaction of zinc powder and silver chloride on 2-hydroxy-4-methoxy-α-chloroacetophenone in benzene and crotonaldehyde mixture at 60-70° [1038].

-Also obtained by reaction of 2 N sodium hydroxide on 2-hydroxy-4-methoxy-α,α,α-trifluoro-acetoacetophenone at r.t. (quantitative yield) [1885].

-Also obtained by acetylation of resorcinol monomethyl ether by treatment with complex mixture (acetyl chloride/acetic anhydride/acetic acid/anisole/sodium perchlorate) at 60° (8%) [1176].

-Also obtained by reaction of aluminium chloride on 2,4-dimethoxyacetophenone in benzene at 100-110° [1626] or in acetonitrile for 6 h at 45° (40%) [962].
-Also obtained on treatment of ethyl 2-acetyl-5-methoxyphenoxyacetate with boron trichloride in methylene chloride, first at -70°, then at r.t. for 5 min (84%). The ethoxycarbonylmethyl group was selectively removed without difficulty [496].

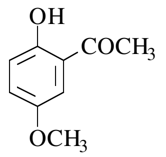
Isolation from natural sources

-From the root bark of *Paeonia Moutan* (Ranunculaceae) [684] [1159] [1285] [1738], of *Paeonia broteroi* [490] and of *Paeonia suffruticosa* Andrews (mudanpi) (Paeoniaceae) [1924] or *Paeania suffruticosa* Anhr. (mudanpi) (Ranunculaceae) (major component) [1098].
-From *paeonia radix* (SM) [696] [1100] [1898]. SM is the dried roots of *paeonia veitchii* Lynch or *paeonia lactiflora* Pall, yet named *paeonia albiflora* Pall.
-From macadamia nuts and shells [1451].
-From the roots of *Pentecost rose* (*paeonia arborea*, also named *paeonia Moutan* in China or *paeonia Botan* in Japan) (Renonculaceae) by hydrolysis of its glucoside [1159] [1201] [1415].
-From the roots of *cynanchum paniculatum* [714] [1114] [1715].
-From the volatile oil of *dioscorea japonica* [1242].
-From the leaves of *ficus krishnae* [849].
-As a major component in the steam distillates of the resins from various species of *Xanthorrhoea (X.); X. tateana* F. Muell. and *X. preissi* [1484], but also from *X. arborea* R. Br. and *X. reflexa* [596].
-By thermal decomposition of the resin from *Ferula pyramidata* (Kar. et Kir.) eug. kor. [982].

m.p. 51°3 [1418], 51° [1038] [1308], 50-51° [1809], 50° [7] [156] [157] [433] [578] [684] [790] [927] [1105] [1196] [1202] [1285] [1345] [1626] [1738], 49-50° [5] [1066], 49° [596] [702] [982] [1484], 48-50° [907] [1415], 48° [971] [1795], 47-49° [1899], 45° [1159];
b.p.$_{0.001}$ 90-100° [1038], b.p.$_3$ 135-137° [982], b.p.$_{20}$ 154° [69], b.p.$_{18}$ 155-165° [596], b.p.$_{20}$ 158° [1484], b.p.$_5$ 180° [1809], b.p.$_{30}$ 210° [1809];
n_D^{15} = 1.5745 [982]; d_{20}^{40} = 1.1604 [982];
TLC [1451] [1832]; HPLC [1100] [1120]; GC [714] [1242]; GC-MS [1242];
^{1}H NMR [43] [44] [490] [683] [1066], ^{13}C NMR [5] [735] [736] [1396] [1400] [1401], IR [490] [1923], UV [43] [490], MS [684] [1832].

1-(2-Hydroxy-5-methoxyphenyl)ethanone

[705-15-7] $C_9H_{10}O_3$ mol.wt. 166.18



Syntheses

-Preparation by reaction of dimethyl sulfate on 2,5-dihydroxyacetophenone [723] [943] [1010] [1200],
*with potassium carbonate in acetone at r.t. (74%) [723];
*with aqueous sodium hydroxide solution at reflux (35%) [1010] [1200].
-Preparation by reaction of aluminium chloride on 2,5-dimethoxyacetophenone in refluxing ethyl ether (53%) [140].
-Preparation by reaction of methyl iodide on 2,5-dihydroxyacetophenone with potassium carbonate in refluxing acetone [1077] [1858], (55-64%) [1858].
-Also obtained by reaction of acetic acid on hydroquinone dimethyl ether with boron trifluoride at 70° (26%) [1345].
-Also obtained by Fries rearrangement of 4-methoxyphenyl acetate with aluminium chloride without solvent at 60-65° (24%) [46].
-Also obtained by reaction of acetyl chloride on hydroquinone dimethyl ether with aluminium chloride,

*in boiling ethyl ether (57%) [1357];
*in nitrobenzene, at r.t. (45%) [1888];
*in methylene chloride, at r.t. (16%) [1635];
*in carbon disulfide, at r.t. (7%) [958] or by heating at 95°, after elimination of the solvent (72%) [374].

-Preparation by UV light irradiation of 4-methoxyphenyl acetate at 25°,
*in hexane (75%) [660];
*in hexane with potassium carbonate, (89%) [660];
*in ethyl ether (38%) [724];
*in ethanol [1575] [1623], (40-42%) [1623].

-Also obtained by UV light irradiation of 4-methoxyphenyl 3-(ethylenedioxy)-butanoate in hexane at r.t. (34%) [42].

-Also obtained by UV light irradiation of 2,4-dimethoxyphenyl acetate in benzene or ethanol (11-13%) [280].

-Also refer to: [289] [1311] [1666].

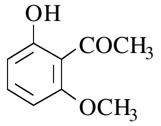
Isolation from natural sources

-From the essential oil of the rhizomes of *Primula acaulis*, an European variety of stemless primrose [693].

m.p. 52° [1010] [1345] [1582] [1888], 51° [1357], 50-51° [46] [140] [958] [1200], 50° [660] [1623], 49-49°5 [1635], 49° [374] [693], 48-50° [1036] [1858], 48-49° [813] [1077], 47-49° [723], 46° [1575];
b.p._{12} 138-142° [140], b.p._{15} 146-150° [1345];
^{1}H NMR [723] [914], ^{13}C NMR [736] [914] [1396] [1759], IR [723] [1923], UV [723] [813]; pK_a [1697].

1-(2-Hydroxy-6-methoxyphenyl)ethanone

[703-23-1] $C_9H_{10}O_3$ mol.wt. 166.18



Syntheses

-Preparation by reaction of methyl iodide on 2,6-dihydroxyacetophenone with potassium carbonate in boiling acetone [736] [1077] [1307], (56%) [1307].

-Preparation by reaction of dimethyl sulfate on 2,6-dihydroxyacetophenone,
*with potassium carbonate in boiling benzene (71-73%) [136] [1111];
*with potassium carbonate in boiling acetone [520] [1873], (quantitative yield) [1873];
*with potassium hydroxide in benzene, in a water bath (54%) [1610];
*with 20% solution of sodium hydroxide (68%) [1867];
*with 30% solution of sodium hydroxide (20%) [447] [1092].

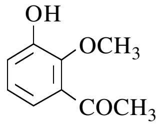
-Also obtained by partial demethylation of 2,6-dimethoxyacetophenone with aluminium chloride in acetonitrile for 6 h at 45° (30%) [962].

-Also obtained from 3-acetyl-5-methoxy-2-methylchromone by refluxing with 2% sodium carbonate solution [1289].

m.p. 60° [136] [1092] [1289] [1867], 59-60° [1610], 58°5 [1307], 58-59° [447], 57-59° [1111], 57-58° [520], 55-56° [1077], 55° [1873];
^{1}H NMR [238], ^{13}C NMR [520] [736], UV [447].

1-(3-Hydroxy-2-methoxyphenyl)ethanone

[204781-71-5] $C_9H_{10}O_3$ mol.wt. 166.18



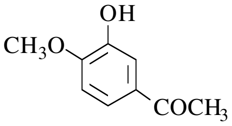
Isolation from natural sources

-Detected in liquid smoke flavouring preparations (compound **61**) [708].

GC [708]; GC/MS [708].

1-(3-Hydroxy-4-methoxyphenyl)ethanone *(Isoacetovanillone)*

[6100-74-9] $C_9H_{10}O_3$ mol.wt. 166.18



Syntheses

-Preparation by saponification of 3-acetoxy-4-methoxyacetophenone [1164] [1568] [1577], (90%) [1577], (59%) [1164].
-Preparation by hydrolysis of 3,4-dimethoxyacetophenone with concentrated sulfuric acid at 65° (58%) [295].
-Preparation by reaction of methyl iodide on 3,4-dihydroxyacetophenone with lithium carbonate in DMF at 55° (90%) [1899].
-Preparation by reaction of activated zinc dust on 3-hydroxy-4-methoxy-α-chloroacetophenone with 10% acetic acid in refluxing ethanol (48%) [1706].
-Preparation by Fries rearrangement of guaiacol acetate,
*with hydrofluoric acid at 0° (28%) [480];
*with zinc chloride at reflux (6%) [1481].
-Preparation by reaction of acetic acid on guaiacol,
*with hydrofluoric acid at 0° (25%) [480];
*with phosphorous oxychloride on a steam bath (20%) [433].
-Preparation by reaction of acetic anhydride on guaiacol,
*with concentrated sulfuric acid at 80° (20-24%) [1568]. (The *in situ* formed sulfoacetic acid during the reaction was the actual acylating agent);
*with zinc chloride [684].
-Obtained by reaction of sodium acetate on 3-chloroacetoxy-4-methoxyacetophenone in refluxing methanol [1831].
-Also refer to: [1368].

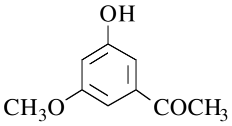
Isolation from natural sources

-From Chinese Moutan Cortex, the root of *Paeonia suffruticosa* Andrews or Anhr. *(mudanpi)* (minor component) (Paeoniaceae) [1924], (Ranunculaceae) [1098].

m.p. (anhydrous): 93° [480], 92-93° [295] [1098], 92° [1164], 91-92° [433] [1577], 91° [1568], 89° [1899], 87-88° [1706];
m.p. (hydrate): 67-68° [1481] [1577], 66-69° [1568], 65-68° [1831], 64-65° [684], 59-60° [433];
b.p.$_{15}$ 180-200° [433], b.p.$_{18}$ 195-200° [1568];
^{1}H NMR (Sadtler: standard n° 28211 M);
IR [1164] and (Sadtler: standard n° 55283); UV [1164], MS [684].

1-(3-Hydroxy-5-methoxyphenyl)ethanone

[35999-23-6] $C_9H_{10}O_3$ mol.wt. 166.18

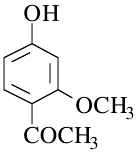


Synthesis

-Refer to: [1791].

1-(4-Hydroxy-2-methoxyphenyl)ethanone *(Isopaeonol)*

[493-33-4] $C_9H_{10}O_3$ mol.wt. 166.18



Syntheses

-Preparation by reaction of acetonitrile on resorcinol monomethyl ether (Hoesch reaction) (27%) [790], (10%) [138].
-Preparation by reaction of acetic acid on resorcinol monomethyl ether,
*with polyphosphoric acid (27%) [1308];
*using perchloric acid liberated *in situ*, at 60° (6%) [1176].
-Preparation by hydrolysis of 4-acetyl-3-methoxyphenyl acetate with boiling 10% sodium hydroxide solution (58%) [1131] or 4-acetyl-3-methoxyphenyl benzoate with potassium hydroxide in refluxing methanol (85%) [874].
-Also obtained (by-product) by Fries rearrangement of 3-methoxyphenyl acetate with aluminium chloride in nitrobenzene at r.t. (11%) [1196] [1202] or at 90° (4%) [138].
-Also refer to: [1311] and [1868] (compound **8**).

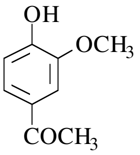
Isolation from natural sources

-This ketone was identified in the extract from "Redgold" apple flowers [1361].

m.p. 139-140° [874] [1131], 138° [138] [790] [1196] [1202], 137-138° [1176], 134° [1308]; ^{13}C NMR [1396].

1-(4-Hydroxy-3-methoxyphenyl)ethanone *(Apocynin; Acetovanillone; Acetoguaiacone)*

[498-02-2] $C_9H_{10}O_3$ mol.wt. 166.18



Syntheses

-Preparation by reaction of acetyl chloride on guaiacol [1568].
-Preparation by reaction of acetic anhydride on guaiacol with polyphosphoric acid in a water bath (29%) [1831].
-Preparation by Fries rearrangement of guaiacol acetate,
*with aluminium chloride in nitrobenzene at r.t. [155] [201] [1268] [1294] [1939], (49-51%) [1268] [1939] or at 80° (40%) [201];
*with hydrofluoric acid at 0° (50%) [480];
*with zinc chloride at 200° (25-26%) [433] [1481].
-Preparation by reaction of acetic acid on guaiacol,
*with hydrofluoric acid at 0° (38%) [480];
*with polyphosphoric acid (36%) [1308];

*with zinc chloride at reflux (4%) [433];
*with aluminium chloride-zinc chloride mixture at 140-150° [1370] [1568], (low yield) [1370].
-Also obtained by hydrolysis of 4-acetyl-2-methoxyphenyl acetate with boiling water [1568].
-Also obtained by saponification of 4-acetyl-2-methoxyphenyl benzoate with boiling aqueous sodium hydroxide (56%) [599].
-Also obtained (low yield) by treatment of 4-hydroxy-3-methoxybenzoic acid (vanillic acid) with calcium carbonate in boiling dilute acetic acid [1317].
-Also obtained from 4-hydroxy-3-methoxy-α-bromoacetophenone [1492] or 4-hydroxy-3-methoxy-α-chloroacetophenone [1442] by reductive removal of the halogen atom with iron filings and 10% sulfuric acid in aqueous ethanol at 60°.
-Also obtained by UV light irradiation,
*of guaiacol acetate in benzene (12-14%) [280] [724];
*of 2,4-dimethoxyphenyl acetate in benzene (8%) [280] or in ethanol (4%) [280].
-Also refer to: [1666] [1702].

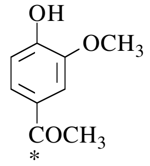
Isolation from natural sources

-From rhizomes of Canadian hemp, *Apocynum cannabinum*, of *Apocynum androsaemifolium* (Apocynaceae) [598] [1258], of several species of *Apocynum* [684].
-From the essential oil of the rhizomes of Iris (Iridaceae) [1312].
-From the roots of *Paeonia broteroi* (Paeoniaceae) [490].
-From the root of *Paeonia suffruticosa* Andrews (Paeoniaceae) [1924].
-From the bulbs of *Buphane disticha*, Herb. (Amaryllidaceae) [1829].
-From spruce lignin sulfonic acid by treatment with hot aqueous alkali (0.2-0.3%) [1079].
-Described by Shimamoto as one of the fragrant components of Soy [1294].

m.p. 116° [480], 115-116° [201] [1481], 115-115°5 [1312],
115° [598] [599] [684] [1258] [1268] [1317] [1370] [1442] [1829],
114-115° [1831], 114° [1308], 113°5-114°5 [1079], 113-114° [433] [1492],
112-114° [1456];
b.p.$_{13}$ 160-170° [1268], b.p.$_{15-20}$ 233-235° [1317], b.p.$_{760}$ 280-300° [1370], b.p. 300° [598];
^{1}H NMR [490], IR [490], UV [490] [1082], MS [684] [1456].

1-(4-Hydroxy-3-methoxyphenyl)ethanone-*1*-^{13}*C*

[199793-91-4] $C_9H_{10}O_3$ mol.wt. 167.17

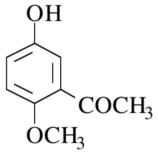


Synthesis

-Obtained by condensation of [1-^{13}C]acetic acid with guaiacol [1682].

1-(5-Hydroxy-2-methoxyphenyl)ethanone

[31405-60-4] $C_9H_{10}O_3$ mol.wt. 166.18



Syntheses

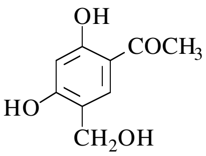
-Preparation by reaction of concentrated hydrochloric acid on 5-(benzyloxy)-2-methoxyacetophenone in acetic acid at 65-70° (31%) [130].
-Also obtained (by-product) by reaction of dimethyl sulfate on 5-acetoxy-2-hydroxyacetophenone with potassium carbonate in acetone at r.t. (4%) [723].

-Preparation by reaction of methyl iodide on quinacetophenone with lithium carbonate in DMF at 60° (54%) [1899].
-Preparation by partial demethylation of 2,5-dimethoxyacetophenone with sulfuric acid at 45-55° (42%) [1078].

m.p. 83° [130], 82-83° [1078], 81-83° [1899], 64-65° [1124], 62-63° [723];
^{1}H NMR [723], IR [723], UV [723] [1124].

1-[2,4-Dihydroxy-5-(hydroxymethyl)phenyl]ethanone

[117705-66-5] $C_9H_{10}O_4$ mol.wt. 182.18



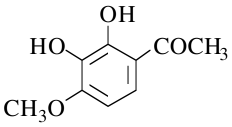
Synthesis

-Preparation by hydrogenation of 5-formyl-2,4-dihydroxyacetophenone in the presence of 10% Pd/C in ethanol (74%) [777].

m.p. 51-52° [777].

1-(2,3-Dihydroxy-4-methoxyphenyl)ethanone

[708-53-2] $C_9H_{10}O_4$ mol.wt. 182.18



Syntheses

-Preparation by reaction of acetic acid on pyrogallol 1-methyl ether,
*with zinc chloride at reflux (155-160°) (Nencki reaction), (62%) [136], (46%) [141];
*with boron trifluoride on a steam bath (77%) [1053].
-Preparation by reaction of methyl iodide on gallacetophenone monopotassium salt in boiling methanol [1409].
-Preparation by hydrolysis of 3-acetoxy-2-hydroxy-4-methoxyacetophenone with concentrated hydrochloric acid in refluxing aqueous ethanol (84%) [814].
-Also obtained by reaction of acetyl chloride on 2,6-dimethoxyphenol with zinc chloride at r.t. (8%) [1194].
-Also obtained by Fries rearrangement of 2,6-dimethoxyphenyl acetate with zinc chloride at 120° (6%) [1194].
-Also obtained by partial dealkylation of 2-hydroxy-3,4-dimethoxyacetophenone [663] [1194] with hydrobromic acid in acetic acid at r.t. (46%) [663] or by partial dealkylation of 3-ethoxy-2-hydroxy-4-methoxyacetophenone in the same conditions (22%) [663].

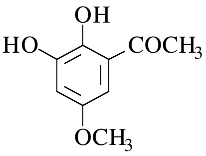
Isolation from natural sources

-From the roots of *Paeonia broteroi* Boiis & Reuter (Paeoniaceae) [490] or from the root cortex of *Paeonia suffruticosa* Anhr. [mudanpi in Chinese] (Ranunculaceae) (minor component) [1098].

m.p. 132-133° [1053] [1194] [1408] [1409], 132° [141], 131-132° [1098], 130-134°5 [814], 130-132° [663];
^{1}H NMR [490] [1053], IR [490] [1053], UV [490], MS [490] [684].

1-(2,3-Dihydroxy-5-methoxyphenyl)ethanone

$C_9H_{10}O_4$ mol.wt. 182.18



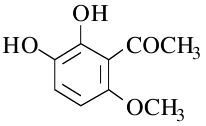
Synthesis

-Obtained by reaction of potassium persulfate on 2-hydroxy-5-methoxyacetophenone in aqueous sodium hydroxide solution (1%) [140].

m.p. 120° [140].

1-(2,3-Dihydroxy-6-methoxyphenyl)ethanone

[56358-73-7] $C_9H_{10}O_4$ mol.wt. 182.18



Syntheses

-Preparation by reaction of 3% hydrogen peroxide on 3-acetyl-2-hydroxy-4-methoxybenzaldehyde into solution of 1 N sodium hydroxide (Dakin reaction) (62-65%) [130] [1305].

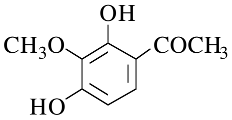
-Preparation by reaction of 3% hydrogen peroxide on the 3-acetyl-2-hydroxy-6-methoxyacetophenone into solution of 1 N sodium hydroxide at r.t. (33%) [130].

-Also obtained by reaction of concentrated hydrochloric acid on 2,3-bis(benzyloxy)-6-methoxyacetophenone in acetic acid at 60° [130].

m.p. 148-149° [130], 147° [1305]; ^{1}H NMR [238], MS [238].

1-(2,4-Dihydroxy-3-methoxyphenyl)ethanone

[62615-26-3] $C_9H_{10}O_4$ mol.wt. 182.18



Syntheses

-Preparation by catalytic hydrogenolysis of 4-(benzyloxy)-2-hydroxy-3-methoxyacetophenone in the presence of 5% Pd/C in ethyl acetate [972] [1571], (90%) [972].

-Preparation by reaction of boron trifluoride-acetic acid complex with the pyrogallol 2-methyl ether at 100° (79-85%) [1053] [1360].

-Preparation by reaction of acetonitrile on pyrogallol 2-methyl ether with triflic acid at r.t. (60%) [1458].

-Also obtained by reaction of aluminium chloride on gallacetophenone trimethyl ether in boiling ethyl ether (15%) [135].

-Also obtained by reaction of methyl iodide on gallacetophenone monopotassium salt in boiling methanol (10%) [1407] [1409].

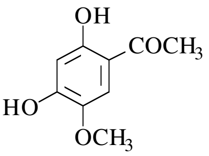
-Also obtained by hydrolysis of 2,4-diacetoxy-3-methoxyacetophenone with boiling aqueous sodium carbonate solution [1406].

N.B.: The melting points of the 1-(2,4-dihydroxy-3-methoxyphenyl)ethanone are conflicting [1458]. One shall thus mention that the melting points of this product, that are in the range 130-135°, can be compared to those of the 1-(2,3-dihydroxy-4-methoxyphenyl)ethanone (132-133°). However, ^{1}H NMR spectral data of this ketone of m.p. 68° [1458] is identical with those reported for the compound of m.p. 141-144° [1571].

m.p. 141-144° [1571], 134-135° [1406], 132-133° [1407] [1409], 130-131° [135], 76° [972] [1360], 75-76° [1053], 68° [1458];
^{1}H NMR [1458] [1571], IR [1053] [1458], MS [1458].

1-(2,4-Dihydroxy-5-methoxyphenyl)ethanone

[7298-21-7] $C_9H_{10}O_4$ mol.wt. 182.18



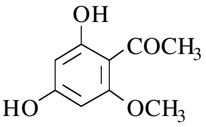
Syntheses

-Preparation by debenzylation of 4-(benzyloxy)-2-hydroxy-5-methoxyacetophenone,
*by catalytic hydrogenolysis with 5 to 10% Pd/C in ethyl acetate at r.t. (quantitative yield) [8] [60];
*with concentrated hydrochloric acid in boiling acetic acid [1068].
-Preparation by partial demethylation of 2,4,5-trimethoxyacetophenone with hydrobromic acid in acetic acid [156] [157].
-Preparation by Fries rearrangement of 2,4-diacetoxyanisole with aluminium chloride [147].

m.p. 174° [1068], 172-173° [60], 171-172° [147], 170-171° [8], 166° [156] [157].

1-(2,4-Dihydroxy-6-methoxyphenyl)ethanone

[3602-54-8] $C_9H_{10}O_4$ mol.wt. 182.18



Syntheses

-Preparation by reaction of acetonitrile on phloroglucinol monomethyl ether (Hoesch reaction) [174] [736] [761] [1673] [1945], (87%) [1945], (73%) [174], (62%) [1673].
-Preparation by catalytic hydrogenolysis of 2,4-bis-(benzyloxy)-6-methoxyacetophenone in the presence of 10% Pd/C (89%) [1822] in ethyl acetate (64%) [841].
-Preparation by reaction of aluminium chloride,
*on the 2,4,6-trimethoxyacetophenone [710] [761] [873] [1140] [1625] in boiling chlorobenzene (29-35%) [710] [1140];
*on the 2-hydroxy-4,6-dimethoxyacetophenone in boiling chlorobenzene [876] [877] [879] [1142], (58%) [877] according to the method [1142], (58%) [879];
*on the 4-hydroxy-2,6-dimethoxyacetophenone in boiling benzene [1037].
-Preparation by partial demethylation of 4-hydroxy-2,6-dimethoxyacetophenone with boron trichloride in cooled methylene chloride (74%) [496].
-Also obtained by hydrolysis of 2,4-dihydroxy-6-methoxyacetophenone diacetate [1131].
-Also obtained by reaction of concentrated hydrochloric acid on 4-(benzyloxy)-2-hydroxy-6-methoxyacetophenone in acetic acid [1281].

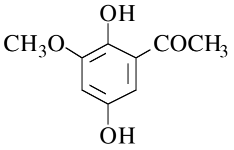
Isolation from natural sources

-From the stem of *Kniphofia fioliosa* (Asphodelaceae) [1917].
-From the aerial parts of *Tanacetum densum* subsp. *eginense* [692].
-From the roots of *Sanguisorba officinalis* [1101].
-From phloroacetophenone 2,4-di-O-(2,3,4,6-tetra-O-acetyl)-β-D-galactopyranoside. This one was methylated with methyl iodide in the presence of silver carbonate in refluxing acetone for 8 h. The obtained methyl ether was deacetylated, then hydrolyzed with 5% sulfuric acid [1008].
-By reductive cleavage of *isofoliosone*, itself isolated from *Kniphofia foliosa* Hochst [1917].
N.B.: Mg (II) salt [1548].

m.p. 207-209° [1037], 207° [1625], 205-207° [85] [1008] [1673] [1675], 205-206° [877], 205° [873], 204-205° [879], 203-204° [1131] [1281], 203° [710] [876] [1142] [1945], 201-202° [841] [1822], 195-198° [1917];
^{1}H NMR [841] [1493] [1917], ^{13}C NMR [117] [736] [1917], IR [841] [1493], UV [1322], MS [841] [1917].

1-(2,5-Dihydroxy-3-methoxyphenyl)ethanone

$C_9H_{10}O_4$ mol.wt. 182.18



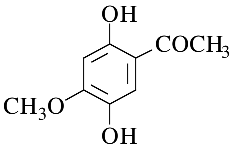
Synthesis

-Obtained by reaction of potassium persulfate on 2-hydroxy-3-methoxyacetophenone in aqueous sodium hydroxide solution (26%) [1643], (2%) [140].

m.p. 172-174° [1643], 172° [140].

1-(2,5-Dihydroxy-4-methoxyphenyl)ethanone

[22089-12-9] $C_9H_{10}O_4$ mol.wt. 182.18



Syntheses

-Preparation by Fries rearrangement of 2-methoxyhydroquinone diacetate,
*with boron trifluoride in acetic acid (97%) [498], (62%) [118];
*with aluminium chloride in nitrobenzene at r.t. [147] [1196] [1202], (38%) [1202], (31%) [1196].

-Preparation by reaction of dimethyl sulfate with 2,4,5-trihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone (65%) [1900].

-Preparation from paeonol by persulfate oxidation [147] [156] [157] [971], (Elbs reaction) (18-22%) [156] [157] [971].

-Preparation by partial demethylation of 2-hydroxy-4,5-dimethoxyacetophenone with hydrobromic acid in refluxing acetic acid [1068].

-Preparation by diazotization of 5-amino-2-hydroxy-4-methoxyacetophenone, followed by decomposition of the diazonium salt obtained [1626].

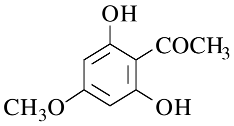
Isolation from natural sources

-From Chinese Moutan Cortex, the root of *Paeonia suffructicosa* Andrews (Paeoniaceae) [Botanpi] in Japanese [1924]. The root cortex of *Paeonia suffruticosa* Anhr. (Ranunculaceae) is also known as [mudanpi] in Chinese. In this, the ketone is a minor component [1098].

m.p. 166-167° [1098], 166° [118] [498], 165-166° [1196] [1202], 164-166° [1900], 164-165° [1068] [1626], 164° [156] [157] [971];
^{1}H NMR [118], IR [118], MS [684].

1-(2,6-Dihydroxy-4-methoxyphenyl)ethanone

[7507-89-3] $C_9H_{10}O_4$ mol.wt. 182.18



Syntheses

-Obtained by reaction of boiling aqueous potassium hydroxide,
*on the Methyl 3-acetyl-2,4-dihydroxy-6-methoxybenzoate (quantitative yield) [73] [1884];
*on the 3-trichloroacetyl-2,6-dihydroxy-4-methoxyacetophenone [5] [73] [1884], (quantitative yield) [73] [1884].
-Preparation by adding a solution of 2,6-diacetoxy-4-hydroxyacetophenone in dioxane at r.t.. The residual pale yellow oil obtained after elimination of solvent was hydrolyzed with dilute hydrochloric acid in refluxing methanol (83%) [311].
-Preparation by selective deacetylation of 2,4-diacetyl-5-methoxyresorcinol with sodium methoxide in refluxing methanol [761] [762] [764], (76%) [761] or with boiling 1 N sodium hydroxide (70%) [342].
-Preparation by reaction of diazomethane on phloroacetophenone in ethyl ether at r.t. [361] [554] [1673] [1674], (37%) [361].
-Preparation by reaction of dimethyl sulfate on phloroacetophenone with potassium carbonate in refluxing acetone (62%) [1006].

Isolation from natural sources

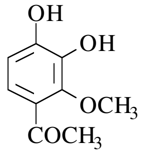
-From the root tissue of *Sanguisorba minor* (Rosaceae) [1006].
-As a decomposition product of sakuranin, a glucoside isolated from the bark of *Prunus pseudocerasus Lindl.*, (Var. Sieboldi Maxim.), also called *Prunus yedoensis Matsumura* [85].
-By alkaline hydrolysis of artocarpetin, a flavonoid pigment isolated from the heartwood of *Artocarpus integrifolia* [481].
-Claimed to be obtained as a minor component in the steam distillates of the resins from various species of *Xanthorrhoea (X.)*; *X. tateana* F. Muell. and *X. preissi* (m.p. 79°) [1484], but also from *X. arborea* R. Br. and *X. reflexa.* (m.p. 79°) [596]. Thus, this compound, the 2,6-dihydroxy-4-methoxyacetophenone has a melting point of 136-137° (see below). Two possibilities may then occur:
*either this compound is a monomethyl ether derived from phloroacetophenone, as the authors do pretend, and in this case, it would be at the time the 2,4-dihydroxy-6-methoxyacetophenone (m.p. 205-207°) [85] [1673] [1675]. It is not possible;
*or, it is a dimethyl ether [1675], and in this case, it would be the 2-hydroxy-4,6-dimethoxy-acetophenone *(Xanthoxylin)* (m.p. 78-79°) [1564], (80°) [1675], (82°) [223], what is later confirmed [223].

m.p. 139-140° [85], 139-139°5 [311], 139° [481], 138-140° [361],
137-139° [342], 136-137° [761] [1037] [1625] [1673] [1675] [1884], 134-136° [5];
b.p.$_{0.5}$ 145-150° [481];

^{1}H NMR [5] [311] [342] [738] [761], ^{13}C NMR [5] [738], IR [761], UV [1006],
MS [1006].

1-(3,4-Dihydroxy-2-methoxyphenyl)ethanone

[27829-93-2] $C_9H_{10}O_4$ mol.wt. 182.18



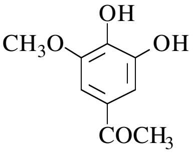
Syntheses

-Obtained by debenzylation of 3,4-bis(benzyloxy)-2-methoxyacetophenone with 15% ethanolic hydrochloric acid, on a steam bath (22%) [1053].
-Also refer to: [1029] (compound 5).

m.p. 84-85° [1053]; ^{1}H NMR [1053], IR [1053].

1-(3,4-Dihydroxy-5-methoxyphenyl)ethanone

[3934-89-2] $C_9H_{10}O_4$ mol.wt. 182.18

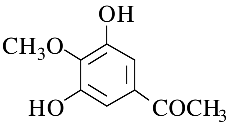


Syntheses

-Cyclic voltammetry showed the electrochemical oxidation of 3,5-dimethoxy-4-hydroxyacetophenone gave 3,4-dihydroxy-5-methoxyacetophenone as the major product by a one electron oxidation process (20% isolated yield), but 30 to 40% estimated by thin layer chromatography [292].
-Also refer to: [617] [618] [1244] [1638].

1-(3,5-Dihydroxy-4-methoxyphenyl)ethanone

[148204-58-4] $C_9H_{10}O_4$ mol.wt. 182.18

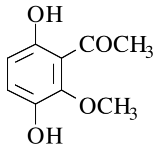


Isolation from natural sources

-Characterization in liquid wastes from eucalyptus wood and kraft lignin charring by flame-ionization gas-chromatography and gas-chromatography/mass-spectrometry [1504].

1-(3,6-Dihydroxy-2-methoxyphenyl)ethanone

[33539-20-7] $C_9H_{10}O_4$ mol.wt. 182.18



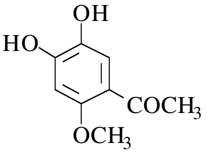
Syntheses

-Preparation from 2-hydroxy-6-methoxyacetophenone by persulfate oxidation (Elbs reaction) (26-33%) [136] [1307] [1867].
-Preparation by reduction of 2-acetyl-3-methoxy-1,4-benzoquinone using conventional methods [587].
-Also obtained (low yield) by reaction of 2-acetyl-1,4-benzoquinone with an excess of methanol at r.t., with exclusion of light [587].

m.p. 91° [1307], 90° [136] [587] [1867]; ^{1}H NMR [238] [587], IR [587], MS [238].

1-(4,5-Dihydroxy-2-methoxyphenyl)ethanone

$C_9H_{10}O_4$ mol.wt. 182.18



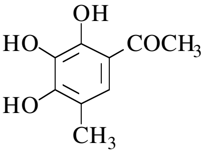
Synthesis

-Obtained by reaction of the Dakin solution on 2,4-diacetyl-5-methoxyphenol [147].

m.p. 173-175° [147].

1-(2,3,4-Trihydroxy-5-methylphenyl)ethanone

[59862-06-5] $C_9H_{10}O_4$ mol.wt. 182.18



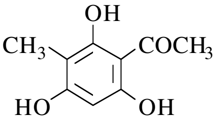
Syntheses

-Preparation by reaction of acetic anhydride and acetic acid on 1,2,3-trihydroxy-4-methylbenzene with zinc chloride at 140-145°, then deacylation of keto esters mixture obtained with boron trifluoride etherate in methanol (25%) [623].
-Also obtained (poor yield) by alkaline degradation of a solution of D-xylose or D-glucose in 0.63 M sodium hydroxide at 96° under nitrogen [623].

m.p. 167-168° [623]; ^{1}H NMR [623], IR [623], MS [623].

1-(2,4,6-Trihydroxy-3-methylphenyl)ethanone

[2657-28-5] $C_9H_{10}O_4$ mol.wt. 182.18



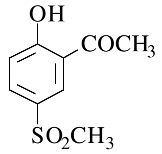
Syntheses

-Preparation by reaction of acetonitrile on 2-methylphloroglucinol (Hoesch reaction) [469] [1185] [1564] [1887], (83%) [1887], (70%) [1185], (33%) [1564].
-Preparation by reduction of 3-formylphloroacetophenone with hydrochloric acid and amalgamated zinc in gently heated aqueous methanol (53%) [1498].
-Preparation by demethylation of 2,4-dimethoxy-6-hydroxy-3-methylacetophenone,
*with boron tribromide in methylene chloride at 0° (77%) [837];
*with aluminium chloride in refluxing benzene (87%) [1272].
-Preparation by reaction of 2-methylphloroglucinol with boron trifluoride-acetic acid complex at 28-30° (50%) [1146].
-Also obtained from phloroacetophenone using methyl iodide and alkali in methanolic solution [623] [628] [875] [883] [1491], (50%) [875], (31%) [883].

m.p. 211-212° [469] [837] [1272] [1564], 211° [1185], 210-211° [875] [1498] [1887], 210° [1146], 209-210° [350], 205-206° [883];
^{1}H NMR [350] [837] [1887], IR [837], UV [1491], MS [1887].

1-[2-Hydroxy-5-(methylsulfonyl)phenyl]ethanone

[20951-24-0] $C_9H_{10}O_4S$ mol.wt. 214.24



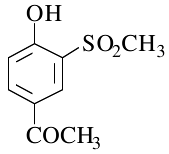
Synthesis

-Preparation by Fries rearrangement of 4-(methylsulfonyl)phenyl acetate with aluminium chloride without solvent at 120° (42%) [318].

m.p. 139-140° [318].

1-[4-Hydroxy-3-(methylsulfonyl)phenyl]ethanone

[56490-43-8] $C_9H_{10}O_4S$ mol.wt. 214.24



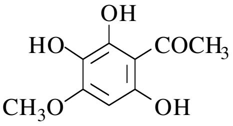
Synthesis

-Preparation by Fries rearrangement of 2-(methylsulfonyl)phenyl acetate in the presence of aluminium chloride in nitrobenzene at 50-60° (75%) [935].

m.p. 168-169° [935].

1-(2,3,6-Trihydroxy-4-methoxyphenyl)ethanone

$C_9H_{10}O_5$ mol.wt. 198.18



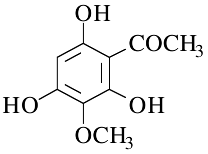
Syntheses

-Preparation by reduction of 2-acetyl-3-hydroxy-5-methoxyquinone,
*with sulfur dioxide in water [1466];
*with sodium hydrosulfite in boiling water (59%) [1845].

m.p. 170-171° [1466] [1845].

1-(2,4,6-Trihydroxy-3-methoxyphenyl)ethanone

[16297-01-1] $C_9H_{10}O_5$ mol.wt. 198.18



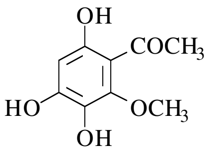
Syntheses

-Preparation by reaction of acetonitrile on 2-methoxy-1,3,5-trihydroxybenzene (2-methoxyphloroglucinol or iretol), (Hoesch reaction) [1341] [1420], (71%) [1420].
-Also obtained (poor yield) by partial demethylation of 2,4-dihydroxy-3,6-dimethoxyacetophenone with aluminium chloride in nitrobenzene at 100° [1605].

m.p. 188° [1605], 169-170° [1341], 168° [1420].

1-(3,4,6-Trihydroxy-2-methoxyphenyl)ethanone

[73239-52-8] $C_9H_{10}O_5$ mol.wt. 198.18



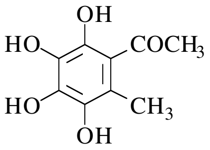
Synthesis

-Refer to: [379].

TLC [379].

1-(2,3,4,5-Tetrahydroxy-6-methylphenyl)ethanone

[66296-85-3] $C_9H_{10}O_5$ mol.wt. 198.18



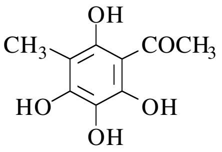
Synthesis

-Obtained (poor yield) by treatment of dihydroxyacetone in aqueous solution (pH 4.5) at 96° (2%) [1434].

m.p. 178-181° [1434]; ^{1}H NMR [1434], MS [1434].

1-(2,3,4,6-Tetrahydroxy-5-methylphenyl)ethanone

$C_9H_{10}O_5$ mol.wt. 198.18



Syntheses

-Preparation by reaction of sulfur dioxide on 2-acetyl-3,5-dihydroxy-6-methyl-2,5-cyclohexadiene-1,4-dione in dilute methanol (92%) [1490].

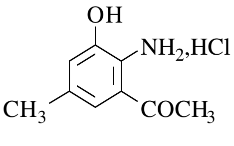
-Preparation by hydrolysis of 3-amino-2,4,6-trihydroxy-5-methylacetophenone hydrochloride (89%) [1490].

-Preparation by reaction of aluminium bromide on 2,5-dihydroxy-4,6-dimethoxy-3-methylacetophenone in chlorobenzene at 80-85° (61%) [1490].

m.p. 191-192° [1490].

1-(2-Amino-3-hydroxy-5-methylphenyl)ethanone *(Hydrochloride)*

$C_9H_{11}NO_2$, HCl mol.wt. 201.65



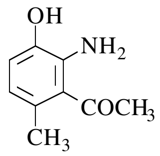
Synthesis

-Preparation by reaction of hydrogen on 3-hydroxy-5-methyl-2-nitroacetophenone with Raney nickel in methanol (80%) [324].

m.p. 194-196° (d) [324]; UV [324].

1-(2-Amino-3-hydroxy-6-methylphenyl)ethanone

[38968-45-5] $C_9H_{11}NO_2$ mol.wt. 165.19

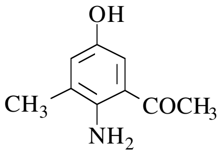


Syntheses

- -Obtained (trace) by photolysis of 3,4-dimethylanthranil in 98% sulfuric acid [545].
- -Also obtained (trace) by thermal decomposition of 2-azido-6-methylacetophenone in 98% sulfuric acid [545].

1-(2-Amino-5-hydroxy-3-methylphenyl)ethanone

$C_9H_{11}NO_2$ mol.wt. 165.19

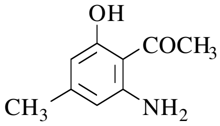


Synthesis

-Refer to: [546] (compound **8e**).

1-(2-Amino-6-hydroxy-4-methylphenyl)ethanone

[97066-15-4] $C_9H_{11}NO_2$ mol.wt. 165.19



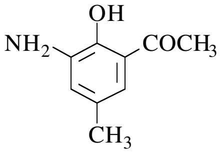
Synthesis

-Obtained by reaction of potassium hydroxide with 2-acetyl-3-amino-5-hydroxy-5-methyl-2-cyclohexenone in ethanol at 40° (44%) [562].

m.p. 91-92° [562]; IR [562], UV [562], MS [562].

1-(3-Amino-2-hydroxy-5-methylphenyl)ethanone

[70977-71-8] $C_9H_{11}NO_2$ mol.wt. 165.19



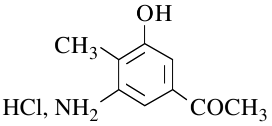
Syntheses

- -Preparation by hydrogenation of 2-hydroxy-5-methyl-3-nitroacetophenone using 5% Pd/C catalyst in ethanol (68%) [1463], (48%) [620].
- -Preparation by reduction of 2-hydroxy-5-methyl-3-nitroacetophenone with stannous chloride dihydrate in hydrochloric acid (50%) [956].

m.p. 71-72° [956], 56-58° [1463], 55-57° [620].

1-(3-Amino-5-hydroxy-4-methylphenyl)ethanone *(Hydrochloride)*

$C_9H_{11}NO_2$, HCl mol.wt. 201.65

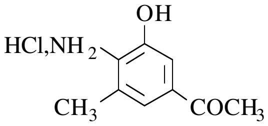


Synthesis

-Preparation by reduction of 3-hydroxy-4-methyl-5-nitroacetophenone with tin and 25% hydrochloric acid heated under reflux on a steam bath (87%) [633].

1-(4-Amino-3-hydroxy-5-methylphenyl)ethanone *(Hydrochloride)*

$C_9H_{11}NO_2$, HCl mol.wt. 201.65



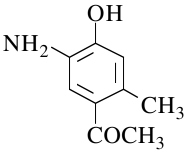
Synthesis

-Preparation by reaction of hydrogen on 3-hydroxy-5-methyl-4-nitroacetophenone with Raney nickel in methanol (92%) [324].

m.p. 195-198° [324]; UV [324].

1-(5-Amino-4-hydroxy-2-methylphenyl)ethanone

$C_9H_{11}NO_2$ mol.wt. 165.19



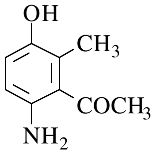
Synthesis

-Obtained by reduction of 4-hydroxy-2-methyl-5-nitroacetophenone with sodium hydrosulfite in boiling alkaline solution (66%) [1377].

m.p. 116° [1377].

1-(6-Amino-3-hydroxy-2-methylphenyl)ethanone

[69976-76-7] $C_9H_{11}NO_2$ mol.wt. 165.19

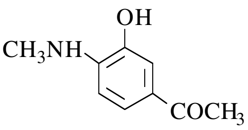


Synthesis

-Preparation by irradiation of 3,4-dimethyl-2,1-benzisoxazole in 96% sulfuric acid (91%) [546].

1-[3-Hydroxy-4-(methylamino)phenyl]ethanone

[54903-57-0] $C_9H_{11}NO_2$ mol.wt. 165.19



Syntheses

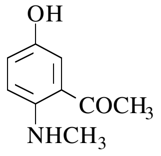
-Preparation from 6-acetyl-3-methylbenzoxazolinone by alkaline hydrolysis with boiling 10% aqueous sodium hydroxide solution (90 to 100%) [266], (60%) [1270].

-Also refer to: [203] (compound VII) and [1269].

m.p. 169-170° [266] [1270].

1-[5-Hydroxy-2-(methylamino)phenyl]ethanone

[63609-52-9] $C_9H_{11}NO_2$ mol.wt. 165.19



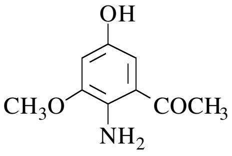
Synthesis

-Preparation by UV light irradiation of 1,3-dimethylindazole in aqueous sulfuric acid at 11-15° (38-44%) [672] [673].

m.p. 142-143° [672];
^{1}H NMR [672], IR [672], UV [672], MS [672].

1-(2-Amino-5-hydroxy-3-methoxyphenyl)ethanone

[126893-27-4] $C_9H_{11}NO_3$ mol.wt. 181.19



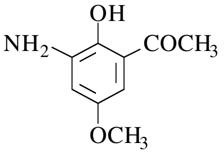
Synthesis

-Obtained (by-product) by reaction of stannous chloride on 3,5-dimethoxy-2-nitroacetophenone in concentrated hydrochloric acid at r.t. [1503].

m.p. 136-138° [1503];
^{1}H NMR [1503], ^{13}C NMR [1503], IR [1503], UV [1503], MS [1503].

1-(3-Amino-2-hydroxy-5-methoxyphenyl)ethanone

[55008-15-6] $C_9H_{11}NO_3$ mol.wt. 181.19



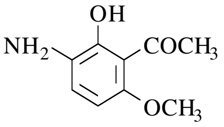
Syntheses

-Preparation by reduction of 2-hydroxy-5-methoxy-3-nitroacetophenone with stannous chloride dihydrate in hydrochloric acid (47%) [956].
-Preparation according to [955] by [1036].

m.p. 107-108° [956].

1-(3-Amino-2-hydroxy-6-methoxyphenyl)ethanone

[75452-86-7] $C_9H_{11}NO_3$ mol.wt. 181.19



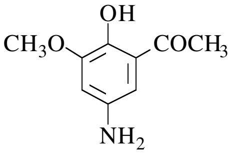
Synthesis

-Preparation by reaction of stannous chloride on 2-hydroxy-6-methoxy-3-nitroacetophenone in refluxing concentrated hydrochloric acid [371] [1213], (51%) [1213].

m.p. 66° [1213].

1-(5-Amino-2-hydroxy-3-methoxyphenyl)ethanone

$C_9H_{11}NO_3$ mol.wt. 181.19



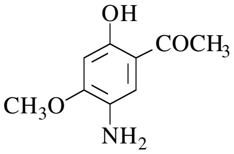
Synthesis

-Preparation from 2-hydroxy-3-methoxyacetophenone that was coupled with diazotized sulfanilic acid and the resulting azo dye reduced with sodium hydrosulfite to 5-amino-2-hydroxy-3-methoxyacetophenone (41%) [1643].

m.p. 145°5-147° [1643].

1-(5-Amino-2-hydroxy-4-methoxyphenyl)ethanone

$C_9H_{11}NO_3$ mol.wt. 181.19



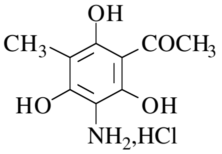
Synthesis

-Preparation by reduction of 2-hydroxy-4-methoxy-5-nitroacetophenone [1626] with tin in concentrated hydrochloric acid heated in a water bath [7] [947].

m.p. 113-114° [1626], 113° [947], 112-113° [7].

1-(3-Amino-2,4,6-trihydroxy-5-methylphenyl)ethanone *(Hydrochloride)*

$C_9H_{11}NO_4$, HCl mol.wt. 233.65



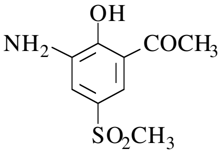
Synthesis

-Preparation by reaction of stannous chloride on 2,4,6-trihydroxy-3-methyl-5-phenylazoacetophenone in acetic acid at 85-90°, in the presence of concentrated hydrochloric acid [1490].

m.p. 210-211° [1490].

1-[3-Amino-2-hydroxy-5-(methylsulfonyl)phenyl]ethanone

[70977-88-7] $C_9H_{11}NO_4S$ mol.wt. 229.26

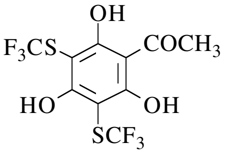


Synthesis

-Preparation by catalytic hydrogenation of 2-hydroxy-5-(methylsulfonyl)-3-nitroacetophenone in the presence of 5% Pd/C in ethanol at 25° [1463].

1-[2,4,6-Trihydroxy-3,5-bis[(trifluoromethyl)thio]phenyl]ethanone

[66625-04-5] $C_{10}H_6F_6O_4S_2$ mol.wt. 368.28



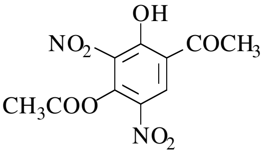
Synthesis

-Preparation by reaction of trifluoromethanesulfenyl chloride with phloroacetophenone in chloroform in the presence of a slight excess of pyridine and a small quantity of iron powder, first at -40°, then at 60° for 3 h (40%) [456].

m.p. 113-115° [456]; ^{1}H NMR [456], IR [456].

1-[4-(Acetyloxy)-2-hydroxy-3,5-dinitrophenyl]ethanone

$C_{10}H_8N_2O_8$ mol.wt. 284.18



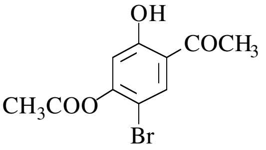
Synthesis

-Preparation by reaction of nitric acid on 4-acetoxy-2-hydroxyacetophenone in acetic acid or in acetic acid-ethanol mixture [7].

m.p. 121-122° [7].

1-[4-(Acetyloxy)-5-bromo-2-hydroxyphenyl]ethanone

$C_{10}H_9BrO_4$ mol.wt. 273.08



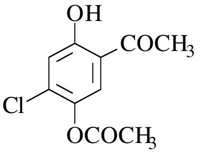
Synthesis

-Preparation by reaction of bromine on 4-acetoxy-2-hydroxyacetophenone in 80% acetic acid at r.t. (34%) [947] [1571].

m.p. 85° [1571], 84° [947]; ^{1}H NMR [1571].

1-[5-(Acetyloxy)-4-chloro-2-hydroxyphenyl]ethanone

$C_{10}H_9ClO_4$ mol.wt. 228.63



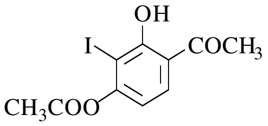
Syntheses

-Preparation by Fries rearrangement of 2-chlorohydroquinone diacetate with aluminium chloride [514].
-Also obtained by partial acetylation of 4-chloro-2,5-dihydroxyacetophenone [514].

m.p. 129° [514].

1-[4-(Acetyloxy)-2-hydroxy-3-iodophenyl]ethanone

[149810-09-3] $C_{10}H_9IO_4$ mol.wt. 320.08



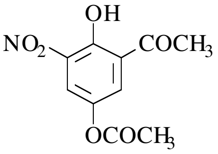
Synthesis

-Preparation by reaction of acetyl chloride with 2,4-dihydroxy-3-iodoacetophenone in the presence of triethylamine in methylene chloride for 1 h at 0° and for 2.5 h at r.t. (77%) [1265].

m.p. 101-102° [1265]; ^1H NMR [1265], IR [1265], MS [1265].

1-[5-(Acetyloxy)-2-hydroxy-3-nitrophenyl]ethanone

[30095-73-9] $C_{10}H_9NO_6$ mol.wt. 239.18



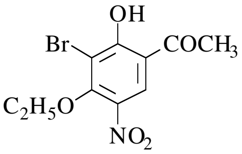
Synthesis

-Preparation by reaction of nitric acid (d = 1.5) on 5-acetoxy-2-hydroxyacetophenone in acetic acid at 10° (41%) [170].

m.p. 112-113° [170];
^1H NMR [170], IR [170], UV [170].

1-(3-Bromo-4-ethoxy-2-hydroxy-5-nitrophenyl)ethanone

[134716-11-3] $C_{10}H_{10}BrNO_5$ mol.wt. 290.09

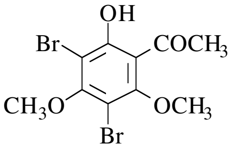


Synthesis

-Refer to: [63] (compound 1h).

1-(3,5-Dibromo-2-hydroxy-4,6-dimethoxyphenyl)ethanone

[3410-83-1] $C_{10}H_{10}Br_2O_4$ mol.wt. 354.00



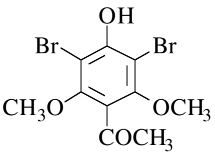
Syntheses

-Preparation by bromination of 2-hydroxy-4,6-dimethoxyacetophenone (Xanthoxylin) in chloroform containing 6% of pyridine (96%) [541].
-Also refer to: [362].

m.p. 111° [541]; IR [541].

1-(3,5-Dibromo-4-hydroxy-2,6-dimethoxyphenyl)ethanone

[57393-65-4] $C_{10}H_{10}Br_2O_4$ mol.wt. 354.00



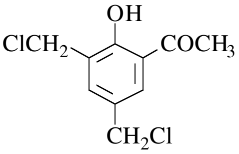
Synthesis

-Obtained (by-product) by reaction of bromine on 4-hydroxy-2,6-dimethoxyacetophenone in chloroform in the presence of aqueous sodium acetate solution (5%) [539].

m.p. 117-118° [539]; ^{1}H NMR [539].

1-[3,5-Bis(chloromethyl)-2-hydroxyphenyl]ethanone

$C_{10}H_{10}Cl_2O_2$ mol.wt. 233.09



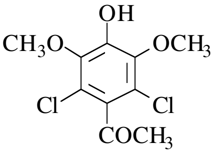
Synthesis

-Preparation by reaction of 37% formaldehyde solution on 2-hydroxyacetophenone with hydrochloric acid in a boiling water bath (81-87%) [1811].

m.p. 83° [1811].

1-(2,6-Dichloro-4-hydroxy-3,5-dimethoxyphenyl)ethanone

[94649-71-5] $C_{10}H_{10}Cl_2O_4$ mol.wt. 265.09



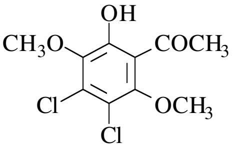
Syntheses

-Preparation by chlorination of acetosyringone (4-hydroxy-3,5-dimethoxyacetophenone) in dioxane with 2.0-2.5 mol. equiv. chlorine in acetic acid [1657] [1659], (37%) [1657].
-Identified in wheat and rye straw pulp bleaching and combined mill effluents [617].
-Identified on control of effluent from the manufacturing of bleached pulp and paper from sugarcane bagasse [616].
-Also refer to: [1658].

m.p. 114-115° [1657] [1659]; ^{1}H NMR [1657], ^{13}C NMR [1657], MS [1657].

1-(3,4-Dichloro-6-hydroxy-2,5-dimethoxyphenyl)ethanone

[88771-63-5] $C_{10}H_{10}Cl_2O_4$ mol.wt. 265.09



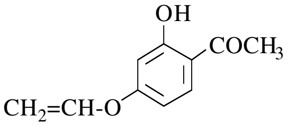
Synthesis

-Preparation by reaction of chlorine on 4-chloro-3,6-dimethoxy-2-hydroxyacetophenone in chloroform at r.t. (57%) [502].

m.p. 96° [502].

1-[4-(Ethenyloxy)-2-hydroxyphenyl]ethanone

[109661-95-2] $C_{10}H_{10}O_3$ mol.wt. 178.19



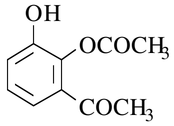
Synthesis

-Preparation by reaction of potassium tert-butoxide with 2-hydroxy-4-(2-chloroethoxy)acetophenone in refluxing tert-butanol (70%) [1529].

^{1}H NMR [1529], IR [1529].

1-[2-(Acetyloxy)-3-hydroxyphenyl]ethanone

[145723-28-0] $C_{10}H_{10}O_4$ mol.wt. 194.19



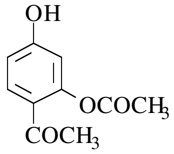
Synthesis

-Obtained by photooxygenation of 2,3-dimethyl-7-hydroxybenzofuran in methylene chloride at -5° (13%) [4].

m.p. 53-55° [4];
^{1}H NMR [4], ^{13}C NMR [4], IR [4], UV [4].

1-[2-(Acetyloxy)-4-hydroxyphenyl]ethanone

[52751-42-5] $C_{10}H_{10}O_4$ mol.wt. 194.19



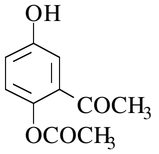
Syntheses

-Preparation by Fries rearrangement of resorcinol diacetate with ferric chloride in boiling acetic acid (46%) [711].
-Also obtained by enzymatic deacylation of 2,4-diacetoxyacetophenone with porcine pancreas lipase in tetrahydrofuran at 42-45° (80%) [1381] [1383].

m.p. 119-120° [711], 87-88° [1383]; ^{1}H NMR [1383].

1-[2-(Acetyloxy)-5-hydroxyphenyl]ethanone

[144152-29-4] $C_{10}H_{10}O_4$ mol.wt. 194.19



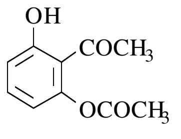
Syntheses

-Obtained by photooxygenation of 2,3-dimethyl-5-hydroxybenzofuran in methylene chloride at -5° (10%) [4].
-Also obtained by alcoholysis of 2,5-diacetoxyacetophenone with n-butanol mediated by *Pseudomonas cepacia* lipase in cyclohexane/tert-amyl alcohol at 40° (65%) [1326].
-Also obtained by enzymatic deacylation of 2,5-diacetoxyacetophenone with porcine pancreas lipase in tetrahydrofuran at 42-45° (60%) [1381] [1383].

m.p. 105-106° [4], 93-95° [1383];
^{1}H NMR [4] [1383], ^{13}C NMR [4], IR [4], UV [4].

1-[2-(Acetyloxy)-6-hydroxyphenyl]ethanone

[26674-05-5] $C_{10}H_{10}O_4$ mol.wt. 194.19

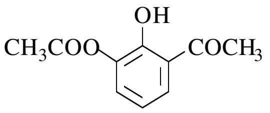


Syntheses

-Preparation by acylation of 2,6-dihydroxyacetophenone (compound **49**) [1335].
-Refer to: [1352]; this reference indicated in Chem. Abstr., **89**, 179792x (1978) for the monoacetate mentioned actually concerns the diacetate, that is to say the 1,3-diacetoxy-2-acetylbenzene.

1-[3-(Acetyloxy)-2-hydroxyphenyl]ethanone

[144224-87-3] $C_{10}H_{10}O_4$ mol.wt. 194.19

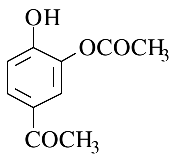


Synthesis

-Refer to: [1264].

1-[3-(Acetyloxy)-4-hydroxyphenyl]ethanone

[115436-75-4] $C_{10}H_{10}O_4$ mol.wt. 194.19



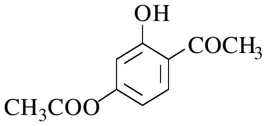
Synthesis

-Obtained (by-product) by reaction of acetic anhydride on pyrocatechol with zinc chloride at 145-150° (8%) [62].

m.p. 74-76° [62].

1-[4-(Acetyloxy)-2-hydroxyphenyl]ethanone

[42059-48-3] $C_{10}H_{10}O_4$ mol.wt. 194.19



Syntheses

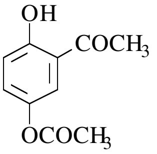
-Preparation by reaction of acetic anhydride on resacetophenone,
*at reflux [1230] [1319] [1637] [1877];
*with sodium acetate [137] [453] [475] [1739], (78%) [137];
*with pyridine (95%) [130], (54-59%) [1571] [1637].
-Preparation by reaction of acetic acid on resacetophenone with polyphosphoric acid (39%) [1298].
-Also obtained by reaction of acetyl chloride on resorcinol at reflux [1138] [1877].
-Also obtained (by-product) by reaction of acetic acid on resorcinol with polyphosphoric acid (3%) [1298].
-Also obtained by reaction of vinyl acetate on resacetophenone mediated by *Pseudomonas cepacia* lipase in cyclohexane/tert-amyl alcohol at 40° (55-65%) [1326].
-Also refer to: [1264].

m.p. 76° [1298], 75-76° [130] [137], 75° [453], 74° [711] [1230], 72-73° [475] [1637], 72° [1319] [1739], 69-71° [1571];

b.p. 303° [1230] [1637];
^{1}H NMR [1326] [1571]; ^{13}C NMR [1326], IR [1326].

1-[5-(Acetyloxy)-2-hydroxyphenyl]ethanone

[21222-04-8] $C_{10}H_{10}O_4$ mol.wt. 194.19



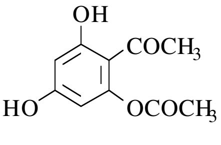
Syntheses

-Preparation by reaction of boiling acetic anhydride on quinacetophenone [993].
-Preparation by reaction of acetic anhydride and sodium acetate mixture on quinacetophenone at 50° [139].
-Preparation by Fries rearrangement of hydroquinone diacetate,
*with boron trifluoride etherate at 120° (90%) [1240];
*with aluminium chloride at 115-120° [723] [1240] [1487], (predominantly) [1487], (31%) [1240].
-Also obtained by UV light irradiation of hydroquinone diacetate in methanol (15%) [1614].
-Also obtained by reaction of vinyl acetate on quinacetophenone mediated by *Pseudomonas cepacia* lipase in cyclohexane/tert-amyl alcohol at 40° (97%) [1326].
-Also obtained by alcoholysis of quinacetophenone diacetate with n-butanol mediated by *Pseudomonas cepacia* lipase in cyclohexane/tert-amyl alcohol at 40° (28%) [1326].

m.p. 91° [139] [993], 83-84° [1614], 81-82° [1240], 80-85° [1487];
^{1}H NMR [723] [1240] [1326] [1614], ^{13}C NMR [1326],
IR [723] [1240] [1326] [1614], UV [723], MS [723]; pK_a [1697].

1-[2-(Acetyloxy)-4,6-dihydroxyphenyl]ethanone

[52751-41-4] $C_{10}H_{10}O_5$ mol.wt. 210.19

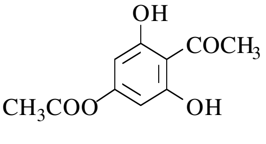


Synthesis

-Refer to: [25].

1-[4-(Acetyloxy)-2,6-dihydroxyphenyl]ethanone

[29376-65-6] $C_{10}H_{10}O_5$ mol.wt. 210.19



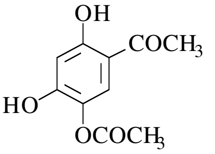
Synthesis

-Preparation by reaction of acetic anhydride on phloroacetophenone in pyridine at r.t. (17-20%) [5] [1019].

m.p. 165-166° [1019]; ^{13}C NMR [5].

1-[5-(Acetyloxy)-2,4-dihydroxyphenyl]ethanone

[55168-29-1] $C_{10}H_{10}O_5$ mol.wt. 210.19



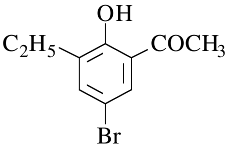
Syntheses

-Obtained by partial Fries rearrangement of 1,2,4-triacetoxybenzene,
*with boron trifluoride-acetic acid complex at 100° (78%) [703];
*with zinc chloride in acetic acid at 120° (21%) [1566] or at 140° (7%) [1335].

m.p. 171° [1566], 169-170° [1335], 163° [703];
^{1}H NMR [703] [1335] [1566], IR [703] [1335] [1566].

1-(5-Bromo-3-ethyl-2-hydroxyphenyl)ethanone

[81591-17-5] $C_{10}H_{11}BrO_2$ mol.wt. 243.10



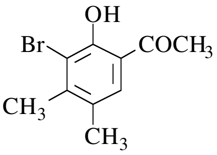
Synthesis

-Preparation by Fries rearrangement of 4-bromo-2-ethylphenyl acetate with aluminium chloride without solvent in an oil bath (40%) [1787].

m.p. 42° [1787].

1-(3-Bromo-2-hydroxy-4,5-dimethylphenyl)ethanone

[112747-62-3] $C_{10}H_{11}BrO_2$ mol.wt. 243.10



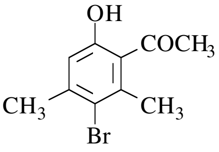
Syntheses

-Preparation by reaction of hydrated sodium sulfide (containing 7 to 9 mol of water) with 2-dimethylamino-4-[3-bromo-2-hydroxy-4,5-dimethylphenyl]-1,3-dithiole bisulfate in refluxing ethanol (85%) [357].
-Preparation by reaction of bromine with 2-hydroxy-4,5-dimethylacetophenone in chloroform (69%) [229].

m.p. 105-106° [357], 100-101° [229]; ^{1}H NMR [229] [357], IR [229] [357].

1-(3-Bromo-6-hydroxy-2,4-dimethylphenyl)ethanone

[71582-57-5] $C_{10}H_{11}BrO_2$ mol.wt. 243.10



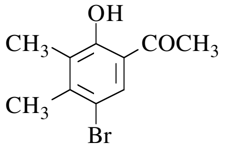
Syntheses

-Preparation by reaction of acetic acid on 4-bromo-3,5-dimethylphenol with boron trifluoride [422].
-Preparation by Fries rearrangement of 4-bromo-3,5-dimethylphenyl acetate (b.p.$_{15}$ 110°) with aluminium chloride at 120° [1085].

m.p. 99-103° [422], 95-97° [1085]; ^{1}H NMR [1085], IR [1085].

1-(5-Bromo-2-hydroxy-3,4-dimethylphenyl)ethanone

[319923-51-8] $C_{10}H_{11}BrO_2$ mol.wt. 243.10



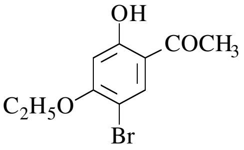
Synthesis

-Preparation by reaction of bromine with 2-hydroxy-3,4-dimethylacetophenone in methylene chloride (61%) [229].

m.p. 65-66° [229]; ^{1}H NMR [229], IR [229].

1-(5-Bromo-4-ethoxy-2-hydroxyphenyl)ethanone

[131359-44-9] $C_{10}H_{11}BrO_3$ mol.wt. 259.10



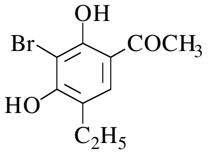
Syntheses

-Preparation by reaction of bromine on 4-ethoxy-2-hydroxyacetophenone in acetic acid [982].
-Also refer to: [63] and [172] (compound 1g).

m.p. 109-110° [982].

1-(3-Bromo-5-ethyl-2,4-dihydroxyphenyl)ethanone

$C_{10}H_{11}BrO_3$ mol.wt. 259.10



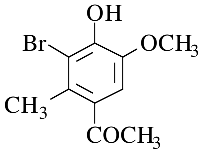
Synthesis

-Preparation by bromination of 2,4-dihydroxy-5-ethylacetophenone with bromine in acetic acid [506] [1151] or in chloroform [1606].

m.p. 131° [1151], 123-125° [1606], 121° [506].

1-(3-Bromo-4-hydroxy-5-methoxy-2-methylphenyl)ethanone

$C_{10}H_{11}BrO_3$ mol.wt. 259.10



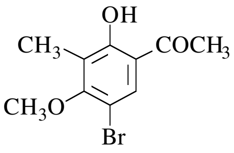
Synthesis

-Preparation by reaction of acetyl chloride on 2-bromo-6-methoxy-3-methylphenol with aluminium chloride in carbon disulfide at 50° (50%) [305].

m.p. 82° [305].

1-(5-Bromo-2-hydroxy-4-methoxy-3-methylphenyl)ethanone

$C_{10}H_{11}BrO_3$ mol.wt. 259.10



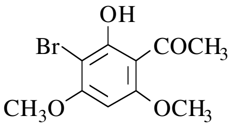
Synthesis

-Preparation by reaction of bromine on 2-hydroxy-4-methoxy-3-methylacetophenone in carbon disulfide [1411].

m.p. 63-64° [1411].

1-(3-Bromo-2-hydroxy-4,6-dimethoxyphenyl)ethanone

[18064-89-6] $C_{10}H_{11}BrO_4$ mol.wt. 275.10



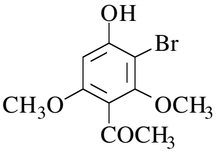
Syntheses

-Preparation by reaction of bromine on 2,4-dimethoxy-6-hydroxyacetophenone [190] [373] [542] [908] [1402] [1559] [1580],
*in acetic acid at r.t. (98%) [190], (43%) [373];
*in carbon tetrachloride (85%) [190];
*in acetic anhydride (50%) [190];
*in chloroform [190] [908], (33%) [190].
-Preparation by bromination of 2,4-dimethoxy-6-hydroxyacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture [391] [894], (62%) [894].
-Preparation by reaction of cupric bromide on 2-acetoxy-4,6-dimethoxyacetophenone in refluxing chloroform-ethyl acetate mixture (76%) [894].

m.p. 188-189° [1402], 187-189° [894], 187° [908] [1559] [1580], 186-187° [190] [373]; ^{1}H NMR [190] [391] [894], MS [391].

1-(3-Bromo-4-hydroxy-2,6-dimethoxyphenyl)ethanone

[57517-42-7] $C_{10}H_{11}BrO_4$ mol.wt. 275.10



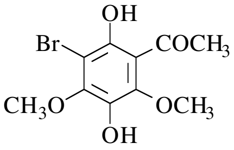
Synthesis

-Preparation by reaction of bromine on 4-hydroxy-2,6-dimethoxyacetophenone in chloroform in the presence of aqueous sodium acetate solution (88%) [539].

m.p. 156-157° [539]; ^{1}H NMR [539].

1-(3-Bromo-2,5-dihydroxy-4,6-dimethoxyphenyl)ethanone

$C_{10}H_{11}BrO_5$ mol.wt. 291.10



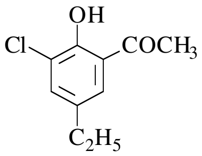
Synthesis

-This compound is obtained by reaction of alkaline potassium persulfate on 3-bromo-2-hydroxy-4,6-dimethoxyacetophenone [542].

m.p. 147-149° [542].

1-(3-Chloro-5-ethyl-2-hydroxyphenyl)ethanone

[58483-48-0] $C_{10}H_{11}ClO_2$ mol.wt. 198.65



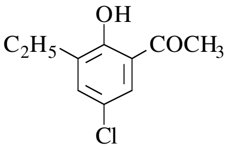
Synthesis

-Preparation by Fries rearrangement of 2-chloro-4-ethylphenyl acetate with aluminium chloride without solvent at 150° (75%) [1041].

m.p. 74° [1041].

1-(5-Chloro-3-ethyl-2-hydroxyphenyl)ethanone

[53347-06-1] $C_{10}H_{11}ClO_2$ mol.wt. 198.65



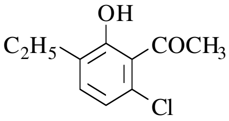
Synthesis

-Preparation by Fries rearrangement of 4-chloro-2-ethylphenyl acetate with aluminium chloride without solvent at 120° [107] or by heating in an oil bath (50%) [1787].

oil [107]; b.p.$_{12}$ 145-146° [107], b.p. 265° [1787].

1-(6-Chloro-3-ethyl-2-hydroxyphenyl)ethanone

[81591-14-2] $C_{10}H_{11}ClO_2$ mol.wt. 198.65



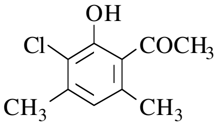
Synthesis

-Preparation by Fries rearrangement of 5-chloro-2-ethylphenyl acetate with aluminium chloride without solvent by heating in an oil bath (40%) [1787].

b.p. 258° [1787].

1-(3-Chloro-2-hydroxy-4,6-dimethylphenyl)ethanone

[71582-56-4] $C_{10}H_{11}ClO_2$ mol.wt. 198.65



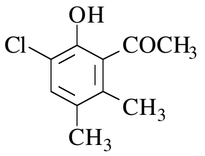
Synthesis

-Preparation by reaction of acetic acid on 2-chloro-3,5-dimethylphenol with boron trifluoride [422].

m.p. 74-75° [422].

1-(3-Chloro-2-hydroxy-5,6-dimethylphenyl)ethanone

[90743-03-6] $C_{10}H_{11}ClO_2$ mol.wt. 198.65

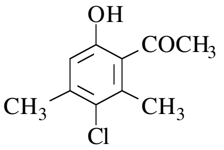


Synthesis

-Refer to: [1347] (ketone 16).

1-(3-Chloro-6-hydroxy-2,4-dimethylphenyl)ethanone

[50343-13-0] $C_{10}H_{11}ClO_2$ mol.wt. 198.65



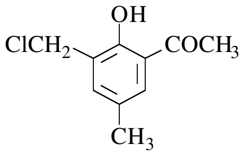
Syntheses

-Preparation by Fries rearrangement of 4-chloro-3,5-dimethylphenyl acetate with aluminium chloride without solvent between 120 to 155° [422] [991] [1587], (90%) [1587].
-Preparation by reaction of aluminium chloride on 3-chloro-6-methoxy-2,4-dimethylacetophenone without solvent at 140-150° [114].
-Also obtained by ozonization of 6-chloro-3,4,5,7-tetramethylcoumarin in ethyl acetate, followed first by hydrolysis of the ozonide so formed, then saponification of the resulting oil by sodium hydroxide in refluxing aqueous methanol for 1 h (59%) [6].

m.p. 110-112° [6], 106-109° [114], 94° [1587], 89°7 [991].

1-[3-(Chloromethyl)-2-hydroxy-5-methylphenyl]ethanone

[87165-62-6] $C_{10}H_{11}ClO_2$ mol.wt. 198.65



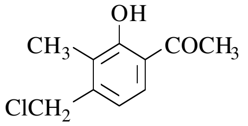
Syntheses

-Preparation from 2-hydroxy-5-methylacetophenone by introduction of the chloromethyl group into aromatic ring by treatment with formaldehyde and hydrogen chloride at 70° [694] according to [1812].
-Also refer to: [273] (compound **11**).

m.p. 59-60° [694]; b.p.$_{0.4}$ 110-116° [289]; ^{1}H NMR [694].

1-[4-(Chloromethyl)-2-hydroxy-3-methylphenyl]ethanone

[97582-37-1] $C_{10}H_{11}ClO_2$ mol.wt. 198.65



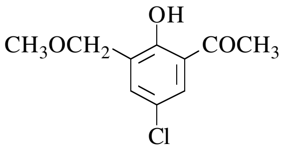
Synthesis

-Preparation by reaction of ethyl chloroformate with 4-(dimethylaminomethyl)-2-hydroxy-3-methylacetophenone in toluene [529] [530], (72%) [530].

m.p. 57-59° [530]; b.p.$_3$ 190-200° [529]; ^{1}H NMR [529], IR [529].

1-[5-Chloro-2-hydroxy-3-(methoxymethyl)phenyl]ethanone

[87165-59-1] $C_{10}H_{11}ClO_3$ mol.wt. 214.65



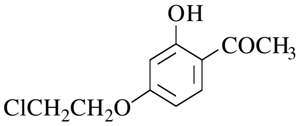
Synthesis

-Obtained by reaction of sodium methoxide with 5-chloro-3-chloromethyl-2-hydroxyacetophenone in refluxing methanol for 2 h (28%) [289].

b.p.$_{0.6}$ 121-131° [289]; ^{1}H NMR [289], IR [289].

1-[4-(2-Chloroethoxy)-2-hydroxyphenyl]ethanone

[109661-96-3] $C_{10}H_{11}ClO_3$ mol.wt. 214.65



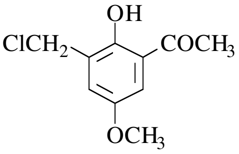
Synthesis

-Preparation by reaction of 1,2-ethylene dichloride with resacetophenone in the presence of n-tetrabutylammonium bromide and potassium hydroxide in water at 60° (41%) [1529].

m.p. 98-100° [1529]; ^{1}H NMR [1529].

1-[3-(Chloromethyl)-2-hydroxy-5-methoxyphenyl]ethanone

[87165-70-6] $C_{10}H_{11}ClO_3$ mol.wt. 214.65



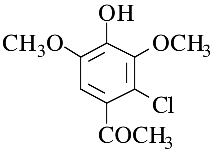
Synthesis

-Preparation by reaction of polyoxymethylene with 2-hydroxy-5-methoxyacetophenone in the presence of concentrated hydrochloric acid at 50° (61%) [289].

m.p. 71° [289]; ^{1}H NMR [289], IR [289].

1-(2-Chloro-4-hydroxy-3,5-dimethoxyphenyl)ethanone

[94649-70-4] $C_{10}H_{11}ClO_4$ mol.wt. 230.65



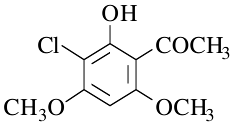
Syntheses

-Preparation by chlorination of acetosyringone (4-hydroxy-3,5-dimethoxyacetophenone) in dioxane with 1.0-1.1 mol. equiv. chlorine in acetic acid [1657] [1659], (24%) [1657].
-Identified in wheat and rye straw pulp bleaching and combined mill effluents [617].
-Identified on control of effluent from the manufacturing of bleached pulp and paper from sugarcane bagasse [616].
-Isolated from the pyrolysis products of beech wood [1439].

m.p. 93-94° [1657] [1659]; GC-MS [1439];
^{1}H NMR [1657], ^{13}C NMR [1657], MS [1657].

1-(3-Chloro-2-hydroxy-4,6-dimethoxyphenyl)ethanone

[81325-85-1] $C_{10}H_{11}ClO_4$ mol.wt. 230.65



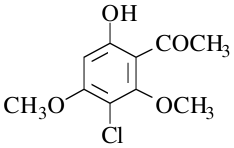
Syntheses

-Preparation by Fries rearrangement of 2-chloro-3,5-dimethoxyphenyl acetate with aluminium chloride in chlorobenzene at reflux (94%) [1424] or in nitrobenzene, from 90 to 130° (24%) [1803].
-Preparation by reaction of acetyl chloride with 2-chloro-3,5-dimethoxyphenol in the presence of aluminium chloride in nitrobenzene at r.t. (87%) [554].
-Also obtained by reaction of chlorine with 2-hydroxy-4,6-dimethoxyacetophenone in carbon tetrachloride (15%) [2].
-Preparation by diazotization of 3-amino-2-hydroxy-4,6-dimethoxyacetophenone and treating with cuprous chloride (Sandmeyer reaction) [2].
-Preparation by partial demethylation of 3-chloro-2,4,6-trimethoxyacetophenone with aluminium chloride in acetonitrile for 4 h at 30° (95%) [962].
-Also refer to: [544].

m.p. 191-192° [2] [554], 188° [1803]; ^{1}H NMR [2] [1803], IR [554].

1-(3-Chloro-6-hydroxy-2,4-dimethoxyphenyl)ethanone

[81325-86-2] $C_{10}H_{11}ClO_4$ mol.wt. 230.65



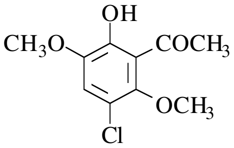
Syntheses

-Preparation by reaction of chlorine with 2-hydroxy-4,6-dimethoxyacetophenone in carbon tetrachloride (57%) [2].
-Also obtained (poor yield) by Fries rearrangement of 4-chloro-3,5-dimethoxyphenyl acetate with aluminium chloride in nitrobenzene at 90° and then 130° (11%) [1087].
-Also refer to: [544] [1802].

m.p. 193-194° [1087], 91° [2]; ^{1}H NMR [2] [1087].

1-(3-Chloro-6-hydroxy-2,5-dimethoxyphenyl)ethanone

[88771-58-8] $C_{10}H_{11}ClO_4$ mol.wt. 230.65



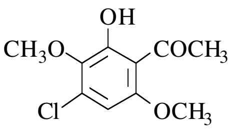
Synthesis

-Preparation by reaction of N-chlorosuccinimide on 3,6-dimethoxy-2-hydroxyacetophenone in refluxing carbon tetrachloride (59%) [502].

m.p. 108° [502]; ^{1}H NMR [502].

1-(4-Chloro-2-hydroxy-3,6-dimethoxyphenyl)ethanone

[88771-46-4] $C_{10}H_{11}ClO_4$ mol.wt. 230.65

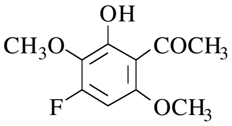


Synthesis

-Refer to: [502].

1-(4-Fluoro-2-hydroxy-3,6-dimethoxyphenyl)ethanone

[88771-57-7] $C_{10}H_{11}FO_4$ mol.wt. 214.19

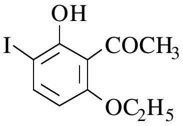


Synthesis

-Refer to: [502].

1-(6-Ethoxy-2-hydroxy-3-iodophenyl)ethanone

[35292-36-5] $C_{10}H_{11}IO_3$ mol.wt. 306.10



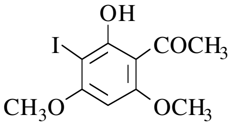
Synthesis

-Preparation by adding an aqueous solution of iodic acid and iodine to an ethanolic solution of 2-ethoxy-6-hydroxyacetophenone (88%) [794].

m.p. 106° [794].

1-(2-Hydroxy-3-iodo-4,6-dimethoxyphenyl)ethanone

[59656-68-7] $C_{10}H_{11}IO_4$ mol.wt. 322.10



Syntheses

-Preparation by adding an ethanolic solution of iodine and phloroacetophenone dimethyl ether to an aqueous solution of iodic acid at r.t. (81%) [388].

-Preparation by adding an acetic acid solution of nitric acid to an acetonic solution of iodine and phloroacetophenone dimethyl ether at 0° [655] [656] [1302], (75%) [1302].

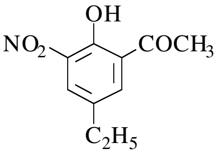
-Preparation by reaction of iodine with phloroacetophenone dimethyl ether in methanol in the presence of potassium hydroxide [1903].

-Also refer to: [544] (compound **23**).

m.p. 201° [1302], 199°5-200°5 [388].

1-(5-Ethyl-2-hydroxy-3-nitrophenyl)ethanone

[71002-71-6] $C_{10}H_{11}NO_4$ mol.wt. 209.20



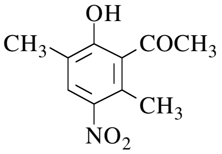
Syntheses

-Preparation by nitration of 5-ethyl-2-hydroxyacetophenone,
*with 100% nitric acid in acetic acid at r.t. (85%) [318];
*with nitric acid (d = 1.42) in concentrated sulfuric acid between -15 to -5° [620] [1463], (44%) [620].

m.p. 127-128° [318], 120-122° [1463], 118-120° [620].

1-(2-Hydroxy-3,6-dimethyl-5-nitrophenyl)ethanone

[207281-53-6] $C_{10}H_{11}NO_4$ mol.wt. 209.20

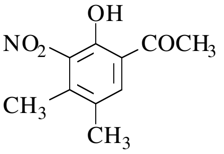


Synthesis

-Refer to: [697].

1-(2-Hydroxy-4,5-dimethyl-3-nitrophenyl)ethanone

$C_{10}H_{11}NO_4$ mol.wt. 209.20



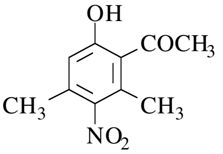
Synthesis

-Preparation by reaction of nitric acid (d = 1.42) on 2-hydroxy-4,5-dimethylacetophenone in acetic acid at r.t. (71%) [142].

m.p. 143-144° [142].

1-(6-Hydroxy-2,4-dimethyl-3-nitrophenyl)ethanone

[125249-30-1] $C_{10}H_{11}NO_4$ mol.wt. 209.20



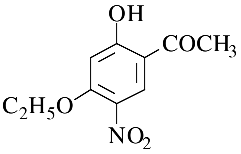
Synthesis

-Preparation is made by adding successively nitromethane, then 3-acetyl-2,6-dimethyl-4*H*-pyran-4-one in a suspension of potassium tert-butoxide in tert-butyl alcohol at 40° under nitrogen (40%) [564].

m.p. 112-114° [564]; ^{1}H NMR [564], IR [564], MS [564].

1-(4-Ethoxy-2-hydroxy-5-nitrophenyl)ethanone

[76951-07-0] $C_{10}H_{11}NO_5$ mol.wt. 225.20



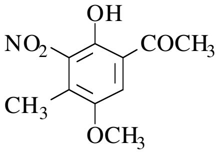
Syntheses

-Prepared by nitration of 2-hydroxy-4-ethoxyacetophenone in glacial acetic acid [922].
-Also refer to: [63] and [172] (compound 1f).

m.p. 132° [922].

1-(2-Hydroxy-5-methoxy-4-methyl-3-nitrophenyl)ethanone

[43140-82-5] $C_{10}H_{11}NO_5$ mol.wt. 225.20



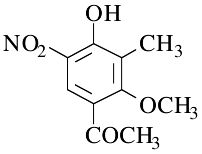
Synthesis

-Preparation by reaction of 10% nitric acid with 2-hydroxy-5-methoxy-4-methylacetophenone at 17-20° (40%) [1741].

m.p. 132° [1741]; ^{1}H NMR [1741], IR [1741].

1-(4-Hydroxy-2-methoxy-3-methyl-5-nitrophenyl)ethanone

[118824-98-9] $C_{10}H_{11}NO_5$ mol.wt. 225.20



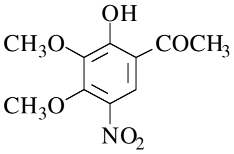
Synthesis

-Preparation by reaction of concentrated nitric acid on 4-hydroxy-2-methoxy-3-methylacetophenone in acetic acid [912] [1470], (64%) [1470].

m.p. 70° [912], 69° [1470];
^{1}H NMR [1470], IR [1470], MS [1470].

1-(2-Hydroxy-3,4-dimethoxy-5-nitrophenyl)ethanone

$C_{10}H_{11}NO_6$ mol.wt. 241.20



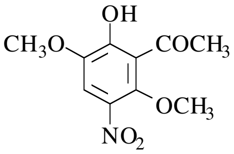
Synthesis

-Preparation by reaction of nitric acid with 3,4-dimethoxy-2-hydroxyacetophenone in ethanol (33%) [663].

m.p. 83-83°8 [663].

1-(2-Hydroxy-3,6-dimethoxy-5-nitrophenyl)ethanone

[88771-59-9] $C_{10}H_{11}NO_6$ mol.wt. 241.20



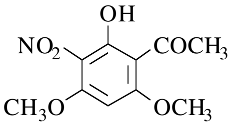
Synthesis

-Preparation by reaction of nitric acid on 3,6-dimethoxy-2-hydroxyacetophenone in acetic acid at 10° (52%) [502].

m.p. 120° [502]; ^{1}H NMR [502].

1-(2-Hydroxy-4,6-dimethoxy-3-nitrophenyl)ethanone

[81325-87-3] $C_{10}H_{11}NO_6$ mol.wt. 241.20



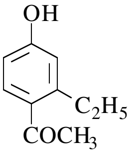
Synthesis

-Obtained (poor yield) by adding nitric acid (d = 1.42) in acetic acid to an ice-cold solution of 2-hydroxy-4,6-dimethoxyacetophenone in acetic anhydride (2%) [2].

m.p. 104-105° [2]; ^{1}H NMR [2].

1-(2-Ethyl-4-hydroxyphenyl)ethanone

$C_{10}H_{12}O_2$ mol.wt. 164.20



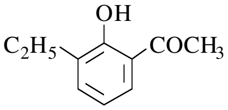
Syntheses

-Obtained by Fries rearrangement of 3-ethylphenyl acetate with aluminium chloride,
*in nitrobenzene at 0° (varying yield, maximum 50%) [970];
*without solvent between 130 and 165° (4-7%) [1461] [1785].

m.p. 102° [970] [1461]; b.p.$_{0.45}$ 150-152° [970], b.p.$_{20}$ 195-200° [1461].

1-(3-Ethyl-2-hydroxyphenyl)ethanone

[103323-22-4] $C_{10}H_{12}O_2$ mol.wt. 164.20



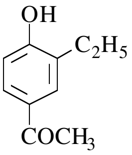
Syntheses

-Obtained by Fries rearrangement of 2-ethylphenyl acetate with aluminium chloride at 130-140° [102].
-Also refer to: [1018] [1457].

b.p.$_3$ 90-95° [1018], b.p. 213° [102].

1-(3-Ethyl-4-hydroxyphenyl)ethanone

[22934-47-0] $C_{10}H_{12}O_2$ mol.wt. 164.20



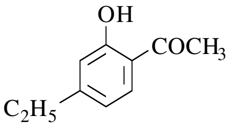
Syntheses

-Preparation by reaction of acetyl chloride on 2-ethylphenol with aluminium chloride,
*in refluxing carbon disulfide (60%) [1069];
*in nitrobenzene at 60° (39%) [186].
-Preparation by acetylation of 2-ethylphenol (60%) [1211].

m.p. 95° [1211], 92-93° [186], 89-91° [1069];
b.p.$_1$ 170-180° [1211], b.p.$_{20}$ 190-195° [186]; UV [186].

1-(4-Ethyl-2-hydroxyphenyl)ethanone

[5896-50-4] $C_{10}H_{12}O_2$ mol.wt. 164.20



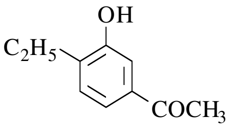
Syntheses

-Preparation by Fries rearrangement of 3-ethylphenyl acetate,
*with aluminium chloride, without solvent between 120 and 165° (80-88%) [550] [1461] [1584] [1585] [1588] [1785], in nitrobenzene at 25° (84-89%) [1585] [1588] or at 60° (65%) [1584], in toluene or in xylene at 100° (56-57%) [1584];
*with titanium tetrachloride, without solvent at 120° (88%) [1585] or in nitrobenzene at 25° (66%) [1585];
*with stannic chloride, without solvent at 120° (84%) [1585] or in nitrobenzene at 25° (86%) [1585];
*with zinc chloride, without solvent at 120° (56%) [1585] or in nitrobenzene at 25° (58%) [1585].

b.p.$_{2.5}$ 97° [550], b.p.$_4$ 140° [1588], b.p.$_{20}$ 142° [1461].

1-(4-Ethyl-3-hydroxyphenyl)ethanone

[73898-20-1] $C_{10}H_{12}O_2$ mol.wt. 164.20



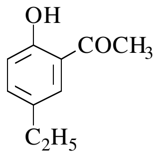
Synthesis

-Preparation by diazotization of 3-amino-4-ethylacetophenone followed by hydrolysis of the diazonium salt obtained (46%) [1069].

m.p. 94-95° [1069].

1-(5-Ethyl-2-hydroxyphenyl)ethanone

[24539-92-2] $C_{10}H_{12}O_2$ mol.wt. 164.20



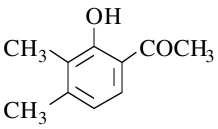
Syntheses

-Preparation by Fries rearrangement of 4-ethylphenyl acetate with aluminium chloride without solvent at 115-120° [102] [318] [683], (96%) [318], (70%) [102].
-Preparation by reaction of acetyl chloride on 4-ethylphenol with aluminium chloride in ethylene dichloride at 110-120° (71%) [1033].

b.p.$_{2.3}$ 94-96° [683], b.p.$_4$ 102-104° [1033], b.p.$_{10}$ 114-116° [318],
b.p.$_{12}$ 119-121° [102]; ^{1}H NMR [683], MS [683].

1-(2-Hydroxy-3,4-dimethylphenyl)ethanone

[5384-55-4] $C_{10}H_{12}O_2$ mol.wt. 164.20



Syntheses

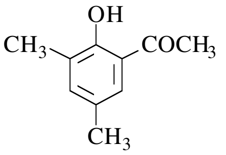
-Preparation by reaction of acetic anhydride on 2,3-dimethylphenol with 70% perchloric acid at 125-135° (35%) [548].

-Preparation by Fries rearrangement of 2,3-dimethylphenyl acetate,
*with aluminium chloride, without solvent, between 100 to 165° (85%) [997], (70-80%) [1026] [1788] [1844], (54-69%) [102] [661] [1025] [1654] or in refluxing carbon disulfide (20%) [1844];
*with titanium tetrachloride at 100° (60%) [113] [1026] [1788].

colourless oil [997]; m.p. 6-8° [1026];
b.p.$_7$ 105-110° [548], b.p.$_8$ 120-124° [1654], b.p.$_{12}$ 122-124° [102],
b.p.$_{10.5}$ 127-129° [1654], b.p.$_{15}$ 131-132° [1026], b.p.$_{12}$ 140° [661];
^{1}H NMR [997], ^{13}C NMR [997], IR [997] [1026], MS [997].

1-(2-Hydroxy-3,5-dimethylphenyl)ethanone

[1198-66-9] $C_{10}H_{12}O_2$ mol.wt. 164.20



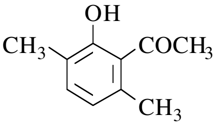
Syntheses

-Preparation by reaction of acetyl chloride on 2,4-dimethylphenol with aluminium chloride in nitrobenzene at 50° (80%) [458].
-Preparation by Fries rearrangement of 2,4-dimethylphenyl acetate with aluminium chloride, in nitrobenzene at 50° (80%) [458] or in the presence of 2,4-dimethylanisole in refluxing carbon disulfide (50%) [103] or without solvent [103] [112] [113] [148] [1788] at 130-140° (good yield) [103], (42%) [148].
-Also obtained by Fries rearrangement of 2,5-dimethylphenyl acetate with aluminium chloride without solvent [101] [112], at 80-90° (25%) [101].
-Also obtained (by-product) by Fries rearrangement of 2,6-dimethyl-4-ethylphenyl acetate with aluminium chloride without solvent (4%) [100].
-Also obtained by reaction of acetyl chloride on 2,4-dimethylanisole with aluminium chloride in refluxing carbon disulfide [101].
-Also obtained by reaction of zinc powder on 3,5-bis(chloromethyl)-2-hydroxyacetophenone in aqueous acetic acid (8%) [1811].
-Preparation by UV light irradiation of 2,4-dimethylphenyl acetate at 25°, in benzene (54%) [280] or in hexane, with potassium carbonate (90%) [660] or without potassium carbonate (34%) [660].
-Preparation by reaction of ethyl acetoacetate with 2-methyl-2-pentenal in the presence of pyridine and piperidine as catalysts, in refluxing benzene (49%). The 2-methyl-2-pentenal was first obtained by self-condensation of propionaldehyde in the presence of 15% potassium hydroxide solution [940] [941] [942].
-Also refer to: [891] [1535].

m.p. 55° [660], 54° [101] [103] [458], 53-54° [112] [113] [1811],
53-53°5 [940] [941] [942];
b.p.$_{12}$ 106-135° [101], b.p.$_{16}$ 124°5-126° [113], b.p.$_{33}$ 126-140° [940] [941] [942];
^{1}H NMR [280] [940] [941] [942], IR [280] [940] [941] [942], UV [940] [941] [942].

1-(2-Hydroxy-3,6-dimethylphenyl)ethanone

[90743-02-5] $C_{10}H_{12}O_2$ mol.wt. 164.20



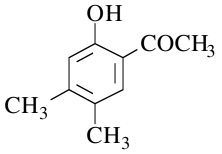
Syntheses

-Obtained by UV irradiation of 2,5-dimethylphenyl acetate in methanol at 254 nm under nitrogen at r.t. (39%) [1703].
-Also refer to: [732] and [1347] (ketone **14**).

viscous oil [1703]; ^{1}H NMR [1703], ^{13}C NMR [1703],
IR [1703], MS [1703].

1-(2-Hydroxy-4,5-dimethylphenyl)ethanone

[36436-65-4] $C_{10}H_{12}O_2$ mol.wt. 164.20



Syntheses

-Preparation by Fries rearrangement of 3,4-dimethylphenyl acetate with aluminium chloride without solvent between 110 to 150° [112] [123] [142] [839] [1528] [1788] [1799] [1844], (86-100%) [123] [1528] [1799], (70-72%) [142] [1844], (23%) [839].

-Preparation by isomerisation of 2-hydroxy-4,6-dimethylacetophenone with an excess of aluminium chloride without solvent at 140-180° (quantitative yield) [123].

-Preparation by reaction of acetic acid on 3,4-dimethylphenol,
*with boron trifluoride at 70° (80%) [980];
*with polyphosphoric acid (75%) [1528].

-Preparation by demethylation of 2-methoxy-4,5-dimethylacetophenone with pyridinium chloride at reflux (81%) [1524].

-Preparation by dehydrogenation of 6-acetyl-3,4-dimethyl-2-cyclohexen-1-one,
*with a 5% palladium-barium sulfate catalyst at reflux [1059];
*with refluxing 16% solution of bromine in acetic acid [1059].

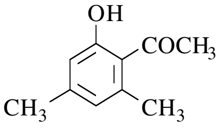
-Also obtained by reaction of sodium methoxide on 2-acetyl-4,5-dimethyl-4-nitro-1,4-dihydrophenyl acetate in methanol [601].

-Also obtained (by-product) by reaction of aluminium chloride on 2,4,5-trimethylphenyl acetate (pseudocumenol acetate) without solvent at 130-140° [112].

m.p. 74° [123], 71°5-72°5 [1059], 71-72°5 [601], 71° [112] [980] [1799] [1844], 70°9-71°7 [839], 70-71° [142], 70° [1524];
b.p.$_{18}$ 143-144° [980];
^{1}H NMR [601] [1698], ^{13}C NMR [736], IR [601] [839], UV [1698], fluorescence spectra [1698], MS [601].

1-(2-Hydroxy-4,6-dimethylphenyl)ethanone

[16108-50-2] $C_{10}H_{12}O_2$ mol.wt. 164.20



Syntheses

-Preparation by reaction of acetic acid on 3,5-dimethylphenol with boron trifluoride at 60-70° (93%) [980].

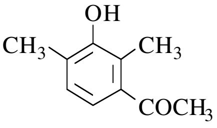
-Preparation by Fries rearrangement of 3,5-dimethylphenyl acetate,
*with aluminium chloride,
  -without solvent, between 100 to 150° [109] [123] [143] [345] [497] [1584] [1585] [1654] [1712] [1788], (81-100%) [123] [1584] [1585], (67-75%) [497] [1654];
  -in nitrobenzene at 25° (78%) [1585] or at 60° (67%) [1584];
  -in toluene or xylene at 100° (61-62%) [1584];
  -in refluxing carbon disulfide (60%) [109].
*with titanium tetrachloride,
  -without solvent at 120° (82%) [1585];
  -in nitrobenzene at 25° (86%) [1585].
*with stannic chloride,
  -without solvent at 120° (78%) [1585];
  -in nitrobenzene at 25° (76%) [1585].
*with zinc chloride,
  -without solvent at 120° (54%) [1585];

-in nitrobenzene at 25° (52%) [1585].
-Also obtained by reaction of 2 N sodium hydroxide on 4,6-dimethyl-2-hydroxy-$_{\alpha,\alpha,\alpha}$-trifluoro-acetoacetophenone at r.t. (quantitative yield) [1885].
-Also obtained by reaction of acetyl chloride,
-with 3,5-dimethylanisole with aluminium chloride (60-70%) [99];
-with 3,5-dimethylphenol in refluxing carbon disulfide (60%) [109].
-Also obtained by heating on a steam bath a mixture of 2-acetoxy-4,6-dimethylacetophenone and aluminium chloride (33%) [1712].
-Also obtained by self-condensation of acetylacetone,
*with refluxing 2 N sodium hydroxide, then by heating the residue at 145° [768];
*catalyzed with potassium fluoride in DMF solution [414] [1753], (64%) [414]; also refer to "ERRATUM" [415].
-Also obtained by reaction of acetic anhydride on 3,5-dimethylanisole with aluminium chloride in refluxing carbon disulfide (46%) [651].
-Preparation by dehydrogenation of 6-acetyl-3,5-dimethyl-2-cyclohexen-1-one with a 5% palladium-barium sulfate catalyst at reflux [1059].
-Also obtained by photoreaction of dehydroacetic acid followed by hydrolysis of the obtained dimer (46%) [1712].
-Also obtained by UV light irradiation of 3,5-dimethylphenyl acetate at 25°, in isopropanol or cyclohexane (32%) [724] or in ethyl ether (9%) [724].
-Also refer to: [1927].

m.p. 62° [980], 60° [123], 59-60° [345], 58-59° [1059], 58° [143] [768], 57-58°5 [1654], 57-58° [99] [109], 56-58° [1712] [1753], 55-56° [414] [415];
b.p.$_{18}$ 140-141° [99] [109], b.p.$_{15}$ 140°5-141°5 [980], b.p.$_{13}$ 144° [1654];
^{1}H NMR [414] [415] [1753], ^{13}C NMR [414] [415] [1540], IR [143] [414] [415], MS [414] [415]; pK$_a$ [1387].

1-(3-Hydroxy-2,4-dimethylphenyl)ethanone

[99892-63-4] $C_{10}H_{12}O_2$ mol.wt. 164.20



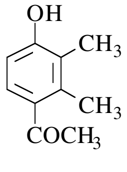
Synthesis

-The 1_{α},6_{α},8_{α}-trimethyl-2_{α}-*H*, 4_{α}-*H*, 5_{α}-*H* -3,9-dioxa-tricyclo[3.3.1.0 ^{2,4}]nonan-7-one was rearranged by treatment with sodium ethoxide in ethanol to form 3-hydroxy-2,4-dimethylacetophenone in 11% yield [615].

m.p. 70° [615]; ^{1}H NMR [378], IR [378], MS [378].

1-(4-Hydroxy-2,3-dimethylphenyl)ethanone

[5384-57-6] $C_{10}H_{12}O_2$ mol.wt. 164.20



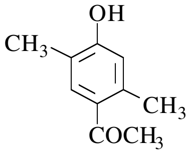
Syntheses

-Obtained by Fries rearrangement of 2,3-dimethylphenyl acetate,
*with aluminium chloride, in nitrobenzene at r.t. (50-60%) [661] [1844], in carbon disulfide at r.t. (10%) [1844] or without solvent at 100° (17%) [1025] [1026];
*with titanium tetrachloride without solvent at 100° (6%) [1025] [1026].

m.p. 148° [1844], 145° [661], 144° [1026].

1-(4-Hydroxy-2,5-dimethylphenyl)ethanone

[26216-10-4] $C_{10}H_{12}O_2$ mol.wt. 164.20



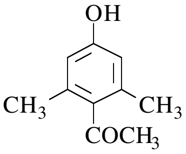
Syntheses

-Preparation by reaction of acetic acid on 2,5-dimethylphenol with boron trifluoride at 70° (95%) [980].
-Preparation by Fries rearrangement of 2,5-dimethylphenyl acetate with aluminium chloride without solvent at 80-90° (65-70%) [104] [112], (49%) [531].

m.p. 131-132° [531] [980], 130-131° [104] [112]; ^{1}H NMR [531], MS [531].

1-(4-Hydroxy-2,6-dimethylphenyl)ethanone

[91060-92-3] $C_{10}H_{12}O_2$ mol.wt. 164.20



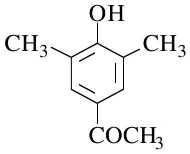
Synthesis

-Preparation by diazotization of 4-amino-2,6-dimethylacetophenone, followed by hydrolysis of the obtained diazonium salt (68%) [36] [1621].

m.p. 119-120° [35] [36] [1540] [1621];
^{1}H NMR [36], ^{13}C NMR [1540], IR [36], MS [36].

1-(4-Hydroxy-3,5-dimethylphenyl)ethanone

[5325-04-2] $C_{10}H_{12}O_2$ mol.wt. 164.20



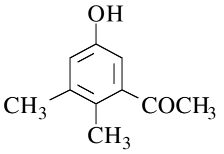
Syntheses

-Preparation by Fries rearrangement of 2,6-dimethylphenyl acetate,
*with aluminium chloride [638], without solvent at 120-140° [102] [603] [604], (81 to 100%) [102], in nitrobenzene at r.t. (75%) [103] or in nitromethane, first at 0°, then at 50° for 48 h under argon atmosphere (61%) [740];
*with aluminium bromide without solvent at 130° (71%) [151].
-Preparation by reaction of 46% hydrobromic acid solution with 4-(benzyloxy)-3,5-dimethylacetophenone in the presence of tetrabutylammonium bromide in refluxing methylene chloride (53%) [205].
-Also obtained by heating various 2,6-dimethyl-4-alkylphenyl acetates** with aluminium chloride without solvent, the reaction being accompanied by an alkyl group elimination,
**alkyl = benzyl (quantitative yield) [100], ethyl (50%) [102], (39%) [100], dodecyl (38%) [100], propyl (31%) [100], butyl (27%) [100] and heptyl (12%) [100].
-Also refer to: [1554].

m.p. 162° [205], 156-157° [638], 151-152° [151] [603] [740], 150-151° [102], 150° [103]
^{1}H NMR [205] [638] [740], ^{13}C NMR [740], IR [205] [740], MS [205] [740].

1-(5-Hydroxy-2,3-dimethylphenyl)ethanone

[127701-70-6] $C_{10}H_{12}O_2$ mol.wt. 164.20



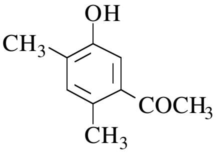
Synthesis

-Preparation by rearrangement of 3-acetyl-4,4-dimethylcyclohexa-2,5-dienone with 49% sulfuric acid at 20° (quantitative yield) [691].

^{1}H NMR [691].

1-(5-Hydroxy-2,4-dimethylphenyl)ethanone

$C_{10}H_{12}O_2$ mol.wt. 164.20



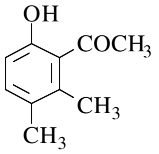
Syntheses

-Preparation by demethylation of 5-methoxy-2,4-dimethylacetophenone with aluminium chloride (50%) [101].
-Also obtained by reaction of acetyl chloride on 2,4-dimethylphenol with aluminium chloride in nitrobenzene at 50° (9%) [458].
-Also obtained (by-product) by Fries rearrangement of 2,4-dimethylphenyl acetate with aluminium chloride, without solvent [148] or in nitrobenzene at 50° (9%) [458].
-Also obtained by reaction of zinc powder on 5-hydroxy-2,4-dimethyl-α-chloroacetophenone in acetic acid [101].

m.p. 135° [458], 130-131°5 [101].

1-(6-Hydroxy-2,3-dimethylphenyl)ethanone

$C_{10}H_{12}O_2$ mol.wt. 164.20



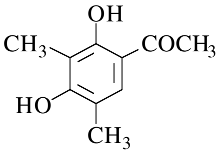
Synthesis

-Preparation by demethylation of 6-methoxy-2,3-dimethylacetophenone with aluminium chloride in boiling benzene (30%) [839]. The above keto anisole itself was obtained by reaction of dimethylcadmium on 6-methoxy-2,3-dimethylbenzoyl chloride in boiling benzene.

m.p. 73°8-75° [839]; b.p.$_{4.5}$ 126° [839]; IR [839].

1-(2,4-Dihydroxy-3,5-dimethylphenyl)ethanone *(Clavatol)*

[577-45-7] $C_{10}H_{12}O_3$ mol.wt. 180.20



Syntheses

-Preparation by reaction of acetonitrile on 2,4-dimethylresorcinol (Hoesch reaction) (56-68%) [755] [1259].
-Preparation by reaction of acetic acid on 2,4-dimethylresorcinol with zinc chloride (Nencki reaction) [665] [1655].
-Also obtained by reaction of methyl iodide with 2,4-di-

hydroxy-5-methylacetophenone in the presence of potassium hydroxide in methanol, in an ice-chest overnight (19%) [448].

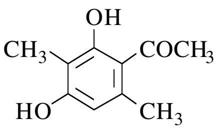
From Microorganisms

-Also obtained by hydrolysis of Sorbicillin (a pigment produced by the mold *Penicillium notatum*) with refluxing 2 N sodium hydroxide solution (16%) [448].
-Also obtained by direct methylation of resacetophenone or 3-methylresacetophenone using washed cells of *Streptomyces risomus* [665].
-Isolated in small quantities from cultures of *Aspergillus clavatus* grown in Czapek-Doz medium with molasses as an additional substrate [199] [665].

m.p. 184-186° [199], 183° [755], 181-182° [448]; UV [447] [448].

1-(2,4-Dihydroxy-3,6-dimethylphenyl)ethanone

[69082-35-5] $C_{10}H_{12}O_3$ mol.wt. 180.20



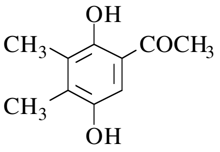
Syntheses

-Obtained by reaction of methyl iodide with 2,4-dihydroxy-6-methylacetophenone in the presence of potassium hydroxide in methanol in an ice-chest overnight (27%) [448].
-Preparation by reaction of acetonitrile on β-orcinol (1,3-dihydroxy-2,5-dimethylbenzene) (Hoesch reaction) [726] [1351], (70%) [726].

m.p. 153° [1351], 149-150° [448]; ^{1}H NMR [726], IR [726], UV [447], MS [726].

1-(2,5-Dihydroxy-3,4-dimethylphenyl)ethanone

[71582-59-7] $C_{10}H_{12}O_3$ mol.wt. 180.20



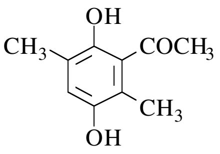
Synthesis

-Preparation by reaction of acetic acid on 2,3-dimethylhydroquinone with boron trifluoride, followed by saponification of the monoacetate [422] [1144] or diacetate [1051] obtained (84-91%) [1051] [1144].

m.p. 151° [1051], 150° [1144].

1-(2,5-Dihydroxy-3,6-dimethylphenyl)ethanone

$C_{10}H_{12}O_3$ mol.wt. 180.20



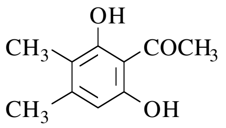
Synthesis

-Obtained (poor yield) by reaction of acetic acid on 2,5-dimethylhydroquinone with boron trifluoride (1%) [1145].

m.p. 88-90° [1145].

1-(2,6-Dihydroxy-3,4-dimethylphenyl)ethanone

[7743-16-0] $C_{10}H_{12}O_3$ mol.wt. 180.20



Syntheses

-Obtained from 4,5-dimethylresorcinol by reaction,
*with acetyl chloride in the presence of aluminium chloride in nitrobenzene, first at r.t., then at 60° (9%) [447];
*with acetic acid in the presence of boron trifluoride etherate at reflux [1178].

-Also obtained (by-product) by Fries rearrangement of 4,5-dimethylresorcinol diacetate in the presence of aluminium chloride at 115-120° (10%) [363].

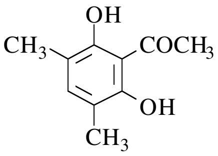
-Preparation by heating a mixture of 2-acetyl-4,5-dihydroxy-4,5-dimethylcyclohexane-1,3-dione and zinc dust in 50% acetic acid at 65° (71%) [363]. The same reaction carried out with 2-acetyl-6-hydroxy-5,6-dimethylcyclohex-4-ene-1,3-dione leads to 82% yield [363].

m.p. 125-127° [363], 122-124° [1178] and 82-83° [447]. One of the reported melting points is obviously wrong.

^{1}H NMR [363], ^{13}C NMR [363], IR [363], UV [363] [447].

1-(2,6-Dihydroxy-3,5-dimethylphenyl)ethanone

[37467-68-8] $C_{10}H_{12}O_3$ mol.wt. 180.20



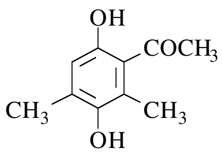
Synthesis

-Obtained by reaction of acetic anhydride with 4,6-dimethylresorcinol in the presence of 45% solution of boron trifluoride etherate at r.t. (15%) [447] or boron trifluoride-acetic acid complex for 2 h at 100° [343].

m.p. 144-146°5 [343], 139-140° [447]; UV [447].

1-(3,6-Dihydroxy-2,4-dimethylphenyl)ethanone

[71582-58-6] $C_{10}H_{12}O_3$ mol.wt. 180.20



Syntheses

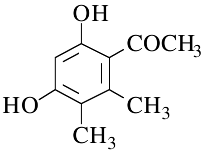
-Preparation by reaction of acetic acid on 2,6-dimethylhydroquinone with boron trifluoride [422] [1145], (76%) [1145].

-Preparation by reaction of ammonium persulfate on 2-hydroxy-4,6-dimethylacetophenone (Elbs reaction) (34%) [67].

m.p. 135-136° [67], 133-134° [1145]; IR [67].

1-(4,6-Dihydroxy-2,3-dimethylphenyl)ethanone

$C_{10}H_{12}O_3$ mol.wt. 180.20



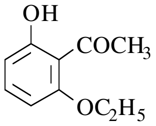
Synthesis

-Preparation by reaction of acetonitrile on 3,5-dihydroxy-o-xylene (Hoesch reaction) (69%) [448].

m.p. 155-156° [448]; UV [447].

1-(2-Ethoxy-6-hydroxyphenyl)ethanone

[2750-25-6] $C_{10}H_{12}O_3$ mol.wt. 180.20



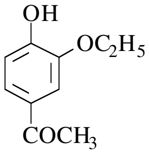
Synthesis

-Preparation by reaction of ethyl iodide on 2,6-dihydroxy acetophenone with potassium carbonate in refluxing acetone (64%) [1567].

m.p. 84-85° [1567].

1-(3-Ethoxy-4-hydroxyphenyl)ethanone

[78268-45-8] $C_{10}H_{12}O_3$ mol.wt. 180.20



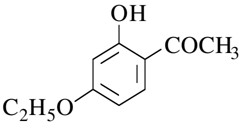
Syntheses

-Preparation by Fries rearrangement of 2-ethoxyphenyl acetate with aluminium chloride in nitrobenzene at r.t. (50%) [501].
-Preparation by refluxing 4-(benzyloxy)-3-ethoxy-acetophenone in mixture of acetic acid and hydrochloric acid [549] according to [670].

m.p. 66° [501], 59-60° [549]; ^{1}H NMR [501].

1-(4-Ethoxy-2-hydroxyphenyl)ethanone

[37470-42-1] $C_{10}H_{12}O_3$ mol.wt. 180.20



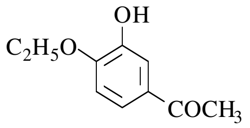
Syntheses

-Preparation by reaction of ethyl iodide on resacetophenone,
*with potassium hydroxide in refluxing ethanol [364] [418] [578] [702] [1012] [1775] [1776], (25%) [364] or boiling acetone [982];
*with potassium carbonate in boiling acetone [313] [1652], (88%) [1652].
-Also obtained by reaction of aluminium chloride on 2,4-diethoxyacetophenone [418].
-Also refer to: [63] and [172] (compound 1e).

m.p. 50° [1776] [1777], 49-50° [982] [1652], 49° [364] [1012], 48° [418] [578] [702], 45-46° [313]; UV [1776] [1777].

1-(4-Ethoxy-3-hydroxyphenyl)ethanone

[78269-19-9] $C_{10}H_{12}O_3$ mol.wt. 180.20



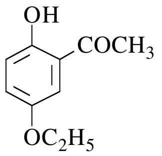
Synthesis

-Preparation by Fries rearrangement of 2-ethoxyphenyl acetate with aluminium chloride in nitrobenzene at r.t. (50%) [501].

m.p. 100° [501]; ^{1}H NMR [501].

1-(5-Ethoxy-2-hydroxyphenyl)ethanone

[56414-14-3] $C_{10}H_{12}O_3$ mol.wt. 180.20



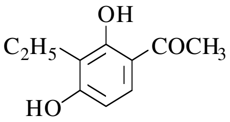
Syntheses

-Preparation by reaction of ethyl bromide with quinacetophenone in the presence of potassium hydroxide in boiling ethanol [1014].
-Also obtained by condensation of hydroquinone diethyl ether with acetyl chloride according to the Friedel-Crafts method [106] [189].
-Also obtained by reaction of aluminium chloride on quinacetophenone diethyl ether [106] [189].
-Also obtained by alkaline degradation of 6,3'-diethoxyflavone* with sodium ethoxide in refluxing ethanol for some hours [236]. **N.B.**: Former nomenclature (2,3'-diethoxyflavone*).
-Refer to: [184] [1479] [1666].

m.p. 57° [1014], 55° [106] [189].

1-(3-Ethyl-2,4-dihydroxyphenyl)ethanone

[111224-13-6] $C_{10}H_{12}O_3$ mol.wt. 180.20



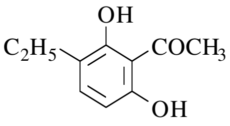
Syntheses

-Preparation by reaction of acetic acid on 2-ethylresorcinol with zinc chloride (Nencki reaction) at 140° [1096] [1499] [1521], (73%) [1096].
-Preparation from 2-ethylresorcinol (SM) by reaction with acetyl chloride in the presence of aluminium chloride. The starting material (SM) was prepared by a three-step procedure from resorcinol dimethyl ether [1158].
-Also obtained by alkaline degradation of 8-acetyl-6-ethyl-4-methylumbelliferone (m.p. 137°) in refluxing N sodium hydroxide for 1 h (96%) [1097].

m.p. 137° [1096], 130° [1097]; ^{1}H NMR [1158], MS [1158].

1-(3-Ethyl-2,6-dihydroxyphenyl)ethanone

[54337-59-6] $C_{10}H_{12}O_3$ mol.wt. 180.20



Syntheses

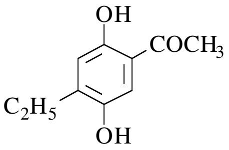
-Preparation by degradation of 8-acetyl-6-ethyl-7-hydroxy-4-methylcoumarin with refluxing 2 N sodium hydroxide [507].

-Preparation by decarboxylation of 3-acetyl-5-ethyl-2,4-dihydroxybenzoic acid,
*with refluxing aqueous hydrochloric acid (62%) [1595];
*with 10% aqueous sodium hydroxide heated in a sand bath [507].
-Also refer to: [343].

m.p. 135° [507], 130° [1595].

1-(4-Ethyl-2,5-dihydroxyphenyl)ethanone

$C_{10}H_{12}O_3$ mol.wt. 180.20



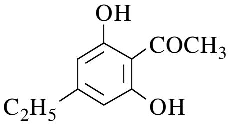
Synthesis

-Obtained (poor yield) by reaction of aqueous ammonium persulfate solution on 4-ethyl-2-hydroxyacetophenone with 10% potassium hydroxide, in aqueous pyridine solution at r.t. (3%) [1461].

m.p. 100° [1461].

1-(4-Ethyl-2,6-dihydroxyphenyl)ethanone

[209746-96-3] $C_{10}H_{12}O_3$ mol.wt. 180.20

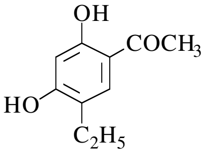


Synthesis

-Refer to: [1819].

1-(5-Ethyl-2,4-dihydroxyphenyl)ethanone

[4460-42-8] $C_{10}H_{12}O_3$ mol.wt. 180.20



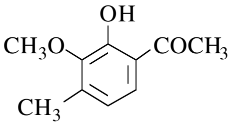
Syntheses

-Preparation by reaction of acetic acid on 4-ethylresorcinol with zinc chloride (Nencki reaction) [777] [930] [1151] [1606] [1879], (67-77%) [777] [1606] [1879].
-Preparation by Fries rearrangement of 4-ethylresorcinol diacetate with aluminium chloride in nitrobenzene at 50-60° (quantitative yield) [1514] or without solvent at 40-50° (47%) [1514].
-Preparation by reaction of acetonitrile on 4-ethylresorcinol (Hoesch reaction) [1151] [1606].
-Preparation from 5-ethyl-2-hydroxy-4-methoxyacetophenone by demethylation with boiling pyridinium chloride (40%) [1521].
-Preparation from 5-ethyl-2,4-dimethoxyacetophenone by demethylation with boron tribromide in methylene chloride at r.t. (36%) [256] [257].
-Also obtained by hydrolysis of 6-ethyl-7-hydroxy-2-methylchromone with refluxing aqueous 1 N sodium hydroxide solution [509].

m.p. 118-119° [1606], 118° [509] [1151], 117-118° [1514], 116° [1521], 115-116° [777], 115° [1277] [1879].

1-(2-Hydroxy-3-methoxy-4-methylphenyl)ethanone

[77869-43-3] $C_{10}H_{12}O_3$ mol.wt. 180.20



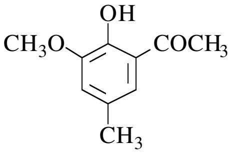
Synthesis

-Isolated as a co-product from the preparation of 2,3-dimethoxy-4-methylacetophenone, obtained by conversion of 2,3-dimethoxy-4-methylbenzoyl chloride with methyl cadmium (10%) [1235].

crystalline compound [1235]; ^{1}H NMR [1235], MS [1235].

1-(2-Hydroxy-3-methoxy-5-methylphenyl)ethanone

[7452-85-9] $C_{10}H_{12}O_3$ mol.wt. 180.20



Syntheses

-Preparation by reaction of methylmagnesium iodide on 2-acetoxy-3-methoxy-5-methylbenzonitrile in refluxing ethyl ether (72%) [298].

-Preparation by Fries rearrangement of 2-methoxy-4-methylphenyl acetate with aluminium chloride without solvent (24%) [148].

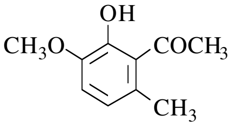
-Also obtained by reaction of dimethyl sulfate on 2,3-dihydroxy-5-methylacetophenone with potassium carbonate in acetone (18%) [473].

-Preparation by UV light irradiation (photo-Fries rearrangement) of 2-methoxy-4-methylphenyl acetate (creosol acetate) in ethanol (68%), in benzene or in hexane (56-55%) [280].

m.p. 84-85° [473], 82-84° [298]; ^{1}H NMR [280], IR [280].

1-(2-Hydroxy-3-methoxy-6-methylphenyl)ethanone

[4223-86-3] $C_{10}H_{12}O_3$ mol.wt. 180.20



Syntheses

-Preparation by partial demethylation of 2,3-dimethoxy-6-methylacetophenone with aluminium chloride in refluxing methylene chloride (77%) [1873].

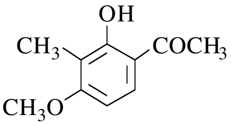
-Preparation by chromic acid degradation of 7-methoxy-2,3,4-trimethylbenzofuran (46%) [1521].

-Also obtained (poor yield) by photo-Fries rearrangement of 2-methoxy-5-methylphenyl acetate in ethanol under nitrogen (2%) [247].

pale yellow oil [247] [1521] [1873]; b.p.$_{12}$ 156-158° [1521];
$n_D^{23} = 1.5527$ [1521]; ^{1}H NMR [247], ^{13}C NMR [1873], IR [247] [1873].

1-(2-Hydroxy-4-methoxy-3-methylphenyl)ethanone

[69469-91-6] $C_{10}H_{12}O_3$ mol.wt. 180.20



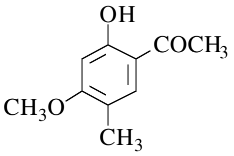
Syntheses

-Preparation by reaction of acetonitrile on 3-methoxy-2-methylphenol (Hoesch reaction) (46%) [910].
-Preparation by reaction of methyl iodide on resacetophenone,
*with potassium hydroxide in refluxing methanol [702] [1455] [1501], (19-25%) [1455] [1464] [1501];
*with sodium methoxide in boiling methanol [1411].

m.p. 83-84° [1411] [1455], 83° [910], 82-83° [1464], 80-82° [1501], 80-81° [702].

1-(2-Hydroxy-4-methoxy-5-methylphenyl)ethanone

[81511-52-6] $C_{10}H_{12}O_3$ mol.wt. 180.20



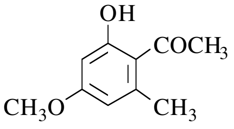
Syntheses

-Preparation by partial methylation of 2,4-dihydroxy-5-methylacetophenone,
*with methyl iodide in the presence of potassium carbonate in refluxing acetone (78%) [1185];
*with diazomethane in solution of ethyl ether-methanol mixture (92%) [1259].

m.p. 94° [1185].

1-(2-Hydroxy-4-methoxy-6-methylphenyl)ethanone *(Acetoevernone)*

[6540-66-5] $C_{10}H_{12}O_3$ mol.wt. 180.20



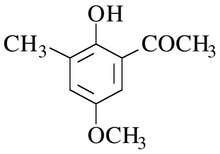
Syntheses

-Preparation by partial methylation of 2,4-dihydroxy-6-methylacetophenone (orcacetophenone or β-orcacetophenone), with diazomethane (78%) [1705] or dimethyl sulfate [790] [1598].
-Preparation by Fries rearrangement of 3-methoxy-5-methylphenyl acetate with aluminium chloride in nitrobenzene at r.t. (52%) [1196] [1202].
-Preparation by reaction of acetonitrile on 3-methoxy-5-methylphenol with zinc chloride and hydrochloric acid in ethyl ether at r.t. (Hoesch reaction) [790] [860], (28%) [790].
-Also obtained (by-product) by reaction of acetyl chloride on orcinol dimethyl ether with aluminium chloride in carbon disulfide at r.t. [14] [723] [1705] [1761], (5-8%) [723] [1705].

m.p. 79-80° [723], 79° [790] [860] [1196] [1202] [1761], 78-78°5 [1705];
^{1}H NMR [723] [1705], IR [723] [1705], UV [723] [1705], MS [723] [1705].

1-(2-Hydroxy-5-methoxy-3-methylphenyl)ethanone

[77936-48-2] $C_{10}H_{12}O_3$ mol.wt. 180.20



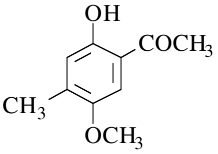
Syntheses

-Preparation by Fries rearrangement of 4-methoxy-2-methylphenyl acetate,
*with boron trifluoride in ethylene dichloride for 3 h (97%) [20];
*with aluminium chloride (11%) [148].

m.p. 52-53° [20]; sublimation 54-58°/0.2 mm [20];
^{1}H NMR [20], IR [20], MS [20] [267].

1-(2-Hydroxy-5-methoxy-4-methylphenyl)ethanone

[4223-84-1] $C_{10}H_{12}O_3$ mol.wt. 180.20



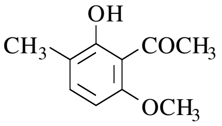
Syntheses

-Obtained by reaction of acetyl chloride on 2,5-dimethoxy-4-isopropyltoluene with aluminium chloride in boiling carbon disulfide (14%) [1524].
-Also obtained by chromic acid degradation of 5-methoxy-2,3,6-trimethylbenzofuran (10%) [1521].
-Also obtained (by-product) by reaction of acetyl chloride with 2,5-dimethoxytoluene in the presence of aluminium chloride in carbon disulfide at 20-25° (4%) [1741].
-Also obtained by photo-Fries rearrangement of 4-methoxy-3-methylphenyl acetate in ethanol under nitrogen (19%) [247].

m.p. 114° [1741], 112° [1524], 111-112° [1521]; ^{1}H NMR [1741], IR [1741].

1-(2-Hydroxy-6-methoxy-3-methylphenyl)ethanone

[56504-43-9] $C_{10}H_{12}O_3$ mol.wt. 180.20



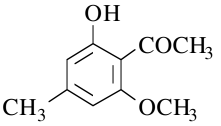
Syntheses

-Preparation by partial methylation of 2,6-dihydroxy-3-methylacetophenone,
*with methyl iodide in the presence of potassium carbonate in refluxing acetone (55%) [1185];
*with diazomethane in ethyl ether at r.t. (16%) [1746].
-Also obtained by reduction of 3-formyl-2-hydroxy-6-methoxyacetophenone with hydrochloric acid and amalgamated zinc in methanol at 50° (11%) [1185].

m.p. 59° [1185], 58° [1746]; ^{1}H NMR [1746], IR [1746].

1-(2-Hydroxy-6-methoxy-4-methylphenyl)ethanone

[31405-63-7] $C_{10}H_{12}O_3$ mol.wt. 180.20



Syntheses

-Preparation by reaction of acetic anhydride on orcinol monomethyl ether with concentrated sulfuric acid, at reflux (45%) [860].

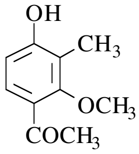
-Also obtained by reaction of dimethyl sulfate on 2,6-dihydroxy-4-methylacetophenone (p-orcacetophenone) with sodium hydroxide [860] or potassium hydroxide [1121].

-Also obtained by reaction of acetyl chloride on orcinol dimethyl ether with aluminium chloride in carbon disulfide at r.t. [723] [1705] [1761], (11%) [723], (4%) [1705].

m.p. 81° [860], 80-81° [1705], 76-77° [1760], 74-75° [723];
^{1}H NMR [723] [1705], IR [723] [1705], UV [723] [1705], MS [723] [1705].

1-(4-Hydroxy-2-methoxy-3-methylphenyl)ethanone

[118824-97-8] $C_{10}H_{12}O_3$ mol.wt. 180.20



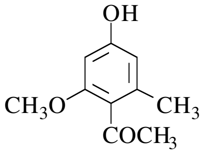
Synthesis

-Preparation by catalytic hydrogenolysis of 4-(benzyloxy)-2-methoxy-3-methylacetophenone at r.t. under pressure in the presence of 10% Pd/C in ethanol (92%) [1470], (84%) [912].

m.p. 130-132° [1470], 130° [912];
^{1}H NMR [1470], IR [1470], MS [1470].

1-(4-Hydroxy-2-methoxy-6-methylphenyl)ethanone *(Isoacetoevernone)*

$C_{10}H_{12}O_3$ mol.wt. 180.20



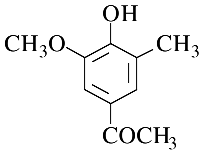
Synthesis

-Preparation by reaction of acetonitrile on orcinol monomethyl ether (Hoesch reaction) (32%) [790].

m.p. 150° [790].

1-(4-Hydroxy-3-methoxy-5-methylphenyl)ethanone

$C_{10}H_{12}O_3$ mol.wt. 180.20



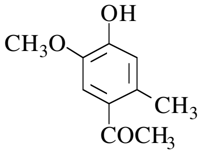
Synthesis

-Preparation by Fries rearrangement of 2-methoxy-6-methylphenyl acetate with aluminium chloride in refluxing carbon disulfide (58%) [561].

m.p. 94° [561].

1-(4-Hydroxy-5-methoxy-2-methylphenyl)ethanone

[162853-20-5] $C_{10}H_{12}O_3$ mol.wt. 180.20



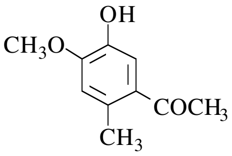
Syntheses

-Preparation by reaction of acetyl chloride on isocreosol (2-methoxy-5-methylphenol) with aluminium chloride in nitrobenzene at r.t. (87%) [582].
-Preparation by Fries rearrangement of isocreosol acetate with aluminium chloride in nitrobenzene at r.t. (75%) [305].
-Also obtained by photo-Fries rearrangement of 2-methoxy-5-methylphenyl acetate under nitrogen in ethanol (20%) [247] or in methanol at 254 nm at r.t. (21%) [1703].

m.p. 167-168° [1703], 124° [305], 123° [582];
^{1}H NMR [1703], ^{13}C NMR [1703], IR [1703], MS [1703].

1-(5-Hydroxy-4-methoxy-2-methylphenyl)ethanone

[6948-37-4] $C_{10}H_{12}O_3$ mol.wt. 180.20



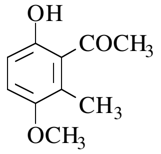
Syntheses

-Preparation by reaction of acetic acid on creosol (2-methoxy-4-methylphenol) with boron trifluoride at 25° [280] [473], (88%) [473].
-Preparation by Fries rearrangement of creosol acetate with aluminium chloride, in methylene chloride at 0° [1275] or at 20° (82%) [1169], in nitrobenzene at 80° (70%) [1150] or without solvent (8%) [148].
-Also obtained by reaction of acetyl chloride on homoveratrole (3,4-dimethoxytoluene) with aluminium chloride in carbon disulfide [585].

m.p. 129-130° [473], 129° [1150] [1169], 128-129° [1275], 124-126° [280], 123° [585];
^{1}H NMR [280] [1169], (Sadtler: standard n°49332 M);
IR [280] [1169], (Sadtler: standard n° 76405 K); UV [1169].

1-(6-Hydroxy-3-methoxy-2-methylphenyl)ethanone

[71452-36-3] $C_{10}H_{12}O_3$ mol.wt. 180.20



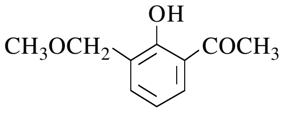
Synthesis

-Obtained by photo-Fries rearrangement of 4-methoxy-3-methylphenyl acetate in ethanol under nitrogen (18%) [247].

oil [247]; ^{1}H NMR [247], IR [247], MS [247].

1-[2-Hydroxy-3-(methoxymethyl)phenyl]ethanone

[87165-50-2] $C_{10}H_{12}O_3$ mol.wt. 180.20



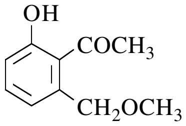
Synthesis

-Preparation from 3-chloromethyl-2-hydroxyacetophenone (m.p. 45°) by reaction with methanol in the presence of concentrated hydrochloric acid and iron powder at reflux for 3.5 to 4 h (88%) [289].

b.p.$_{0.3}$ 89-91° [289]; ^{1}H NMR [289], IR [289].

1-[2-Hydroxy-6-(methoxymethyl)phenyl]ethanone

[161358-64-1] $C_{10}H_{12}O_3$ mol.wt. 180.20



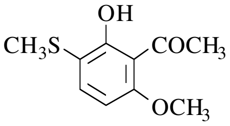
Synthesis

-Obtained by treatment of 2-(methoxymethoxy)-6-(methoxymethyl)acetophenone with aqueous trifluoroacetic acid at r.t. for 16 h (93%) [435].

pale yellow oil [435]; b.p.$_1$ 165-170° [435];
^{1}H NMR [435], IR [435], MS [435].

1-[2-Hydroxy-6-methoxy-3-(methylthio)phenyl]ethanone

[126405-81-0] $C_{10}H_{12}O_3S$ mol.wt. 212.27



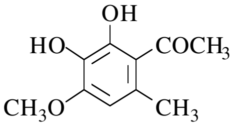
Synthesis

-Preparation by adding 2-hydroxy-3-iodo-6-methoxyacetophenone and cuprous oxide to a solution of sodium methyl sulfhydrate, first prepared from methanethiol and sodium hydride in DMF [1873].

m.p. 83° [1873]; ^{1}H NMR [1873], IR [1873].

1-(2,3-Dihydroxy-4-methoxy-6-methylphenyl)ethanone

[127940-12-9] $C_{10}H_{12}O_4$ mol.wt. 196.20



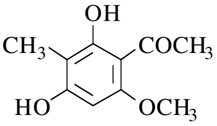
Synthesis

-Preparation by reaction of acetyl chloride on 1,2,3-trimethoxy-5-methylbenzene with aluminium chloride in refluxing methylene chloride (45%) [1782].

m.p. 132° [1782]; ^{1}H NMR [1782], ^{13}C NMR [1782], IR [1782], MS [1782].

1-(2,4-Dihydroxy-6-methoxy-3-methylphenyl)ethanone

[83459-37-4] $C_{10}H_{12}O_4$ mol.wt. 196.20



Syntheses

-Preparation by reduction of 3-formyl-2,4-dihydroxy-6-methoxyacetophenone with hydrochloric acid and amalgamated zinc in gently heated aqueous methanol (64%) [1500].

-Also obtained by reaction of acetonitrile on 3,5-dihydroxy-4-methylanisole (Hoesch reaction) [470].

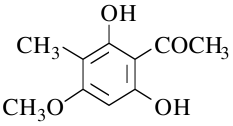
Isolation from natural sources

-From Yuexiandaji *(Euphorbia ebracteolata)* [1951].
-From the roots of *Euphorbia ebracteolata* Hayata [536] [1950].
-From *Pancratium maritimum* (Amaryllidaceae) [1931].

m.p. 225° [1500], 224° [470], 202-203° (d) [1931]; HPLC [1951];
^{1}H NMR [1931], ^{13}C NMR [1931], IR [1931], EIMS [1931], HRMS [1931].

1-(2,6-Dihydroxy-4-methoxy-3-methylphenyl)ethanone

[69480-06-4] $C_{10}H_{12}O_4$ mol.wt. 196.20



Syntheses

-Preparation by reaction of acetonitrile on 3,5-dihydroxy-2-methylanisole (Hoesch reaction) (73%) [470].

-Also obtained by reaction of 2 N aqueous sodium hydroxide on 2,4-diacetyl-3,5-dihydoxy-6-methylanisole at 80° (decarbonylation reaction) [494].

-Preparation by catalytic hydrogenolysis of 6-(benzyloxy)-2-hydroxy-4-methoxy-3-methyl-acetophenone in the presence of Pd/C in acetic acid (75%) [1186].

-Also obtained (by-product) by reaction of acetic anhydride on 3,5-dihydroxy-2-methylanisole with boron trifluoride in ethyl ether at 20° [494].

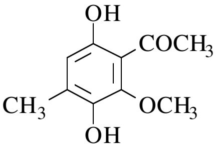
Isolation from natural sources

-From the pericarps of *Mallotus japonicus* Muell. Arg. (Euphorbiaceae) [77] [78] [1017].
-Also obtained by reductive alkaline cleavage of 3-(3,3-dimethylallyl)-5-(3-acetyl-2,4-dihydroxy-5-methyl-6-methoxybenzyl)phloroacetophenone (**I**) [1622], according to [1115]. The ketone (**I**) was isolated from *Mallotus japonicus* (Euphorbiaceae) [1622].

m.p. 200-201° [1017], 198° [494], 197-200° [1622], 197-198° [470], 196-198° [78], 196° [1186];
^{1}H NMR [78] [1017] [1622], UV [78], MS [78] [1017] [1622].

1-(3,6-Dihydroxy-2-methoxy-4-methylphenyl)ethanone

[90377-24-5] $C_{10}H_{12}O_4$ mol.wt. 196.20

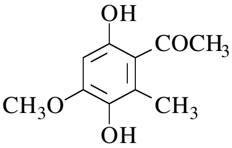


Isolation from natural sources

-From *Trocholejeunea sandvicensis* (Lejeuneaceae) [87].

1-(3,6-Dihydroxy-4-methoxy-2-methylphenyl)ethanone

[68531-86-2] $C_{10}H_{12}O_4$ mol.wt. 196.20



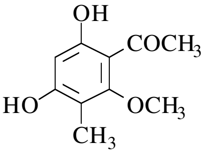
Synthesis

-Preparation by nuclear oxidation of 2-hydroxy-4-methoxy-6-methylacetophenone with alkaline persulfate (Elbs reaction) (45%) [16].

m.p. 164-165° [16].

1-(4,6-Dihydroxy-2-methoxy-3-methylphenyl)ethanone *(Pseudoaspidinol-A)*

[52200-61-0] $C_{10}H_{12}O_4$ mol.wt. 196.20



Syntheses

-Preparation by catalytic hydrogenolysis of 4,6-bis-(benzyloxy)-2-methoxy-3-methylacetophenone in the presence of Pd/C in acetic acid (quantitative yield) [1883], (86%) [1186].
-Preparation by reaction of dimethyl sulfate on 4,6-bis-(benzoyloxy)-2-hydroxy-3-methylacetophenone with potassium carbonate in boiling acetone (46%) [1883].
-Also obtained by heating methyl 5-acetyl-2,6-dihydroxy-4-methoxy-3-methylbenzoate in aqueous glycerol at 180-200° for 30 min (29%) [1563].
-Also refer to: [219] [1184].

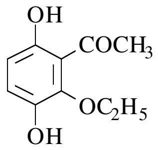
Isolation from natural sources

-From *stereocaulon vesuvianum,* a foliose lichen, abundantly growing over volcanic rocks [258].

m.p. 143-144° [258], 142° [1186] [1883], 138-140° [1563]; TLC [258];
^{1}H NMR [258] [1563], IR [258] [1563], UV [258], MS [258].

1-(2-Ethoxy-3,6-dihydroxyphenyl)ethanone

[33539-21-8] $C_{10}H_{12}O_4$ mol.wt. 196.20



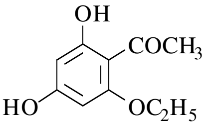
Syntheses

-Easy preparation by reduction of 2-acetyl-3-ethoxy-1,4-benzoquinone using conventional methods [587].
-Also obtained (low yield) by reaction of 2-acetyl-1,4-benzoquinone with an excess of ethanol at r.t., with exclusion of light [587].

m.p. 102-103°5 [587]; ^{1}H NMR [587], IR [587].

1-(2-Ethoxy-4,6-dihydroxyphenyl)ethanone

$C_{10}H_{12}O_4$ mol.wt. 196.20



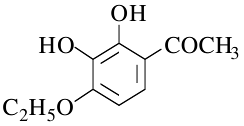
Synthesis

-Preparation by reaction of acetonitrile on phloroglucinol monoethyl ether (Hoesch reaction) (63%) [73].

m.p. 178° [73].

1-(4-Ethoxy-2,3-dihydroxyphenyl)ethanone

$C_{10}H_{12}O_4$ mol.wt. 196.20



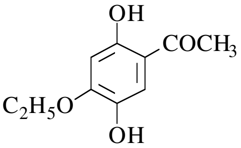
Syntheses

-Preparation by reaction of ethyl iodide on gallacetophenone monopotassium salt in boiling methanol [1409].
-Preparation by reaction of hydrobromic acid with 2,4-diethoxy-3-methoxyacetophenone (43%) or 3,4-diethoxy-2-hydroxyacetophenone (20%) in acetic acid at r.t. [663].

m.p. 102°2-103°2 [663], 102° [1408] [1409].

1-(4-Ethoxy-2,5-dihydroxyphenyl)ethanone

[58084-93-8] $C_{10}H_{12}O_4$ mol.wt. 196.20



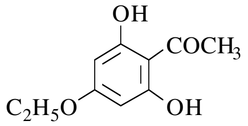
Synthesis

-Preparation from 4-ethoxy-2-hydroxyacetophenone by persulfate oxidation (Elbs reaction) (quantitative yield) [1652], (24%) [212].

m.p. 129-130° [212], 125-126° [1652]; ^{1}H NMR [1652].

1-(4-Ethoxy-2,6-dihydroxyphenyl)ethanone

[35028-01-4] $C_{10}H_{12}O_4$ mol.wt. 196.20



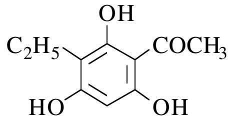
Synthesis

-Preparation from 2,4-diacetyl-5-ethoxyresorcinol by selective deacetylation by refluxing in 1 N sodium hydroxide for 1 h [342].

m.p. 164-165° [342]; ^{1}H NMR [342].

1-(3-Ethyl-2,4,6-trihydroxyphenyl)ethanone

[84653-58-7] $C_{10}H_{12}O_4$ mol.wt. 196.20



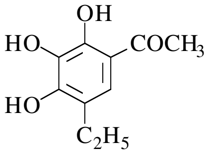
Synthesis

-Refer to: [350] (compound **VII**).

m.p. 187-189° [350]; ^{1}H NMR [350].

1-(5-Ethyl-2,3,4-trihydroxyphenyl)ethanone

[86989-84-6] $C_{10}H_{12}O_4$ mol.wt. 196.20



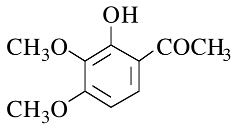
Syntheses

-Preparation by reaction of acetyl chloride on 4-ethylpyrogallol with aluminium chloride [420].
-Preparation by reaction of acetic acid with 4-ethylpyrogallol in the presence of boron trifluoride in ethyl ether at 0° (78%) [347].

m.p. 141° [347] [420]; UV [347].

1-(2-Hydroxy-3,4-dimethoxyphenyl)ethanone

[5396-18-9] $C_{10}H_{12}O_4$ mol.wt. 196.20



Syntheses

-Preparation by reaction of acetyl chloride on pyrogallol trimethyl ether,
*with aluminium chloride in carbon disulfide [169] [282] [1412] [1413] [1444], (50%) [1444], in boiling ethyl ether (77%) [1357] or in benzene at 45-50° (77%) [635];
*with mercuric chloride without solvent at 100° (40%) [1153] [1154].
-Preparation by Fries rearrangement of 2,3-dimethoxyphenyl acetate with aluminium chloride in nitrobenzene at r.t. (61%) [1196] [1202].
-Preparation by partial methylation of gallacetophenone,
*with methyl iodide,
    -in the presence of sodium methoxide in boiling methanol [1410] [1411];
    -in the presence of potassium carbonate in refluxing acetone (47%) [196] or in acetone-DMF mixture [831].

*with dimethyl sulfate,
  -in the presence of potassium carbonate in refluxing benzene (65%) [135], (51%) [141];
  -in the presence of 40% potassium hydroxide [282] [483] [1194].

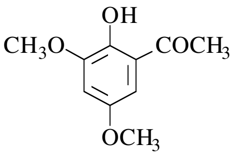
-Preparation by partial methylation of 2,3-dihydroxy-4-methoxyacetophenone with methyl iodide in the presence of potassium hydroxide in methanol [1408] [1409].

-Also obtained by selective demethylation of 2,3,4-trimethoxyacetophenone,
*with boron trichloride in methylene chloride at 0° (88%) [1083];
*with aluminium chloride in refluxing ethyl ether [736] or in acetonitrile at 30° for 3 h (95%) [962];
*with aniline hydriodide in aniline for 7 h at 95° (54%) [1351];
*with cupric bromide in refluxing chloroform-ethyl acetate mixture (4%) [894].

m.p. 83° [169] [1351], 78-80° [282], 78-79° [196] [483] [635] [1194] [1196] [1202], 78° [831], 77-78° [1409] [1410] [1411], 77° [135] [1412] [1413] [1444], 75-77° [141], 72-76° [1083], 68-72° [894],
^{1}H NMR [635] [894] [1083], ^{13}C NMR [736], IR [635] [1083].

1-(2-Hydroxy-3,5-dimethoxyphenyl)ethanone

[17605-00-4] $C_{10}H_{12}O_4$ mol.wt. 196.20



Syntheses

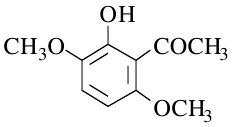
-Preparation by reaction of dimethyl sulfate on 2,5-dihydroxy-3-methoxyacetophenone with potassium carbonate in refluxing acetone (54%) [1643].

-Preparation by photo-Fries rearrangement of 2,4-dimethoxyphenyl acetate in ethanol (61%) or in benzene (55%) [280].

m.p. 84-86° [1643]; ^{1}H NMR [280], IR [280].

1-(2-Hydroxy-3,6-dimethoxyphenyl)ethanone

[52099-27-1] $C_{10}H_{12}O_4$ mol.wt. 196.20



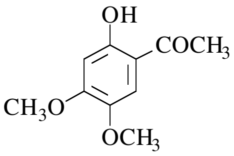
Synthesis

-Preparation by reaction of concentrated hydrochloric acid on 2-(benzyloxy)-3,6-dimethoxyacetophenone in acetic acid at 60° (99%) [140].

m.p. 61° [140].

1-(2-Hydroxy-4,5-dimethoxyphenyl)ethanone

[20628-06-2] $C_{10}H_{12}O_4$ mol.wt. 196.20



Syntheses

-Preparation by partial methylation of 2,5-dihydroxy-4-methoxyacetophenone,
*with methyl iodide in the presence of potassium carbonate in refluxing acetone (81%) [118];
*with dimethyl sulfate in the presence of potassium

carbonate in refluxing acetone (71%) [1900], in the presence of sodium methoxide in methanol (by-product) [147] [156] [157] [164] or in the presence of sodium hydroxide in boiling aqueous ethanol (37%) [1196] [1202];

*with an excess of ethereal diazomethane in methanol (93%) [971].

-Preparation by reaction of acetonitrile on 3,4-dimethoxyphenol with zinc chloride (Hoesch reaction) (47%) [911].

-Also obtained (by-product) by reaction of acetyl chloride on 1,2,4-trimethoxybenzene with aluminium chloride in carbon disulfide at r.t. [147] [158] [164].

-Also obtained by partial demethylation of 2,4,5-trimethoxyacetophenone with boiling aqueous hydrochloric acid [147] [164] or aluminium chloride in acetonitrile for 6 h at 45° (50%) [962].

-Preparation by reaction of boiling acetic acid on 3,4-dimethoxyphenyldiazonium borofluoride. The 3,4-dimethoxyphenyl acetate which was first formed was rearranged by the boron trifluoride produced during the reaction (62%) [1653].

-Also refer to: [41].

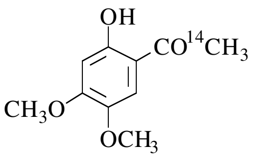
Isolation from natural sources

-From various plants belonging to the Polypodiaceae family, namely Inomotosou (*Pteris multifide* Poiret), Oobainomotosou (*Pteris cretica* L.) and Hitotsuba (*Pyrrosia"ingua* Farw.) [1353].

m.p. 115° [164], 114-116° [1900], 114-115° [156] [157], 112-114° [971],
112° [118] [911] [1653], 111-112° [1196] [1202]; b.p.$_{0.004}$ 125° [911];
GC [1353], GC-MS [1353];
^{1}H NMR [118], ^{13}C NMR [897], IR [118] [1353].

1-(2-Hydroxy-4,5-dimethoxyphenyl)ethanone-*2-^{14}C*

[77184-92-0] $C_{10}H_{12}O_4$ mol.wt. 198.20



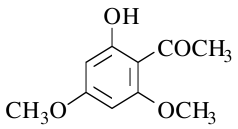
Synthesis

-Preparation by heating a mixture of 3,4-dimethoxyphenol, boron trifluoride-acetic acid complex and sodium acetate-2-^{14}C (250 μCi) at 100° for 25 min (54%) [729].

m.p. 112-113° [729];
specific radioactivity 1.50 μCi/mmol [729].

1-(2-Hydroxy-4,6-dimethoxyphenyl)ethanone *(Xanthoxylin; Brevifolin)*

[90-24-4] $C_{10}H_{12}O_4$ mol.wt. 196.20



Syntheses

-Preparation by reaction of acetonitrile on phloroglucinol dimethyl ether (Hoesch reaction) [352] [1037].

-Also obtained by partial methylation of phloroacetophenone,

*with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone [481] [866], (86%) [481] or in solution of acetone-benzene mixture at reflux (78-83%) [416] [721] [1302], (65%) [1551];

*with diazomethane in ethyl ether, at r.t. [1262] [1673];

*with methyl iodide in the presence of potassium carbonate in boiling acetone (83%) [841], (6%) [1564].

-Also obtained by partial methylation of 2,4-dihydroxy-6-methoxyacetophenone [1675] or 2,6-dihydroxy-4-methoxyacetophenone with diazomethane [85] [1675], (quantitative yield) [85].

-Preparation by acetylation of phloroglucinol dimethyl ether,

*with the boron trifluoride-acetic acid complex at 100° (24%) [1146];
*with a mixture of acetic anhydride-acetic acid in the presence of boron trifluoride at 0° (54%) [1129];
*with acetic anhydride in the presence of boron trifluoride in ethyl ether at 15° (49%) [494];
*with acetylating complex mixture at 60° (17%) [1176].
-Preparation by partial demethylation of phloroacetophenone trimethyl ether,
*with hydriodic acid in acetic anhydride at r.t. (96%) [840];
*with aluminium chloride [194] [962] [1013] [1140] [1625], in nitrobenzene (sole product) [1140], in acetonitrile for 6 h at 45° (90%) [962], in boiling ethyl ether (79%) [194] or without solvent at 110° (30%) [1013];
*with hydrobromic acid in acetic acid [840].
-Also obtained by reaction of boron trifluoride etherate on 2,4-diacetyl-3,5-dimethoxyphenol in acetic acid (61%) [494].
-Also obtained (major product) by reaction of acetyl chloride on phloroglucinol trimethyl ether with aluminium chloride in boiling petroleum ether [630].
-Preparation by UV light irradiation of 3,5-dimethoxyphenyl acetate at 25° [724] (photo-Fries rearrangement), in cyclohexane (62%), in isopropanol (45%) or in ethyl ether (32%).

Isolation from natural sources

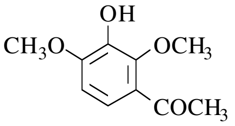
-From the Bark of *Phytophthora* — and *Hendersonula* — infected *Citrus limon* [752].
-From *Xanthoxylum piperitum* De Candolle [1688] [1689], from the essential oils of *Xanthoxylum aubertia* (*Evodia aubertia*) (10%) [1580] and of *Xanthoxylum alatum* Roxb. (Rutaceae) [1580].
-From the root bark of *Fagara okinawaensis* Nakai (0.5%) [1262].
-From the leaves of *Hippomane mancinella* L. [1559].
-From the essential oil of *Artemisia brevifolia* Wallich [1656] or indigenous species of *Artemisia gallica* Willd. [890].
-From the essential oil of *Eucalyptus Bakeri* Maiden [1402].
-From various species of *Geijera* [1402].
-From *Blumea balsamifera* DC [908] [909].
-A new flavone, hinokiflavone was obtained from the leaves of *Chamaecyparis obtusa* Endlicher (Cupressaceae) [951]. Hinokiflavone pentamethyl ether treated with alkali gave Xanthoxylin,
*with potassium hydroxide [644];
*by boiling in methanolic barium hydroxide solution (77%) [952].
-A flavonoid, Sciadopitysin, was obtained from the leaves of *Sciadopitys verticillata*. Xanthoxylin was obtained in high yield by degradation of sciadopitysin trimethyl ether in boiling methanolic barium hydroxide solution [952] [965].
-A flavonoid, Tricin, was obtained from the Khapli wheat leaves *(Triticum Dicoccum)*. Xanthoxylin was obtained by degradation of tricin trimethyl ether in boiling 80% solution of potassium hydroxide in ethanol [56].
-In the steam distillates of resins from *Xanthorrhoea preissi*, *Xanthorrhoea reflexa*, *Xanthorrhoea tateana* F. Muell. and *Xanthorrhoea arborea* R. Br. [223] [596] [875] [1484].

m.p. 87-88° [879], 86° [866], 85-88° [630], 85° [1580], 84-85° [1037] [1176],
83°5 [1559], 83° [721] [1673],
82-83° [373] [908] [1013] [1262] [1263] [1302] [1402] [1551],
82° [223] [481] [570] [1129] [1146], 81°5 [494], 81° [194], 80°5-81° [752],
80-85° [56], 80-81° [2] [352], 80° [1656], 79° [596] [1484], 78°5-79°5 [841],
78-80° [1689], 78-79° [416] [1564];
b.p.$_{18}$ 175-185° [596], b.p.$_{20}$ 185° [1484].

^{1}H NMR [622] [752] [841], ^{13}C NMR [736], IR [622] [752] [841] [866] [1262],
UV [570] [752] [1559], MS [752] [841].

1-(3-Hydroxy-2,4-dimethoxyphenyl)ethanone

[23133-83-7] $C_{10}H_{12}O_4$ mol.wt. 196.20



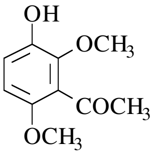
Syntheses

-Preparation from 2,6-dimethoxyphenol or its acetate by reaction of refluxing acetic anhydride in the presence of few drops of concentrated sulfuric acid, followed by saponification of 3-acetoxy-2,4-dimethoxyacetophenone formed with 2 N sodium hydroxide (good yield) [282].
-Preparation from 3-acetoxy-2,4-dimethoxyacetophenone by hydrolysis with 2 N hydrochloric acid in refluxing methanol (78%) [1053].

m.p. 79-80° [282] [1053]; ^{1}H NMR [1053], IR [1053].

1-(3-Hydroxy-2,6-dimethoxyphenyl)ethanone

[56358-74-8] $C_{10}H_{12}O_4$ mol.wt. 196.20



Isolation from natural sources

-Identification in liquid wastes from eucalyptus wood and kraft lignin charring [1504].

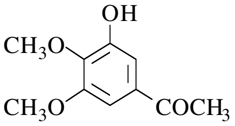
From Microorganisms

-Ketone identified from metabolism of 2,6-dimethoxyacetophenone in the rat [238].

^{1}H NMR [238], MS [238].

1-(3-Hydroxy-4,5-dimethoxyphenyl)ethanone

[114012-82-7] $C_{10}H_{12}O_4$ mol.wt. 196.20

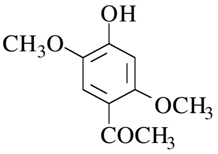


Isolation from natural sources

-Identified by flame-ionization gas-chromatography and gas chromatography-mass spectrometry into liquid wastes from eucalyptus wood and kraft lignin charring [1504].

1-(4-Hydroxy-2,5-dimethoxyphenyl)ethanone

[13909-71-2] $C_{10}H_{12}O_4$ mol.wt. 196.20



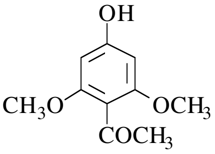
Syntheses

-Preparation by Fries rearrangement of 2,5-dimethoxyphenyl acetate with aluminium chloride [147].
-Preparation by nuclear oxidation of 2,5-dimethoxyacetophenone with peracetic acid [147].

m.p. 117-118° [147].

1-(4-Hydroxy-2,6-dimethoxyphenyl)ethanone

[13246-14-5] $C_{10}H_{12}O_4$ mol.wt. 196.20



Syntheses

-Preparation by reaction of acetic anhydride on phloroglucinol dimethyl ether with boron trifluoride,
*in ethyl ether at 15° (49%) [494];
*in acetic acid at 0° (24%) [1129].
-Preparation by reaction of phloroglucinol dimethyl ether with boron trifluoride-acetic acid complex at 100° (40%) [1146].
-Preparation by reaction of acetonitrile on phloroglucinol dimethyl ether (Hoesch reaction) [352] [1037], (32%) [352].
-Preparation by reaction of aluminium chloride on phloroacetophenone trimethyl ether in refluxing chlorobenzene [1037].
-Also obtained from 4-(benzyloxy)-2,6-dimethoxyacetophenone by heating with concentrated hydrochloric acid in acetic acid [1281].
-Also obtained by saponification of 4-(benzoyloxy)-2,6-dimethoxyacetophenone with 8% methanolic potassium hydroxide at r.t. [352].

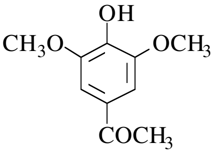
Isolation from natural sources

-From *Pancratium maritimum* (Amaryllidaceae) [1931].

m.p. 186° [1037], 185°5 [352], 185° [1146], 184-185° [1129], 183-184° [1281], 76-78° [1931]. One of the reported melting points is obviously wrong.
^{1}H NMR [1931], ^{13}C NMR [1931], IR [1931], EIMS [1931].

1-(4-Hydroxy-3,5-dimethoxyphenyl)ethanone *(Acetosyringone)*

[2478-38-8] $C_{10}H_{12}O_4$ mol.wt. 196.20



Syntheses

-Preparation by adding a solution of 4-hydroxy-3-iodo-5-methoxyacetophenone and cupric chloride in DMF to a solution of sodium methoxide in methanol and heating between 105 to 120° (86%) [1937].
-Preparation by reaction of sodium methoxide with 5-iodoacetovanillone in methanol in the presence of copper catalyst (53%) [451].
-Also obtained by debenzylation of 4-(benzyloxy)-3,5-dimethoxyacetophenone by means of a cold saturated solution of hydrogen bromide in acetic acid (52%) [279].
-Also obtained by Fries rearrangement of 2,6-dimethoxyphenyl acetate with aluminium chloride in nitrobenzene at r.t. (8-14%) [1079] [1195] [1403].
-Also refer to: [1702].

Isolation from natural sources

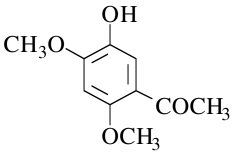
-From hairy roots cultures of *Nicotiana tabacum* and of *Atropa belladonna* [1672].
-In cell suspension cultures of *Hyoscyamus albus* [1231].
-From birch lignin sulfonic acid by treatment with hot aqueous "alkali" (0.8%) [1079].
-Identified by flame-ionization gas chromatography and gas chromatography-mass spectrometry into liquid wastes from eucalyptus wood and kraft lignin charring [1504].

m.p. 125° [1937], 123-124° [451], 122-123° [1195], 121-122° [1403],

120°5-121°5 [1079], 120-125° [1938], 117° [279];
^{1}H NMR [1672], UV[1082] [1672], MS [1672].

1-(5-Hydroxy-2,4-dimethoxyphenyl)ethanone

[91061-75-5] $C_{10}H_{12}O_4$ mol.wt. 196.20



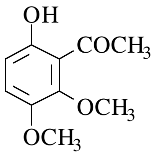
Syntheses

-Preparation by Fries rearrangement of 2,4-dimethoxyphenyl acetate,
*with aluminium chloride in nitrobenzene at 25° [147] [149], (50%) [149];
*with 36.2% boron trifluoride in acetic acid, first at r.t. overnight, then at 70° for 2 h (81%) [1397].
-Preparation by saponification of 5-acetyl-2,4-dimethoxyphenyl acetate with sodium hydroxide in dilute ethanol at 40° (90%) [498].

m.p. 155-156° [149] [1397], 154° [498].

1-(6-Hydroxy-2,3-dimethoxyphenyl)ethanone

[22248-13-1] $C_{10}H_{12}O_4$ mol.wt. 196.20



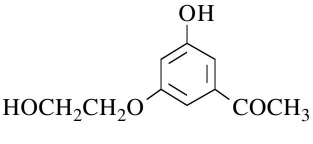
Syntheses

-Preparation by reaction of dimethyl sulfate on 3,6-dihydroxy-2-methoxyacetophenone with potassium carbonate in boiling benzene (67%) [136].
-Also refer to: [1708] (compound III).

b.p.$_{22}$ 162-163° [136].

1-[3-Hydroxy-5-(2-hydroxyethoxy)phenyl]ethanone

[63437-86-5] $C_{10}H_{12}O_4$ mol.wt. 196.20



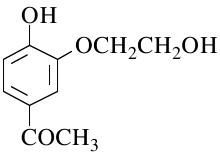
Synthesis

-Obtained by reaction of 2-chloroethanol with 3,5-dihydroxyacetophenone in refluxing aqueous sodium hydroxide for 5 h under nitrogen atmosphere (29%) [486].

m.p. 140° [486].

1-[4-Hydroxy-3-(2-hydroxyethoxy)phenyl]ethanone

[63437-85-4] $C_{10}H_{12}O_4$ mol.wt. 196.20



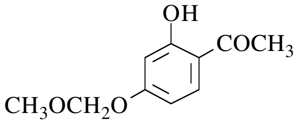
Synthesis

-Preparation by hydrogenolysis of 4-(benzyloxy)-3-(2-hydroxyethoxy)acetophenone in ethanol under hydrogen atmosphere in the presence of 5% Pd/C for 45 min (98%) [486].

m.p. 108-109° [486].

1-[2-Hydroxy-4-(methoxymethoxy)phenyl]ethanone

[65490-08-6] $C_{10}H_{12}O_4$ mol.wt. 196.20



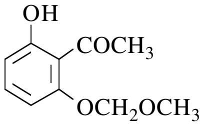
Syntheses

-Preparation by reaction of chloromethyl methyl ether,
*with resacetophenone in the presence of potassium carbonate in acetone at r.t. for 2.5 h (65%) [1395], at 20° for 20 h (70-75%) [1720] or at reflux for 3-6 h [1505];
*with resacetophenone disodium salt in a methanol/toluene mixture (27%) [193].
N.B.: Preparation by selective methoxymethylation of resacetophenone (no accuracy) (91%) [945].
-Also refer to: [1612].

oily residue [1395], colourless oil [945]; TLC [1720];
b.p.$_{0.15}$ 110° [1720], b.p.$_{0.2}$ 118-122° [193], b.p.$_3$ 138° [1395].
CAUTION! Traces of acids or water in the residue may result in a violent decomposition of the material during distillation [1395]; m.p. 36° [193];
^{1}H NMR [945] [1395] [1720], ^{13}C NMR [1720], IR [1395] [1720], MS [945] [1720].

1-[2-Hydroxy-6-(methoxymethoxy)phenyl]ethanone

[78646-28-3] $C_{10}H_{12}O_4$ mol.wt. 196.20



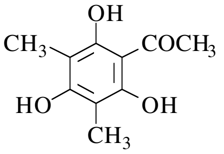
Syntheses

-Obtained by treatment of 2,6-dihydroxyacetophenone with methoxymethyl chloride in the presence of potassium carbonate in refluxing acetone for 2 h (85%) [824].
-Also obtained by adding methoxymethyl chloride to a solution of 2,6-dihydroxyacetophenone monosodium salt prepared by reaction of sodium hydride with the keto phenol in DMF at r.t. (60%) [1107].

light yellow oil [824]; ^{1}H NMR [824], IR [824], EIMS [824].

1-(2,4,6-Trihydroxy-3,5-dimethylphenyl)ethanone

[13383-63-6] $C_{10}H_{12}O_4$ mol.wt. 196.20



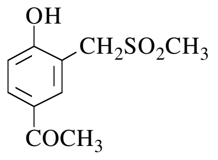
Syntheses

-Preparation by reaction of acetonitrile on 1,3-dimethylphloroglucinol (Hoesch reaction) [262] [346], (66%) [262].
-Preparation by Friedel-Crafts acylation of 1,3-dimethylphloroglucinol with acetic acid in the presence of boron trifluoride (63%) [1902].
-Also obtained by reaction of methyl iodide with phloroacetophenone in the presence of potassium hydroxide in 80% aqueous methanol (12%) [1489], of potassium hydroxide in anhydrous methanol (5%) [645] [875] or sodium methoxide in methanol [1491].
-Also obtained by demethylation of 2-hydroxy-4,6-dimethoxy-3,5-dimethylacetophenone [1118].
-Also refer to: [861] [1090] [1871].

m.p. 226-229° [1902], 221-222° [346], 220-222° [875], 219° [1489], 218° [262];
UV [1489] [1491], MS [262].

1-[4-Hydroxy-3-[(methylsulfonyl)methyl]phenyl]ethanone

[49640-12-2] $C_{10}H_{12}O_4S$ mol.wt. 228.27



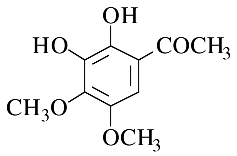
Syntheses

-Obtained by reaction of 3'-chloromethyl-4'-hydroxyacetophenone with magnesium methylsulfinate in refluxing aqueous methanol for 18 h (52%) [935].
-Also refer to: [425] [932] [933] [934].

m.p. 207-209° [935].

1-(2,3-Dihydroxy-4,5-dimethoxyphenyl)ethanone

[119892-31-8] $C_{10}H_{12}O_5$ mol.wt. 212.20

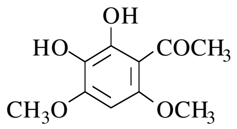


Synthesis

-Refer to: [981] (Japanese patent).

1-(2,3-Dihydroxy-4,6-dimethoxyphenyl)ethanone

[21919-66-4] $C_{10}H_{12}O_5$ mol.wt. 212.20



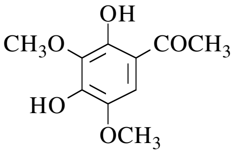
Syntheses

-Preparation by hydrolysis of 3-acetoxy-2-hydroxy-4,6-dimethoxyacetophenone,
*with 6 N hydrochloric acid in refluxing ethanol (92%) [815];
*with 10% potassium hydroxide at r.t. [1303] [1309], (90%) [1303].
-Preparation by hydrolysis of 2-hydroxy-3,4,6-trimethoxyacetophenone with 30% hydrobromic acid in acetic acid at r.t. (42%) [663].
-Preparation by catalytic hydrogenolysis of 2,3-bis(benzyloxy)-4,6-dimethoxyacetophenone in the presence of 10% Pd/C in ethyl acetate (89%) [215].
-Also obtained by reaction of hydrobromic acid with 3-ethoxy-2-hydroxy-4,6-dimethoxyacetophenone in acetic acid at r.t. (major compound) [198].
-Also obtained (by-product) by reaction of acetyl chloride with 1,2,3,5-tetramethoxybenzene in ethyl ether (3%) [198].
-Also refer to: [799] [1295].

m.p. 165°2-166°5 [663], 165-167°5 [198], 164-165° [1303], 160-165° [815], 160-162° [215];
^{1}H NMR [198], IR [198] [215], MS [198].

1-(2,4-Dihydroxy-3,5-dimethoxyphenyl)ethanone

[198203-68-8] $C_{10}H_{12}O_5$ mol.wt. 212.20

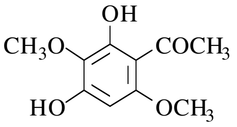


Synthesis

-Obtained (poor yields) by treatment of 4-hydroxy-3,5-dimethoxyacetophenone or 3,4,5-trimethoxyacetophenone with alkaline hydrogen peroxide (pH 11) irradiating with UV light (254 nm) at 40° for 2 h (< 1%) [1716]. **N.B.**: The silylated product was analyzed by gas chromatography-mass spectrometry (GC-MS).

1-(2,4-Dihydroxy-3,6-dimethoxyphenyl)ethanone

[7499-99-2] $C_{10}H_{12}O_5$ mol.wt. 212.20



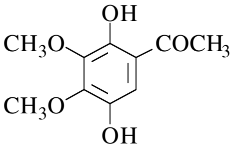
Syntheses

-Preparation by reaction of acetonitrile, (Hoesch reaction),
*on 2,6-bis(benzyloxy)-1,4-dimethoxybenzene (47%) [1452], (71%) [1552];
*on 2,5-dimethoxyresorcinol [664] [1605] [1882].

m.p. 129° [1605] [1882], 128-129° [1552], 125-130° [1452].

1-(2,5-Dihydroxy-3,4-dimethoxyphenyl)ethanone

[69616-56-4] $C_{10}H_{12}O_5$ mol.wt. 212.20



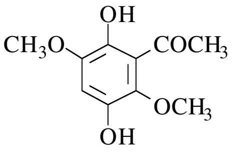
Synthesis

-Obtained from 2-hydroxy-3,4-dimethoxyacetophenone by persulfate oxidation (Elbs reaction) (30%) [135], (10%) [169].

m.p. 119-121° [169], 119° [135].

1-(2,5-Dihydroxy-3,6-dimethoxyphenyl)ethanone

[6212-45-9] $C_{10}H_{12}O_5$ mol.wt. 212.20



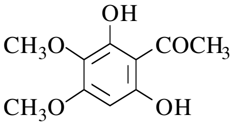
Syntheses

-Preparation by metallation of 2,5-dimethoxyhydroquinone-bis-[tetrahydropyranyl-(2)-ether], followed by treatment of the intermediate aryllithium compound with acetic anhydride in tetrahydrofuran at r.t. (82%) [1561].
-Preparation by reaction of acetic acid on 2,5-dimethoxyhydroquinone diacetate with boron trifluoride etherate at 75° [67] [1460], (55%) [1460].
-Preparation by catalytic hydrogenolysis of 2,5-bis(benzyloxy)-3,6-dimethoxyacetophenone in the presence of palladium oxide in ethanol (96%) [1560].

m.p. 170° [1460], 94° [1560] [1561].

1-(2,6-Dihydroxy-3,4-dimethoxyphenyl)ethanone

[74556-32-4] $C_{10}H_{12}O_5$ mol.wt. 212.20



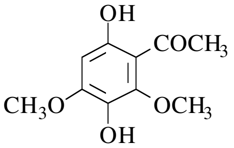
Syntheses

-Preparation by reaction of dimethyl sulfate on 2,3,4,6-tetrahydroxyacetophenone with sodium hydroxide in boiling ethanol (94%) [1328].
-Also obtained by reaction of acetyl chloride on 5-hydroxy-1,2,3-trimethoxybenzene (antiarol) with aluminium chloride in nitrobenzene [375].
-Also obtained by reaction of acetyl chloride on 1,2,3,5-tetramethoxybenzene with aluminium chloride in nitrobenzene at r.t. [160] [163] [375].
-Preparation by cleavage of 2,6-dihydroxy-3,4-dimethoxyacetophenone mono-2,4-dinitrophenyl ether with piperidine by heating in a steam bath (76%) [815].
-Also obtained by cleavage of 2,3,4-trimethoxy-6-isopropoxyacetophenone or 6-hydroxy-2,3,4-trimethoxyacetophenone with hydrobromic acid in acetic acid (23%) [815].

m.p. 166-168° [1328], 162-163° [160] [163], 160-161° [375], 135°6-135°9 [815].

1-(3,6-Dihydroxy-2,4-dimethoxyphenyl)ethanone

[6962-57-8] $C_{10}H_{12}O_5$ mol.wt. 212.20



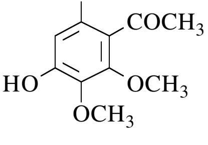
Syntheses

-Preparation by Fries rearrangement of 1,4-diacetoxy-2,6-dimethoxybenzene with aluminium chloride in nitrobenzene at r.t. [815] [858] [1199] [1354], (57%) [1354], (47-56%) [858] and (34%) [1199].
-Preparation by reaction of 2,6-dimethoxyhydroquinone with boron trifluoride-acetic acid complex at 28-30° (60%) [1146].
-Preparation from 2-hydroxy-4,6-dimethoxyacetophenone by persulfate oxidation (Elbs reaction) (36%) [1551], (7%) [841].
-Also obtained (by-product) by reaction of acetyl chloride on 1,2,3,5-tetramethoxybenzene with aluminium chloride in carbon disulfide [161].
-Preparation by hydrolysis of 3-acetoxy-6-hydroxy-2,4-dimethoxyacetophenone with refluxing 5% methanolic hydrochloric acid (major product) [1055] or refluxing 10% ethanolic hydrochloric acid [815].
-Also refer to: [783] [1311].

m.p. 164-165° [1551], 162-163° [161] [1055] [1199] [1354], 162-162°5 [815], 162° [858] [1146], 161-162° [841];
^{1}H NMR [841] [1055], ^{13}C NMR [1396], IR [841] [1055], UV [1055], MS [841] [1055].

1-(4,6-Dihydroxy-2,3-dimethoxyphenyl)ethanone

[103777-42-0] $C_{10}H_{12}O_5$ mol.wt. 212.20

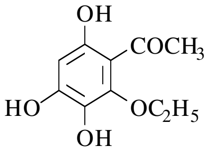


Synthesis

-Preparation from 4-(benzyloxy)-6-hydroxy-2,3-dimethoxyacetophenone by hydrogenolysis with hydrogen in the presence of Pd/C [807].

1-(2-Ethoxy-3,4,6-trihydroxyphenyl)ethanone

[63635-41-6] $C_{10}H_{12}O_5$ mol.wt. 212.20



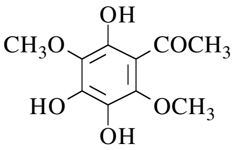
Synthesis

-Preparation by hydrogenolysis of 2-ethoxy-3,4,6-tris-(benzyloxy)acetophenone with 5% Pd/C in ethanol at r.t. (96%) [757] [758].

m.p. 169° [757] [758];
^{1}H NMR [757] [758], IR [757] [758].

1-(2,4,5-Trihydroxy-3,6-dimethoxyphenyl)ethanone

[15994-32-8] $C_{10}H_{12}O_6$ mol.wt. 228.20



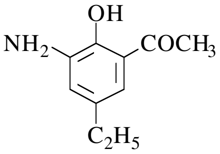
Syntheses

-Obtained by hydrogenolysis of 4-benzyloxy-2,5-dihydroxy-3,6-dimethoxyacetophenone with hydrogen in the presence of 30% Pd/C [1071].
-Also obtained by persulfate oxidation of 2,4-dihydroxy-3,6-dimethoxyacetophenone (Elbs reaction) [844].
-Also refer to: [290] [291].

m.p. 142-144° [290], 140-142° [640], 137°5-138°5 [1071], 131-134° [54];
^{1}H NMR [844], IR [640] [844].

1-(3-Amino-5-ethyl-2-hydroxyphenyl)ethanone

[70977-78-5] $C_{10}H_{13}NO_2$ mol.wt. 179.22



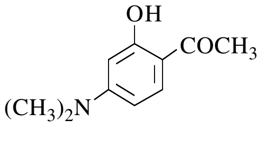
Synthesis

-Preparation by catalytic hydrogenation of 5-ethyl-2-hydroxy-3-nitroacetophenone in the presence of 5% Pd/C in ethanol at 25° (70%) [1463], (60%) [620].

m.p. 50-51° [1463], 48-51° [620].

1-[4-(Dimethylamino)-2-hydroxyphenyl]ethanone

[107070-69-9] $C_{10}H_{13}NO_2$ mol.wt. 179.22



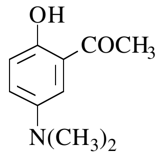
Syntheses

-Preparation by reaction of dimethyl sulfate with 4-amino-2-hydroxyacetophenone in the presence of sodium carbonate in boiling water for 40 min (49%) [1495].
-Also refer to: [1544] [1751].

m.p. 118° [1495]; ^{1}H NMR [1495], ^{13}C NMR [1494], IR [1495].

1-[5-(Dimethylamino)-2-hydroxyphenyl]ethanone

[49619-68-3] $C_{10}H_{13}NO_2$ mol.wt. 179.22



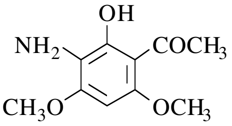
Synthesis

-Preparation by catalytic hydrogenation of 2-hydroxy-5-nitroacetophenone with formalin in the presence of palladium chloride (82%) [1335].

m.p. 76°5-77°5 [1335]; ^{1}H NMR [1335], IR [1335].

1-(3-Amino-2-hydroxy-4,6-dimethoxyphenyl)ethanone

[81325-91-9] $C_{10}H_{13}NO_4$ mol.wt. 211.22



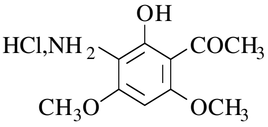
Synthesis

-Preparation by adding a hot solution of stannous chloride in hydrochloric acid to a solution of 2-acetoxy-4,6-dimethoxy-3-nitroacetophenone in ethanol containing zinc dust and heating the mixture in a steam bath (48%) [2].

m.p. 118-119° [2]; ^{1}H NMR [2], IR [2].

1-(3-Amino-2-hydroxy-4,6-dimethoxyphenyl)ethanone *(Hydrochloride)*

[81325-92-0] $C_{10}H_{13}NO_4$, HCl mol.wt. 247.68



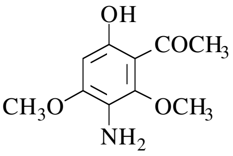
Synthesis

-Preparation by treatment of a solution of 2-hydroxy-4,6-dimethoxy-3-nitroacetophenone in ethanol with zinc dust and a solution of stannous chloride in hydrochloric acid, and heating in a steam bath (50%) [2].

m.p. 171° [2].

1-(3-Amino-6-hydroxy-2,4-dimethoxyphenyl)ethanone

[81325-95-3] $C_{10}H_{13}NO_4$ mol.wt. 211.22



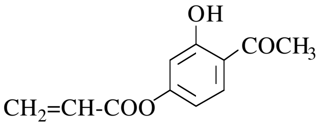
Synthesis

-Preparation by adding a solution of stannous chloride in hydrochloric acid to a hot solution of 6-hydroxy-2,4-dimethoxy-3-phenylazoacetophenone in ethanol containing zinc dust, and heating the mixture in a steam bath (73%) [2].

m.p. 75° [2]; ^{1}H NMR [2].

1-[4-(Acryloyloxy)-2-hydroxyphenyl]ethanone

$C_{11}H_{10}O_4$ mol.wt. 206.20



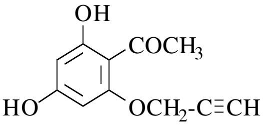
Synthesis

-Preparation by reaction of acryloyl chloride with resacetophenone in the presence of triethylamine in ethyl ether (25%) [1529].

m.p. 55-57° [1529]; ^{1}H NMR [1529], IR [1529].

1-[2,4-Dihydroxy-6-(2-propynyloxy)phenyl]ethanone

[53771-24-7] $C_{11}H_{10}O_4$ mol.wt. 206.20



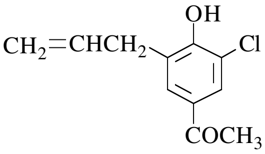
Synthesis

-Obtained (poor yield) by reaction of 2-propynyl bromide with phloroacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (5%) [427].

m.p. 142-143° [427]; UV [427].

1-[3-Chloro-4-hydroxy-5-(2-propenyl)phenyl]ethanone

[51832-82-7] $C_{11}H_{11}ClO_2$ mol.wt. 210.66

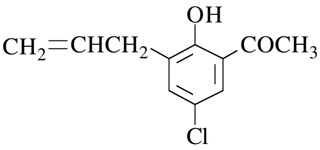


Synthesis

-Preparation by Claisen rearrangement of 4-(allyloxy)-3-chloroacetophenone [275] [950].

1-[5-Chloro-2-hydroxy-3-(2-propenyl)phenyl]ethanone

[186956-46-7] $C_{11}H_{11}ClO_2$ mol.wt. 210.66



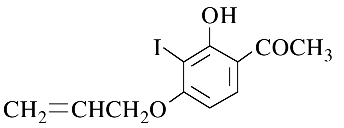
Synthesis

-Obtained by Claisen rearrangement of 2-(allyloxy)-5-chloroacetophenone in refluxing N,N-diethylaniline at 220° for 4 h [1476].

Colourless oil [1476]; b.p.$_{0.1}$ 140° [1476];
^{1}H NMR [1476], IR [1476].

1-[2-Hydroxy-3-iodo-4-(2-propenyloxy)phenyl]ethanone

[72511-76-3] $C_{11}H_{11}IO_3$ mol.wt. 318.11



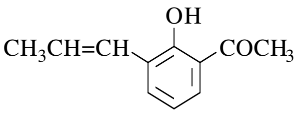
Synthesis

-Obtained by partial allylation of 2,4-dihydroxy-3-iodoacetophenone with allyl bromide in the presence of potassium carbonate in refluxing acetone for 4-5 h (52%) [17].

m.p. 91-92° [17]; ^{1}H NMR [17].

1-[2-Hydroxy-3-(1-propenyl)phenyl]ethanone

[67127-96-2] $C_{11}H_{12}O_2$ mol.wt. 176.22



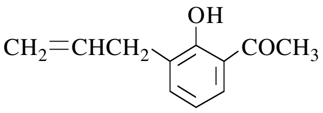
Synthesis

-Preparation by isomerization of 3-allyl-2-hydroxyacetophenone using bis(benzonitrile)-palladous chloride in refluxing toluene (90%) [620] [621].

b.p.$_{18}$ 153-155° [620] [621].

1-[2-Hydroxy-3-(2-propenyl)phenyl]ethanone

[58621-39-9] $C_{11}H_{12}O_2$ mol.wt. 176.22



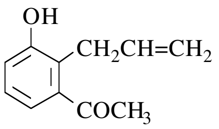
Syntheses

-Preparation by thermal Claisen rearrangement of 2-(allyloxy)acetophenone (m.p. 19-21°) [29],
*in refluxing N,N-diethylaniline at 220° for 4 h [1476];
*in boiling dichlorobenzene (30%) [677];
*without solvent at 260-270° (85%) [1747];
*without solvent at reflux under nitrogen atmosphere for 5 h [27], (66%) [29].
-Also obtained by photolysis of o-allylphenyl acetate in cyclohexane (major product) (photo-Fries rearrangement) [1238].
-Also refer to: [28] [504] [1836].

light yellow liquid [29], colourless oil [1476];
b.p.$_{0.3}$ 110° [29], b.p.$_{20}$ 135-138° [1747], b.p.$_{0.1}$ 135-138° [1476], b.p. 258° [504];
^{1}H NMR [29] [677] [1476], ^{13}C NMR [29], IR [29] [677] [1476], MS [29].

1-[3-Hydroxy-2-(2-propenyl)phenyl]ethanone

[58621-37-7] $C_{11}H_{12}O_2$ mol.wt. 176.22



Syntheses

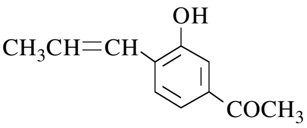
-Preparation by thermal Claisen rearrangement of 3-(allyloxy)acetophenone,
*in boiling dichlorobenzene (10%) [677];
*in DMF at 220° (53%) [303];

*without solvent at 220° (43%) [303].

oil [303]; ^{1}H NMR [303] [677], IR [303] [677], MS [303].

1-[3-Hydroxy-4-(1*E*)-1-propenylphenyl]ethanone

[430474-15-0] $C_{11}H_{12}O_2$ mol.wt. 176.22



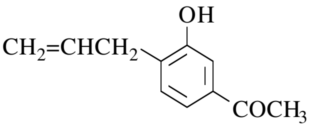
Synthesis

-Obtained by isomerization of 1-[3-hydroxy-4-(2-propenyl)phenyl]ethanone in the presence of polymer-supported iridium catalyst in THF at r.t. (92% *trans)* [177] [178].

^{1}H NMR [178].

1-[3-Hydroxy-4-(2-propenyl)phenyl]ethanone

[58621-38-8] $C_{11}H_{12}O_2$ mol.wt. 176.22



Syntheses

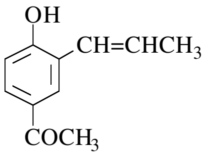
-Preparation by thermal Claisen rearrangement of 3-(allyloxy)acetophenone,
*in boiling dichlorobenzene (50%) [677];
*in DMF at 220° (27%) [303];
*without solvent at 220° (22%) [303].

-Also obtained by UV light irradiation of 3-(allyloxy)acetophenone in benzene or cyclohexane under nitrogen (8%) [677].

m.p. 75-76° [677], 62-64° [303]; ^{1}H NMR [303] [677], IR [303] [677], MS [303].

1-[4-Hydroxy-3-(1-propenyl)phenyl]ethanone

[53889-99-9] $C_{11}H_{12}O_2$ mol.wt. 176.22

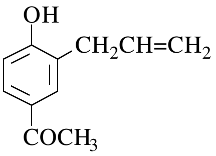


Synthesis

-Refer to: [239].

1-[4-Hydroxy-3-(2-propenyl)phenyl]ethanone

[1132-05-4] $C_{11}H_{12}O_2$ mol.wt. 176.22



Syntheses

-Preparation by thermal Claisen rearrangement of 4-(allyloxy)acetophenone,
*in boiling N,N-dimethylaniline [333];
*in diphenyl ether at 185° [688] or at reflux (76%) [1886];
*without solvent at 200-210° (78%) [80], at 200-230°

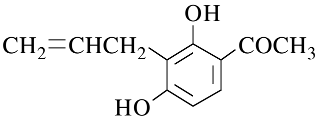
(96%) [1156] or at 260-270° (64%) [1747].

-Also obtained by UV light irradiation of 4-(allyloxy)acetophenone in benzene or cyclohexane under nitrogen (13%) [677].

m.p. 115°9-116°7 [1886], 115-116° [80], 115° [333];
b.p.$_4$ 164-165° [1747], b.p.$_{21}$ 200-201° [333];
^{1}H NMR [677], IR [677], UV [1886], MS [1156].

1-[2,4-Dihydroxy-3-(2-propenyl)phenyl]ethanone

[38987-00-7] $C_{11}H_{12}O_3$ mol.wt. 192.21



Syntheses

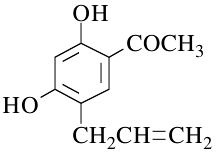
-Preparation by thermal Claisen rearrangement of 4-(allyloxy)-2-hydroxyacetophenone without solvent at 200-210° (85%) [132].

-Also refer to: [132] [1028] [1372].

m.p. 133° [132]; UV [1028].

1-[2,4-Dihydroxy-5-(2-propenyl)phenyl]ethanone

[38987-01-8] $C_{11}H_{12}O_3$ mol.wt. 192.21



Syntheses

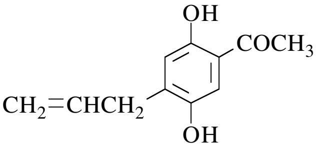
-Preparation by demethylation of 5-allyl-4-hydroxy-2-methoxyacetophenone with aluminium chloride in ethyl ether or acetonitrile [1028].

-Preparation by reaction of boron tribromide on 5-allyl-4-hydroxy-2-methoxyacetophenone in methylene chloride, first at -78°, then at -45° (52%) [256] [257] [777].

m.p. 74-76° [256] [257] [777], 55° [1028]; ^{1}H NMR [256] [257], UV [1028].

1-[2,5-Dihydroxy-4-(2-propenyl)phenyl]ethanone

[174901-51-0] $C_{11}H_{12}O_3$ mol.wt. 192.21

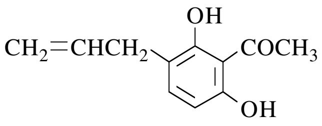


Synthesis

-Refer to: [700].

1-[2,6-Dihydroxy-3-(2-propenyl)phenyl]ethanone

[17488-71-0] $C_{11}H_{12}O_3$ mol.wt. 192.21



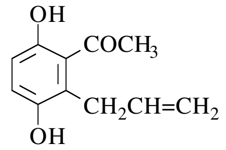
Syntheses

-Obtained from 8-acetyl-6-allyl-7-hydroxy-4-methylcoumarin by alkaline degradation with 12% aqueous sodium hydroxide solution by heating in a water bath (80%) [1648].
-Also refer to: [343] [734].

m.p. 63-65° [1648]; ^{13}C NMR [734].

1-[3,6-Dihydroxy-2-(2-propenyl)phenyl]ethanone

[40815-79-0] $C_{11}H_{12}O_3$ mol.wt. 192.21



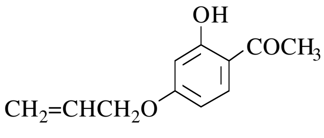
Syntheses

-Preparation by thermal Claisen rearrangement of 5-(allyloxy)-2-hydroxyacetophenone without solvent at 200-220° (36%) [1156] or at 220-230° (74-75%) [131] [303].
-Also obtained by thermal reaction of 2-acetyl-1,4-benzoquinone,
*with allyltrimethylstannane in benzene (27%) or acetonitrile (18%) [1171];
*with allyltributylstannane in benzene (29%) [1171].

m.p. 107°5 [131], 103-104° [303], 78-80° [1171];
^{1}H NMR [303] [1156] [1171], IR [303] [1171], MS [303] [1156] [1171].

1-[2-Hydroxy-4-(2-propenyloxy)phenyl]ethanone

[40815-74-5] $C_{11}H_{12}O_3$ mol.wt. 192.21



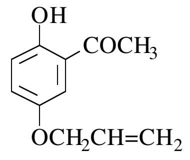
Syntheses

-Preparation by reaction of allyl bromide on resacetophenone with potassium carbonate,
*in refluxing methyl ethyl ketone (90%) [256] [257] [777];
*in refluxing acetone (70%) [132].

oil [256] [257] [777]; b.p.$_9$ 156-157° [132].

1-[2-Hydroxy-5-(2-propenyloxy)phenyl]ethanone

[40815-75-6] $C_{11}H_{12}O_3$ mol.wt. 192.21



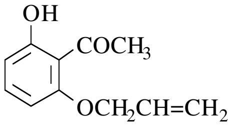
Synthesis

-Preparation by reaction of allyl bromide on quinacetophenone with potassium carbonate in refluxing acetone (86%) [302] [303], (73%) [131] or in refluxing methyl ethyl ketone (52%) [1156].

m.p. 59-60° [131] [302] [303];
^{1}H NMR [303] [1156], IR [303], MS [303] [1156].

1-[2-Hydroxy-6-(2-propenyloxy)phenyl]ethanone

[23226-84-8] $C_{11}H_{12}O_3$ mol.wt. 192.21



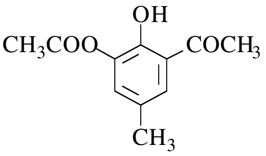
Synthesis

-Preparation by reaction of allyl bromide with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone (52%) [343].

m.p. 45°5-46°5 [343]; b.p.$_{0.15}$ 128-132° [343].

1-[3-(Acetyloxy)-2-hydroxy-5-methylphenyl]ethanone

[77347-23-0] $C_{11}H_{12}O_4$ mol.wt. 208.21



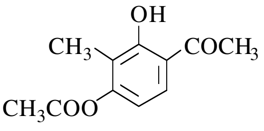
Synthesis

-Preparation by reaction of m-chloroperoxybenzoic acid with 2,6-diacetyl-4-methylphenol using chloroform and trifluoroacetic acid as solvent at r.t. (39%) [171].

m.p. 80-81° [171]; ^{1}H NMR [171], MS [171].

1-[4-(Acetyloxy)-2-hydroxy-3-methylphenyl]ethanone

[144224-86-2] $C_{11}H_{12}O_4$ mol.wt. 208.21



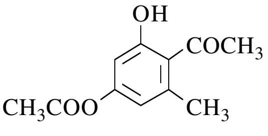
Syntheses

-Preparation by reaction of acetyl chloride with 2,4-dihydroxy-3-methylacetophenone in the presence of triethylamine in methylene chloride at 0° for 2 h then at r.t. overnight (82%) [1265].
-Also refer to: [1264].

m.p. 71-73° [1265]; ^{1}H NMR [1265], ^{13}C NMR [1265], IR [1265].

1-[4-(Acetyloxy)-2-hydroxy-6-methylphenyl]ethanone

[57600-87-0] $C_{11}H_{12}O_4$ mol.wt. 208.21

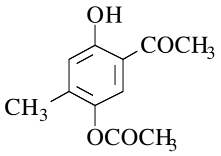


Synthesis

-Preparation by treatment of a mixture of alkylated resorcinols with acetic anhydride and acetic acid in the presence of zinc chloride at 140-145°, followed by suitable separation [936].

1-[5-(Acetyloxy)-2-hydroxy-4-methylphenyl]ethanone

[126570-32-9] $C_{11}H_{12}O_4$ mol.wt. 208.21



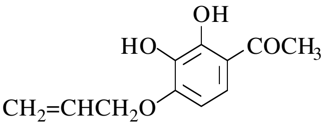
Syntheses

-Preparation by partial acetylation of 2,5-dihydroxy-4-methylacetophenone [514].
-Also obtained (by-product) by Fries rearrangement of 2-methylhydroquinone diacetate with aluminium chloride [514].

m.p. 109° [514].

1-[2,3-Dihydroxy-4-(2-propenyloxy)phenyl]ethanone

$C_{11}H_{12}O_4$ mol.wt. 208.21



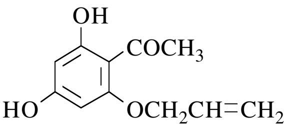
Synthesis

-Obtained by reaction of allyl bromide on gallacetophenone with sodium bicarbonate in refluxing acetone-ethanol mixture (16%) [972].

m.p. 84° [972].

1-[2,4-Dihydroxy-6-(2-propenyloxy)phenyl]ethanone

[76609-35-3] $C_{11}H_{12}O_4$ mol.wt. 208.21



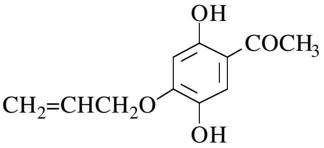
Synthesis

-Preparation by tosylation of phloroacetophenone with p-toluenesulfonyl chloride (2.2 mol) in acetone in the presence of potassium carbonate, followed by allylation with allyl bromide (1.2 mol) and final detosylation with methanolic potassium hydroxide [13].

m.p. 144-145° [13].

1-[2,5-Dihydroxy-4-(2-propenyloxy)phenyl]ethanone

[92831-82-8] $C_{11}H_{12}O_4$ mol.wt. 208.21



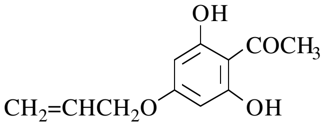
Synthesis

-Preparation from 4-(allyloxy)-2-hydroxyacetophenone by persulfate oxidation (Elbs reaction) (24%) [82].

m.p. 79-80° [82]; ^{1}H NMR [82].

1-[2,6-Dihydroxy-4-(2-propenyloxy)phenyl]ethanone

[35028-03-6] $C_{11}H_{12}O_4$ mol.wt. 208.21



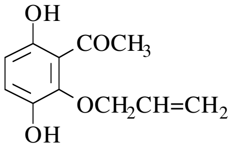
Synthesis

-Preparation from 2,4-diacetyl-5-(allyloxy)resorcinol by selective deacetylation by refluxing in 1 N sodium hydroxide for 1 h [342].

m.p. 145-146° [342]; ^{1}H NMR [342].

1-[3,6-Dihydroxy-2-(2-propenyloxy)phenyl]ethanone

[33539-24-1] $C_{11}H_{12}O_4$ mol.wt. 208.21



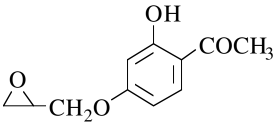
Syntheses

-Easy preparation by reduction of 2-acetyl-3-(allyloxy)-1,4-benzoquinone using conventional methods [587].
-Obtained (low yield) by reaction of 2-acetyl-1,4-benzoquinone with an excess of allyl alcohol at r.t., with exclusion of light [587].

m.p. 68-69° [587]; ^{1}H NMR [587], IR [587].

1-[2-Hydroxy-4-(oxiranylmethoxy)phenyl]ethanone

[61270-24-4] $C_{11}H_{12}O_4$ mol.wt. 208.21



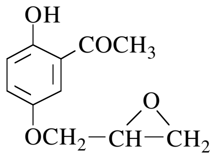
Synthesis

-Preparation by reaction of epichlorohydrin with resacetophenone in the presence of potassium hydroxide, in refluxing ethanol [71] or in a concentrated aqueous solution at 120° [1284].

m.p. 78° [1284], 72-73° [71].

1-[2-Hydroxy-5-(oxiranylmethoxy)phenyl]ethanone

[16139-53-0] $C_{11}H_{12}O_4$ mol.wt. 208.21



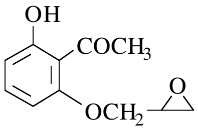
Synthesis

-Refer to: [610] [611].

m.p. 76-79° [611].

1-[2-Hydroxy-6-(oxiranylmethoxy)phenyl]ethanone

[16130-28-2] $C_{11}H_{12}O_4$ mol.wt. 208.21



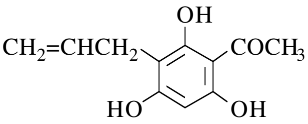
Synthesis

-Preparation by reaction of epichlorohydrin with 2,6-dihydroxyacetophenone in the presence of potassium hydroxide in refluxing ethanol [71].

m.p. 61-63° [71].

1-[2,4,6-Trihydroxy-3-(2-propenyl)phenyl]ethanone

[118062-86-5] $C_{11}H_{12}O_4$ mol.wt. 208.21

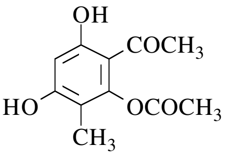


Synthesis

-Refer to: [402] (Japanese patent).

1-[2-(Acetyloxy)-4,6-dihydroxy-3-methylphenyl]ethanone

$C_{11}H_{12}O_5$ mol.wt. 224.21



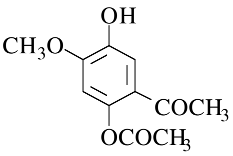
Synthesis

-Obtained (poor yield) by hydrolysis of the ozonide formed from 4,6-dihydroxy-2,3,7-trimethylbenzofuran (m.p. 178°(d)) with dilute ozone (7%) [745] in ethyl acetate at -30° (13%) [1570].

m.p. 161-164° [1570].

1-[2-(Acetyloxy)-5-hydroxy-4-methoxyphenyl]ethanone

[144152-30-7] $C_{11}H_{12}O_5$ mol.wt. 224.21



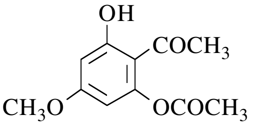
Synthesis

-Obtained by enzymatic deacylation of 2,5-diacetoxy-4-methoxyacetophenone with *Candida cylindracea* lipase in diisopropyl ether at 42-45° (65%) [1381] [1383].

pale yellow viscous oil [1383]; ^{1}H NMR [1383].

1-[2-(Acetyloxy)-6-hydroxy-4-methoxyphenyl]ethanone

[63013-36-5] $C_{11}H_{12}O_5$ mol.wt. 224.21

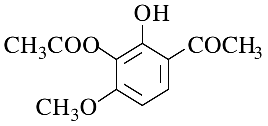


Synthesis

-Refer to: [1046] (compound 5) (48%).

1-[3-(Acetyloxy)-2-hydroxy-4-methoxyphenyl]ethanone

$C_{11}H_{12}O_5$ mol.wt. 224.21



Syntheses

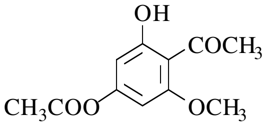
-Preparation by reaction of a mixture of acetic anhydride and acetic acid with 2,6-dimethoxyphenol in the presence of boron trifluoride at 30° (67%) [814].

-Preparation by reaction of acetyl chloride with 2,3-dihydroxy-4-methoxyacetophenone in pyridine at 0° (52%) [1053].

m.p. 123°4-125° [814], 122-123° [1053]; ^{1}H NMR [1053], IR [1053].

1-[4-(Acetyloxy)-2-hydroxy-6-methoxyphenyl]ethanone

[29376-66-7] $C_{11}H_{12}O_5$ mol.wt. 224.21



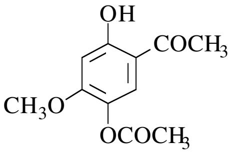
Synthesis

-Preparation by reaction of diazomethane with 4-acetoxy-2,6-dihydroxyacetophenone in tetrahydrofuran at r.t. (55%) [1019].

m.p. 86-89° [1019].

1-[5-(Acetyloxy)-2-hydroxy-4-methoxyphenyl]ethanone

[69470-86-6] $C_{11}H_{12}O_5$ mol.wt. 224.21



Syntheses

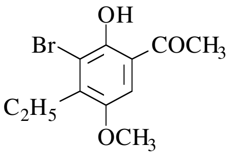
-Preparation by Fries rearrangement of 2-methoxyhydroquinone diacetate with boron trifluoride in acetic acid (90%) [498].

-Obtained by reaction of methyl iodide with 5-acetoxy-2,4-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone (19%) [703].

m.p. 104° [498] [703].

1-(3-Bromo-4-ethyl-2-hydroxy-5-methoxyphenyl)ethanone

$C_{11}H_{13}BrO_3$ mol.wt. 273.13



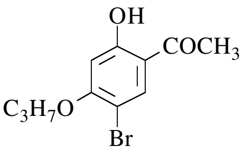
Synthesis

-Obtained by reaction of bromine on 4-ethyl-2-hydroxy-5-methoxyacetophenone in ethyl ether containing a trace of aluminium chloride [1459].

m.p. 83° [1459].

1-(5-Bromo-2-hydroxy-4-propoxyphenyl)ethanone

[57442-27-0] $C_{11}H_{13}BrO_3$ mol.wt. 273.13



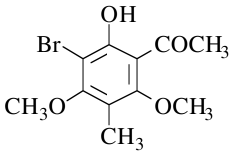
Synthesis

-Preparation by bromination of 2-hydroxy-4-propoxyacetophenone (1 mol) in 80% acetic acid with bromine (1 mol) at r.t. (25-30°) (90%) [1148].

m.p. 118° [1148].

1-(3-Bromo-2-hydroxy-4,6-dimethoxy-5-methylphenyl)ethanone

[39701-15-0] $C_{11}H_{13}BrO_4$ mol.wt. 289.13



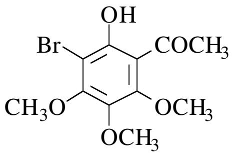
Synthesis

-Preparation by adding an aqueous solution of bromine and potassium bromide to an ethanolic solution of 2-hydroxy-4,6-dimethoxy-5-methylacetophenone (46%) [837].

m.p. 75-76° [837]; ^{1}H NMR [837], IR [837].

1-(3-Bromo-2-hydroxy-4,5,6-trimethoxyphenyl)ethanone

$C_{11}H_{13}BrO_5$ mol.wt. 305.13



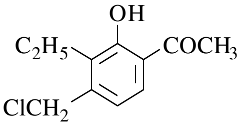
Syntheses

-Preparation by methylation of 3-bromo-2,5-dihydroxy-4,6-dimethoxyacetophenone [542].
-Preparation by bromination of 6-hydroxy-2,3,4-trimethoxyacetophenone [542].

m.p. 89-90° [542].

1-[4-(Chloromethyl)-3-ethyl-2-hydroxyphenyl]ethanone

[97582-38-2] $C_{11}H_{13}ClO_2$ mol.wt. 212.68



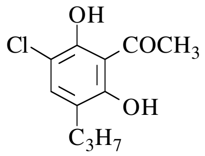
Synthesis

-Preparation by reaction of ethyl chloroformate with 4-(dimethylaminomethyl)-3-ethyl-2-hydroxyacetophenone [529] [530], (71%) [530].

m.p. 55-57° [530]; b.p.$_{0.5}$ 120-130° [529]; ^{1}H NMR [529], IR [529].

1-(3-Chloro-2,6-dihydroxy-5-propylphenyl)ethanone

[102624-59-9] $C_{11}H_{13}ClO_3$ mol.wt. 228.68

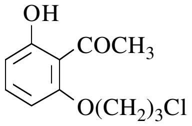


Syntheses

-Preparation according to literature procedures [1067] (compound 1c).
-Also refer to: [92].

1-[2-(3-Chloropropoxy)-6-hydroxyphenyl]ethanone

[105277-74-5] $C_{11}H_{13}ClO_3$ mol.wt. 228.68



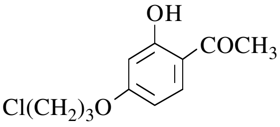
Synthesis

-Preparation by reaction of 1-bromo-3-chloropropane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 24 h (quantitative yield) [872].

m.p. 60°5-62°5 [872]; ^{1}H NMR [872], MS [872].

1-[4-(3-Chloropropoxy)-2-hydroxyphenyl]ethanone

[172739-45-6] $C_{11}H_{13}ClO_3$ mol.wt. 228.68



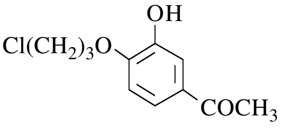
Syntheses

-Preparation by reaction of 1-bromo-3-chloropropane with resacetophenone [614], in the presence of potassium carbonate in refluxing acetone for 5 h (84%) [314] or for 16 h (69%) [260].
-Also refer to: [261].

m.p. 73-74° [260], 73° [314]; ^{1}H NMR [260], IR [260].

1-[4-(3-Chloropropoxy)-3-hydroxyphenyl]ethanone

[151719-65-2] $C_{11}H_{13}ClO_3$ mol.wt. 228.68



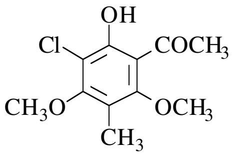
Syntheses

-Obtained by demethylation of 1-[4-(3-chloropropoxy)-3-methoxyphenyl]ethanone in concentrated sulfuric acid at 65° for 23 h (22%) [1701].
-Also refer to: [1283].

m.p. 101-103° [1701]; ^{1}H NMR [1701], MS [1701].

1-(3-Chloro-2-hydroxy-4,6-dimethoxy-5-methylphenyl)ethanone

[31913-64-1] $C_{11}H_{13}ClO_4$ mol.wt. 244.67



Synthesis

-Preparation by reaction of sulfuryl chloride with 6-hydroxy-2,4-dimethoxy-3-methylacetophenone in chloroform at -3° (59%) [1359].

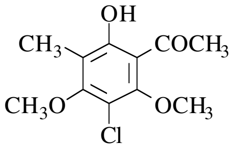
Isolation from natural sources

-Also obtained by alkaline hydrolysis of sordidone dimethyl ether (8-chloro-5,7-dimethoxy-2,6-dimethylchromone) [83] [1359] with refluxing 5% aqueous potassium hydroxide under nitrogen (83%) [1359]. Sordidone is a metabolite isolated from the lichen *Lecanora rupicola* (L) Zahlbr. (syn. *Lecanora sordida* Th. Fr.) [1359].

m.p. 94° [83] [1359]; ^{1}H NMR [1359], IR [1359], MS [1359].

1-(3-Chloro-6-hydroxy-2,4-dimethoxy-5-methylphenyl)ethanone

[23053-45-4] $C_{11}H_{13}ClO_4$ mol.wt. 244.67



Syntheses

-Preparation by adding of ethereal solution of diazomethane to a solution of 3-chloro-2,4,6-trihydroxy-5-methylacetophenone in a mixture of acetone-ethyl ether at r.t. (76%) [836].

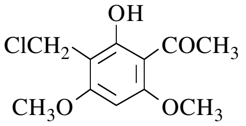
-Preparation by reaction of sulfuryl chloride with 2-hydroxy-4,6-dimethoxy-3-methylacetophenone in chloroform at -3° (43%) [1359].

-Also obtained by alkaline hydrolysis of isosordidone dimethyl ether (6-chloro-5,7-dimethoxy-2,8-dimethylchromone) with refluxing 5% aqueous potassium hydroxide under nitrogen (55%) [1359].

m.p. 108-109° [836], 108° [1359]; ^{1}H NMR [1359], IR [1359], MS [1359].

1-[3-(Chloromethyl)-2-hydroxy-4,6-dimethoxyphenyl]ethanone

[40356-82-9] $C_{11}H_{13}ClO_4$ mol.wt. 244.67



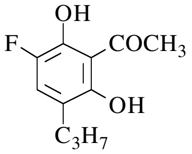
Synthesis

-Preparation by chloromethylation of 2-hydroxy-4,6-dimethoxyacetophenone with chloromethyl methyl ether in acetic acid for 1 h at r.t. (57%) [1300] [1301].

m.p. 133-135° (d) [1300] [1301].

1-(3-Fluoro-2,6-dihydroxy-5-propylphenyl)ethanone

[102624-71-5] $C_{11}H_{13}FO_3$ mol.wt. 212.22

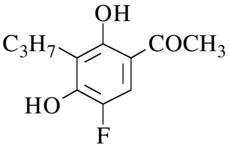


Syntheses

-Preparation according to literature procedures [1067] (compound 1f).
-Also refer to: [92].

1-(5-Fluoro-2,4-dihydroxy-3-propylphenyl)ethanone

[119257-53-3] $C_{11}H_{13}FO_3$ mol.wt. 212.22

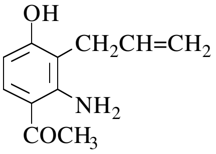


Synthesis

-Refer to: [1889].

1-[2-Amino-4-hydroxy-3-(2-propenyl)phenyl]ethanone

[118684-00-7] $C_{11}H_{13}NO_2$ mol.wt. 191.23



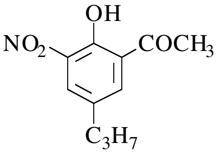
Synthesis

-Preparation by thermal Claisen rearrangement of 4-(allyloxy)-2-aminoacetophenone without solvent at 200° (54%) [297].

colourless oil [297]; ^{1}H NMR [297].

1-(2-Hydroxy-3-nitro-5-propylphenyl)ethanone

[70978-38-0] $C_{11}H_{13}NO_4$ mol.wt. 223.23



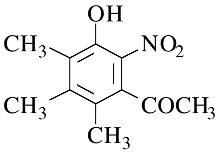
Synthesis

-Preparation by reaction of nitric acid (d = 1.42) on 2-hydroxy-5-propylacetophenone in concentrated sulfuric acid between -15 to -5° [620] [1463], (42%) [620].

m.p. 67-69° [1463], 67-68° [620].

1-(3-Hydroxy-4,5,6-trimethyl-2-nitrophenyl)ethanone

[13667-21-5] $C_{11}H_{13}NO_4$ mol.wt. 223.23



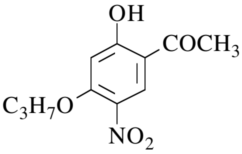
Synthesis

-Preparation by adding a solution of nitric acid (d = 1.38) in concentrated sulfuric acid to a solution of 5-hydroxy-2,3,4-trimethylacetophenone in acetic acid and carbon tetrachloride mixture between -5° and 0° (80%) [1034] [1804].

m.p. 99-100° [1034] [1804]; IR [1804].

1-(2-Hydroxy-5-nitro-4-propoxyphenyl)ethanone

[70668-14-3] $C_{11}H_{13}NO_5$ mol.wt. 239.23



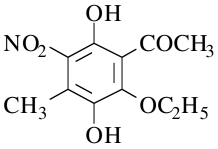
Synthesis

-Preparation by nitration of 2-hydroxy-4-propoxyacetophenone in acetic acid with concentrated nitric acid at 0° [1601].

m.p. 104° [1601].

1-(2-Ethoxy-3,6-dihydroxy-4-methyl-5-nitrophenyl)ethanone

[43140-85-8] $C_{11}H_{13}NO_6$ mol.wt. 255.23



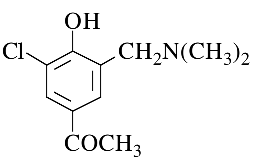
Synthesis

-Preparation by adding to a solution of 5-acetyl-2-methyl-3-nitro-1,4-benzoquinone in ethanol, a solution of pyrrolidine in ethanol. After stirring for 3 min, the solvent was eliminated, excess sulfurous acid was added, and the mixture was allowed to stand overnight (31%) [1741].

yellow viscous oil [1741]; ^{1}H NMR [1741], IR [1741].

1-[3-Chloro-4-hydroxy-5-[(dimethylamino)methyl]phenyl]ethanone

$C_{11}H_{14}ClNO_2$ mol.wt. 227.69



Synthesis

-Preparation by aminomethylation of 3-chloro-4-hydroxyacetophenone with dimethylamine and formalin in water at 35-40° for 4 h (60%) [1040].

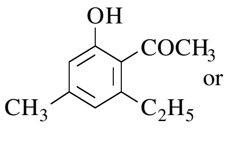
m.p. 112° [1040]; ^{1}H NMR [1040], IR [1040].

1-(2-Ethyl-6-hydroxy-4-methylphenyl)ethanone

or

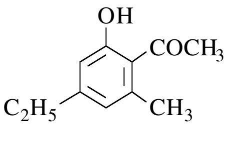
1-(4-Ethyl-2-hydroxy-6-methylphenyl)ethanone

$C_{11}H_{14}O_2$ mol.wt. 178.23



(**I**)

or



(**II**)

Syntheses

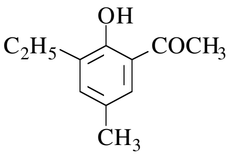
-Mixture obtained by Fries rearrangement of 3-ethyl-5-methylphenyl acetate with aluminium chloride,
*at 160-170° for 3 h. The two isomeric ketones were separated *via* their semicarbazide derivatives. However, the respective structures of the isolated ketones have not been attributed. The melting point of one of them (**I**) or (**II**) is 93° (6% yield) and the melting point of the other (**II**) or (**I**) is 18-19° (30% yield) [954];
*without solvent at 130° (80%) [1589];
*in nitrobenzene at 25° (85%) [1589].

N.B.: The 4-ethyl-2-hydroxy-6-methylacetophenone (**II**) is the most likely formula. However, one does not exclude to deal with a mixture (**I** + **II**), especially if working without solvent at 130° [1589].

b.p.$_{8}$ 170° [1589].

1-(3-Ethyl-2-hydroxy-5-methylphenyl)ethanone

[81591-15-3] $C_{11}H_{14}O_2$ mol.wt. 178.23



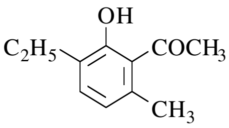
Syntheses

-Obtained by reaction of acetyl chloride on 2-ethyl-4-methylanisole with aluminium chloride in boiling carbon disulfide [101].
-Also obtained by Fries rearrangement of 2-ethyl-4-methylphenyl acetate [112] [1787], (40%) [1787] or 2-ethyl-5-methylphenyl acetate (41%) [112] with aluminium chloride at 130-140°.

b.p.$_{25}$ 144-146° [101], b.p.$_{30}$ 153° [112], b.p. 260° [1787].

1-(3-Ethyl-2-hydroxy-6-methylphenyl)ethanone

[81591-16-4] $C_{11}H_{14}O_2$ mol.wt. 178.23



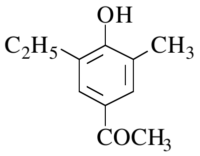
Syntheses

-Obtained (by-product) by reaction of acetyl chloride on 2-ethyl-5-methylanisole with aluminium chloride in carbon disulfide [102].
-Preparation by Fries rearrangement of 2-ethyl-5-methylphenyl acetate by heating with aluminium chloride (30%) [1787].

b.p.$_{12}$ 137-138° [102], b.p. 270° [1787].

1-(3-Ethyl-4-hydroxy-5-methylphenyl)ethanone

$C_{11}H_{14}O_2$ mol.wt. 178.23



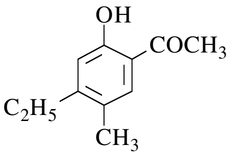
Syntheses

-Preparation by Fries rearrangement at high temperature of 2-ethyl-6-methylphenyl acetate with aluminium chloride (50%) [102].
-Also obtained (poor yield) by Fries rearrangement of 4-dodecyl-2-ethyl-6-methylphenyl acetate with aluminium chloride (13%) [100].

m.p. 101-102° [100], 95°5-96°5 [102]; b.p.$_{12}$ 180-200° [100].

1-(4-Ethyl-2-hydroxy-5-methylphenyl)ethanone

[93351-16-7] $C_{11}H_{14}O_2$ mol.wt. 178.23



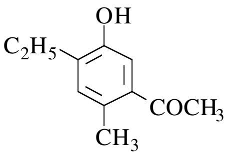
Syntheses

-Obtained by oxidation of 6-ethyl-2,3,5-trimethylbenzofuran with chromium trioxide in acetic acid at 50° for 30 min, followed by saponification of the resulting keto ester with potassium hydroxide in boiling aqueous ethanol for 2 h (65%) [1527].
-Also obtained by Friedel-Crafts acylation of 2,5-diethyl-4-methylanisole (SM) (1 mol) with acetyl chloride (1.5 mol) in the presence of aluminium chloride (1.5 mol) in boiling carbon disulfide. There is elimination of the ortho ethyl group in SM during the reaction [101].
-Also obtained by dehydrogenation of 6-acetyl-3-ethyl-4-methyl-2-cyclohexen-1-one,
*with a 5% palladium-barium sulfate catalyst at reflux [1059];
*with a refluxing solution of bromine (16%) in acetic acid [1059] [1060].
-Also refer to: [532].

yellow oil [101]; m.p. 52° [532] [1059] [1060] [1527];
b.p.$_{15}$ 144-147° [101], b.p.$_{18}$ 154-155° [1527]; IR [1527].

1-(4-Ethyl-5-hydroxy-2-methylphenyl)ethanone

$C_{11}H_{14}O_2$ mol.wt. 178.23



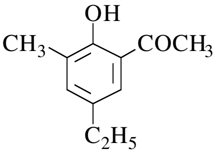
Syntheses

-Preparation by reaction of acetyl chloride on 2-ethyl-4-methylanisole with aluminium chloride in boiling carbon disulfide [101].
-Preparation by reaction of aluminium chloride on 4-ethyl-5-methoxy-2-methylacetophenone [101].

m.p. 120-121° [101].

1-(5-Ethyl-2-hydroxy-3-methylphenyl)ethanone

$C_{11}H_{14}O_2$ mol.wt. 178.23



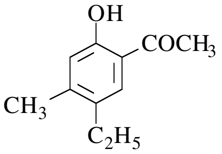
Syntheses

-Preparation by Fries rearrangement of 4-ethyl-2-methylphenyl acetate with aluminium chloride (77%) [102].
-Also obtained by heating the following phenyl esters with aluminium chloride at high temperature (in these reactions, there is elimination or migration of the bulky alkyl or arylalkyl group located in ortho position of the ester group),
*from 2-allyl-4-ethyl-6-methylphenyl acetate (74%) [100];
*from 2-benzyl-4-ethyl-6-methylphenyl acetate (54%) [100];
*from 2-ethyl-6-methylphenyl acetate (noticeable quantity) [102];
*from 4-ethyl-2-methyl-6-propylphenyl acetate (12%) [100].

b.p.$_{20}$ 120-136° [100], b.p.$_{11}$ 129-131° [102], b.p.$_{12}$ 130-132° [102], b.p.$_{18}$ 130-142° [100], b.p.$_{13}$ 142-150° [100].

1-(5-Ethyl-2-hydroxy-4-methylphenyl)ethanone

[27513-07-1] $C_{11}H_{14}O_2$ mol.wt. 178.23



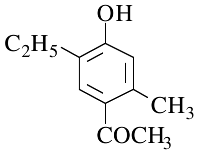
Syntheses

-Preparation by Fries rearrangement of 4-ethyl-3-methylphenyl acetate with aluminium chloride at 120° (quantitative yield) [1512], (70%) [102], (52%) [1518].
-Also obtained (by-product) by reaction of acetyl chloride on 2,4-diethyl-5-methylanisole with aluminium chloride in carbon disulfide [102].
-Preparation by chromic acid degradation of 5-ethyl-2,3,6-trimethylbenzofuran (60%) [1518].
-Preparation by dehydrogenation of 6-acetyl-4-ethyl-3-methyl-2-cyclohexen-1-one,
*with a 5% palladium-barium sulfate catalyst at reflux [313] [1059];
*with a refluxing solution of bromine (16%) in acetic acid [313] [1059].

m.p. 96°5-97° [1059], 96-97° [1512], 94-95° [102], 94° [1518], 92-94° [313];
b.p.$_{15}$ 142-143° [1512].

1-(5-Ethyl-4-hydroxy-2-methylphenyl)ethanone

$C_{11}H_{14}O_2$ mol.wt. 178.23



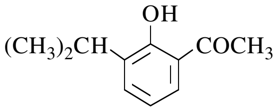
Synthesis

-Obtained (by-product) by Fries rearrangement of 2-ethyl-5-methylphenyl acetate with aluminium chloride at 130-140° [112].

m.p. 117-118° [112].

1-[2-Hydroxy-3-(1-methylethyl)phenyl]ethanone

[104175-18-0] $C_{11}H_{14}O_2$ mol.wt. 178.23



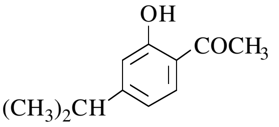
Synthesis

-Preparation by reaction of acetyl chloride with a suspension of aluminium tri-o-isopropylphenoxide in benzene in the presence of aluminium chloride, first at r.t. for 1 h, then on a water bath for 2 h (50%) [1018].

b.p.$_3$ 108-110° [1018].

1-[2-Hydroxy-4-(1-methylethyl)phenyl]ethanone

[91969-72-1] $C_{11}H_{14}O_2$ mol.wt. 178.23



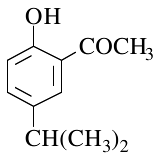
Synthesis

-Obtained by Fries rearrangement of 2-isopropylphenyl acetate with aluminium chloride without solvent at 140°, accompanied by an alkyl group migration (22%) [503].

b.p.$_{12}$ 129-130° [503].

1-[2-Hydroxy-5-(1-methylethyl)phenyl]ethanone

[1634-36-2] $C_{11}H_{14}O_2$ mol.wt. 178.23



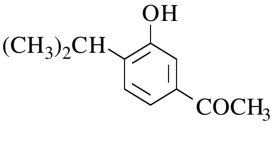
Syntheses

-Preparation by reaction of acetyl chloride on 4-isopropylanisole with aluminium chloride in carbon disulfide at r.t. (48%) [967].
-Also refer to: [1666].

b.p.$_{10}$ 130-132° [967].

1-[3-Hydroxy-4-(1-methylethyl)phenyl]ethanone

[1634-62-4] $C_{11}H_{14}O_2$ mol.wt. 178.23



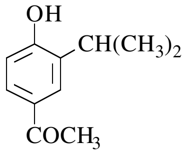
Synthesis

-Preparation by diazotization of 3-amino-4-isopropylacetophenone, followed by hydrolysis of the diazonium salt obtained (50%) [1069], (26%) [967].

m.p. 100-101° [967], 97-100° [1069].

1-[4-Hydroxy-3-(1-methylethyl)phenyl]ethanone

[1632-59-3] $C_{11}H_{14}O_2$ mol.wt. 178.23



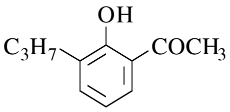
Syntheses

-Preparation by reaction of acetyl chloride on 2-isopropylphenol with aluminium chloride in boiling carbon disulfide (44%) [1069].
-Preparation by demethylation of 4-methoxy-3-isopropylacetophenone with boiling pyridinium chloride (30%) [967].
-Also obtained (poor yield) by Fries rearrangement of 2-isopropylphenyl acetate with aluminium chloride, without solvent at 104° (14%) [503] or in nitrobenzene at r.t. (13%) [967].

m.p. 143° [967], 140° [503], 139-140° [1069].

1-(2-Hydroxy-3-propylphenyl)ethanone

[93915-84-5] $C_{11}H_{14}O_2$ mol.wt. 178.23



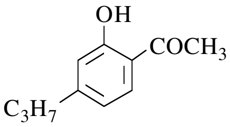
Syntheses

-Preparation by hydrogenation of 3-allyl-2-hydroxyacetophenone in the presence of 10% Pd/C and sodium hypophosphite,
*in dilute ethanol at 20° (92%) [1539];
*in aqueous sodium hydroxide at 50° (88%) [1539].
-Refer to: [851] [852] (Japanese patents).

^{1}H NMR [1539].

1-(2-Hydroxy-4-propylphenyl)ethanone

$C_{11}H_{14}O_2$ mol.wt. 178.23



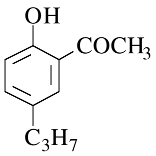
Synthesis

-Preparation by reaction of acetic acid with 3-propylphenol in the presence of zinc chloride for 5 h at 180° (reflux) (Nencki reaction) (40%) [434].

b.p.$_{0.7}$ 93° [434], b.p.$_{16}$ 128-131° [434].

1-(2-Hydroxy-5-propylphenyl)ethanone

[1990-24-5] $C_{11}H_{14}O_2$ mol.wt. 178.23



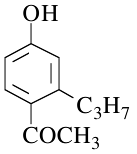
Syntheses

-Preparation by Fries rearrangement of 4-propylphenyl acetate with aluminium chloride [100] [1172] without solvent at 140° [1172].
-Preparation by reaction of acetyl chloride with 4-propylanisole in the presence of aluminium chloride in methylene chloride, first at 0°, then at reflux under nitrogen (86%) [1216].

yellow liquid [1216];
b.p.$_{0.25}$ 80-85° [1172], b.p.$_{1.2}$ 98-105° [1216], b.p.$_{20}$ 145-147° [100];
^{1}H NMR [1216]; n_D^{20} = 1.5365 [1172].

1-(4-Hydroxy-2-propylphenyl)ethanone

[104174-27-8] $C_{11}H_{14}O_2$ mol.wt. 178.23



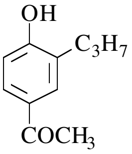
Syntheses

-Obtained by boiling 3-propylphenol with acetic anhydride in the presence of a little sulfuric acid [434].
-Also refer to: [126].

b.p.$_{18}$ 121-123° [434].

1-(4-Hydroxy-3-propylphenyl)ethanone

[61270-28-8] $C_{11}H_{14}O_2$ mol.wt. 178.23



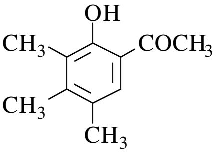
Syntheses

-Preparation by reaction of acetyl chloride on 2-propylphenol with aluminium chloride in nitrobenzene at r.t. [1513].
-Also obtained by catalytic hydrogenation of 3-allyl-4-hydroxyacetophenone in the presence of Pd/C in ethanol [71] [777] [1211], (90-100%) [71] [1211] or Raney nickel in ethyl acetate (80%) [1156].

m.p. 90-91° [71], 89-90° [1211], 87° [1513]; b.p.$_{25}$ 210° [1513];
MS [1156]; pK$_a$ [1156].

1-(2-Hydroxy-3,4,5-trimethylphenyl)ethanone

[58972-39-7] $C_{11}H_{14}O_2$ mol.wt. 178.23



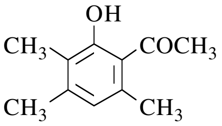
Syntheses

-Preparation by Fries rearrangement of 2,3,4-trimethylphenyl acetate with aluminium chloride at 130-140° (good yield) [112].
-Preparation by reaction of acetyl chloride on 2,3,4-trimethylphenol with aluminium chloride in carbon disulfide at r.t. (55%) [1808].
-Also obtained from various aryl esters by heating with aluminium chloride between 130 to 150°, the reaction being accompanied by a migration of methyl groups,
*2,3,5-trimethylphenyl acetate [112] [123], (86%) [112];
*2,4,5-trimethylphenyl acetate (major compound) [112];
*2,4,6-trimethylphenyl acetate [103] [112], (major compound) [112].
-Also obtained (poor yield) by heating a mixture of 2,4,6-trimethylphenyl acetate and 4-methylphenyl chloroacetate with aluminium chloride (10%) [103].
-Also obtained by isomerization of 2-hydroxy-3,4,6-trimethylacetophenone by heating with aluminium chloride [123].

m.p. 43-44° [112], 42° [103] [123]; b.p.$_{11}$ 142-144° [112], b.p. 275-276° [112];
^{1}H NMR [1808], IR [1808].

1-(2-Hydroxy-3,4,6-trimethylphenyl)ethanone

[163429-79-6] $C_{11}H_{14}O_2$ mol.wt. 178.23



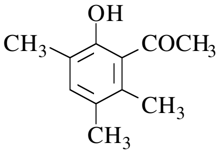
Syntheses

-Preparation by Fries rearrangement of 2,3,5-trimethylphenyl acetate (isopseudocumenol acetate) with aluminium chloride [123], at 100° for 1.5 h (85%) [204].
-Also refer to: [983].

m.p. 46° [123], 32-34° [204]; ^1H NMR [204], ^{13}C NMR [204], IR [204].

1-(2-Hydroxy-3,5,6-trimethylphenyl)ethanone

$C_{11}H_{14}O_2$ mol.wt. 178.23



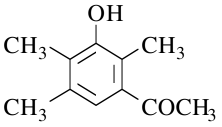
Synthesis

-Obtained (by-product) by Fries rearrangement of 2,4,5-trimethylphenyl acetate (pseudocumenol acetate) with aluminium chloride at 130-140° [112].

b.p.$_{11}$ 145-146° [112].

1-(3-Hydroxy-2,4,5-trimethylphenyl)ethanone

[99892-62-3] $C_{11}H_{14}O_2$ mol.wt. 178.23



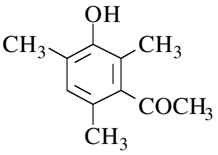
Synthesis

-Preparation by rearrangement of 1_α, 5_α, 6_α, 8_α-tetramethyl-2_α-*H*, 4_α-*H* -3,9-dioxatricyclo [3.3.1.0 ^{2,4}] nonan-7-one by treatment with sodium ethoxide in ethanol (81%) [615].

m.p. 115° [615]; ^1H NMR [615], IR [615], MS [615].

1-(3-Hydroxy-2,4,6-trimethylphenyl)ethanone

$C_{11}H_{14}O_2$ mol.wt. 178.23



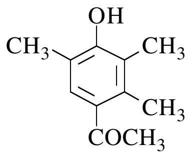
Synthesis

-Preparation by reaction of acetyl chloride on 2,4,6-trimethylanisole (mesitol methyl ether) with aluminium chloride in boiling carbon disulfide (20%) [101].

m.p. 81-82° [101].

1-(4-Hydroxy-2,3,5-trimethylphenyl)ethanone

[61405-64-9] $C_{11}H_{14}O_2$ mol.wt. 178.23



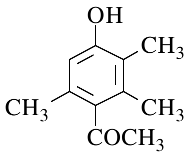
Syntheses

-Preparation by Fries rearrangement of 2,3,6-trimethylphenyl acetate with aluminium chloride at 165-170° for 15 min (94%) [1060].
-Also obtained by dehydrogenation of 4-acetyl-2,3,6-trimethyl-2-cyclohexen-1-one at reflux for 30 min in the presence of 5% palladium-barium sulfate [1059], (10%) [1060].

m.p. 132-133° [1059] [1060]; IR [1060], UV [1060].

1-(4-Hydroxy-2,3,6-trimethylphenyl)ethanone

[156483-08-8] $C_{11}H_{14}O_2$ mol.wt. 178.23

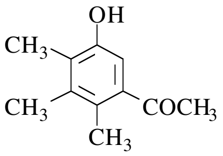


Synthesis

-Refer to: [1631].

1-(5-Hydroxy-2,3,4-trimethylphenyl)ethanone

[13667-28-2] $C_{11}H_{14}O_2$ mol.wt. 178.23



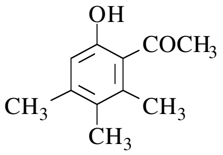
Syntheses

-Preparation from 2,3,4-trimethyl-5-nitroacetophenone *via* reduction with stannous chloride and following diazotization of the resulting 5-amino-2,3,4-trimethylacetophenone (68%) [1805], (53%) [1034].
-Also obtained by rearrangement of 3-acetyl-4,4,5-trimethyl-2,5-cyclohexadiene-1-one in 68% sulfuric acid at 40° (29%) [691].

m.p. 168° [1034] [1805]; ^{1}H NMR [691], IR [691] [1805], MS [691].

1-(6-Hydroxy-2,3,4-trimethylphenyl)ethanone

[27192-99-0] $C_{11}H_{14}O_2$ mol.wt. 178.23



Syntheses

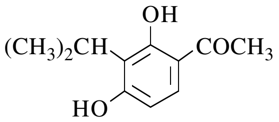
-Preparation by Fries rearrangement of 3,4,5-trimethylphenyl acetate with aluminium chloride without solvent at 130° [112] [733], (50%) [733].
-Preparation by reaction of acetyl chloride on 3,4,5-trimethylanisole with aluminium chloride in boiling carbon disulfide (45%) [114].

-Also obtained *via* pyrolysis of 1,3,7,8-tetramethyl-2-oxabicyclo[4.2.0]octa-3,7-dien-5-one (2,6-dimethyl-4-pyrone - Butyne-2 - Adduct) in refluxing o-dichlorobenzene [733].

m.p. 83°5-84°5 [114], 83-84° [112], 58-60° [733]; b.p.$_{13}$ 163-166° [112];
^{1}H NMR [733], IR [733], UV [733], MS [733].

1-[2,4-Dihydroxy-3-(1-methylethyl)phenyl]ethanone

[118604-45-8]	$C_{11}H_{14}O_3$	mol.wt. 194.23

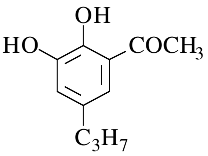


Synthesis

-Preparation by total demethylation of 2,4-dimethoxy-3-isopropylacetophenone with 48% hydrobromic acid in refluxing acetic acid [1157].

1-(2,3-Dihydroxy-5-propylphenyl)ethanone

[86253-71-6]	$C_{11}H_{14}O_3$	mol.wt. 194.23



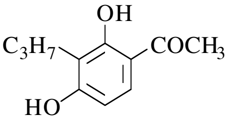
Synthesis

-Preparation by reaction of acetic acid with 2-methoxy-4-propylphenol in the presence of boron trifluoride at 150-155° (81%) [1216].

oil [1216].

1-(2,4-Dihydroxy-3-propylphenyl)ethanone

[40786-69-4]	$C_{11}H_{14}O_3$	mol.wt. 194.23



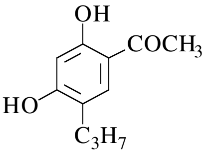
Syntheses

-Preparation by reaction of acetonitrile on 2-propylresorcinol (Hoesch reaction) (86%) [132].
-Preparation by catalytic hydrogenation of 3-allyl-2,4-dihydroxyacetophenone using palladium chloride as catalyst in ethanol (quantitative yield) [132] or Raney nickel in ethyl acetate [777].
-Preparation by total demethylation of 2,4-dimethoxy-3-propylacetophenone with 48% hydrobromic acid in refluxing acetic acid for 19 h (73%) [1157].
-Also refer to: [43] [44] [1372].
N.B.: Pr indicates the *propyl* group -C_3H_7 in Chem. Abstr., **92**, 6368x (1980) and **98**, 54239b (1983), an usual abbreviation. However, in the two references [43] [44], Pr represented the *prenyl* group -$CH_2CH=C(CH_3)_2$. Therefore they concern the 2,4-dihydroxy-3-prenylacetophenone and not the above mentioned 2,4-dihydroxy-3-propylacetophenone.

m.p. 127-128° [132].

1-(2,4-Dihydroxy-5-propylphenyl)ethanone

[63411-87-0] $C_{11}H_{14}O_3$ mol.wt. 194.23



Syntheses

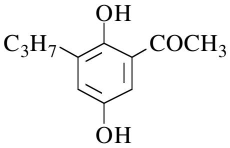
-Preparation by reaction of acetic acid on 4-propylresorcinol with zinc chloride (Nencki reaction) [506] [930].
-Preparation by reaction of acetonitrile on 4-propylresorcinol (Hoesch reaction) (75%) [1277].
-Preparation by Fries rearrangement of 4-propylresorcinol diacetate in the presence of 4-propylresorcinol with aluminium chloride in nitrobenzene at 50° (quantitative yield) [1514].
-Also refer to: [43] [44].

N.B.: Pr indicates the *propyl* group -C_3H_7 in Chem. Abstr., **92**, 6368x (1980) and **98**, 54239b (1983), an usual abbreviation. However, in the two references [43] [44], Pr represented the *prenyl* group -$CH_2CH=C(CH_3)_2$. Therefore they concern the 2,4-dihydroxy-5-prenylacetophenone and not the above mentioned 2,4-dihydroxy-5-propylacetophenone.

m.p. 110-111° [506], 108-109° [1514], 108° [1277].

1-(2,5-Dihydroxy-3-propylphenyl)ethanone

[83812-26-4] $C_{11}H_{14}O_3$ mol.wt. 194.23

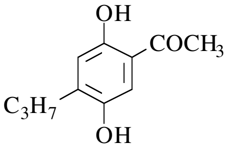


Synthesis

-Refer to: [742] [1680] (patents).

1-(2,5-Dihydroxy-4-propylphenyl)ethanone

$C_{11}H_{14}O_3$ mol.wt. 194.23



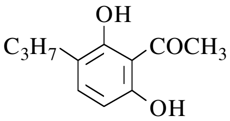
Synthesis

-Obtained (by-product) by reaction of acetyl chloride on 2-propylhydroquinone dimethyl ether with aluminium chloride in boiling carbon disulfide (3%) [457].

m.p. 85° [457].

1-(2,6-Dihydroxy-3-propylphenyl)ethanone

[53542-79-3] $C_{11}H_{14}O_3$ mol.wt. 194.23



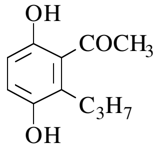
Syntheses

-Preparation from 2,6-dihydroxyacetophenone according to the method [1532], (64%) [237].
-Also refer to: [92] [93] [94] [95] [191] [1067].

m.p. 84-85° [237].

1-(3,6-Dihydroxy-2-propylphenyl)ethanone

[106627-41-2] $C_{11}H_{14}O_3$ mol.wt. 194.23



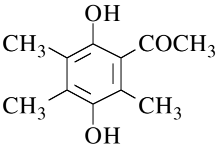
Synthesis

-Preparation by catalytic hydrogenation of 2-allyl-3,6-dihydroxyacetophenone using palladised strontium carbonate catalyst [457] or Raney nickel (60%) [1156] in ethyl acetate.

m.p. 88° [457] (monohydrate); MS [1156].

1-(2,5-Dihydroxy-3,4,6-trimethylphenyl)ethanone

[64794-45-2] $C_{11}H_{14}O_3$ mol.wt. 194.23



Syntheses

-Obtained by oxidation of 2,4,5,7,8-pentamethyl-4*H*-1,3-benzodioxin-6-ol (PBD)* in aqueous media *via* 2-(1-hydroxyethyl)-3,5,6-trimethylbenzo-1,4-quinone, without or with aldehyde trapping (method A or B, respectively) [1507].

oxidant	method	yield (%)
$FeCl_3.6\ H_2O$	A (B)	38 (85)
$K_2Cr_2O_7$	A (B)	38 (86)
$AgNO_3$	A (B)	44 (83)
H_2O_2	A (B)	44 (82)
$KMnO_4$	A (B)	32 (68)
NMMO**	- (B)	- (81)

N.B.:

-PBD* is a novel 3-oxa-tocopherol-type stabilizer which is obtained as a mixture of two diastereoisomers by condensation of trimethylhydroquinone with acetaldehyde.
-NMMO** = N-methylmorpholine-N-oxide.

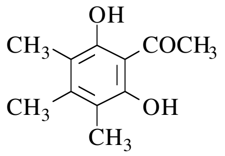
-Preparation by Fries rearrangement of 2,3,5-trimethylhydroquinone diacetate,
*with aluminium chloride at 220° (51%) [1880];
*with boron trifluoride-acetic acid complex, followed by saponification of the 3-acetoxy-6-hydroxy-2,4,5-trimethylacetophenone obtained [422] [424] [1144], (71%) [424], (65%) [1144].
-Also obtained by hydrolysis of 3-(acetyloxy)-6-hydroxy-2,4,5-trimethylacetophenone with 5% methanolic hydrogen chloride (50%) [1872].

-Also refer to: [1928].

m.p. 152° [1880], 111° [1144], 110-113° [1507], 107-109° [1872], 107-108°5 [424];
^1H NMR [424] [1507] [1872], ^{13}C NMR [1507] [1872], IR [424] [1507],
UV [424] [1880], MS [424].

1-(2,6-Dihydroxy-3,4,5-trimethylphenyl)ethanone

[66842-24-8] $C_{11}H_{14}O_3$ mol.wt. 194.23



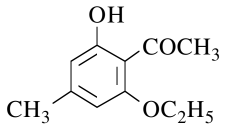
Syntheses

-Obtained by Fries rearrangement of trimethylhydroquinone diacetate with aluminium chloride at 220°, *via* a secondary rearrangement of the normal product (I) (50%) [424].
-Also obtained by reaction of aluminium chloride on 5-acetoxy-2-hydroxy-3,4,6-trimethylacetophenone at 220° (53-55%) [424].
-Also obtained by rearrangement of 2,5-dihydroxy-3,4,6-trimethylacetophenone (I) with aluminium chloride at 220° (29-34%) [424].

m.p. 136-145° [424]; ^{1}H NMR [424], IR [424], UV [424], MS [424].

1-(2-Ethoxy-6-hydroxy-4-methylphenyl)ethanone

[78274-02-9] $C_{11}H_{14}O_3$ mol.wt. 194.23



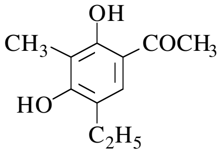
Syntheses

-Obtained by reaction of sodium ethoxide with 3,5-diacetyl-2,6-dimethyl-*4H*-pyran-4-one in ethanol at r.t. (20%) [563].
-Also obtained by heating 3-acetyl-2,6-dimethyl-*4H*-pyran-4-one with sodium ethoxide in ethanol (17%) [564].

m.p. 95° [563] [564] [1784]; ^{1}H NMR [563], IR [563], MS [563] [564].

1-(5-Ethyl-2,4-dihydroxy-3-methylphenyl)ethanone

[140660-34-0] $C_{11}H_{14}O_3$ mol.wt. 194.23



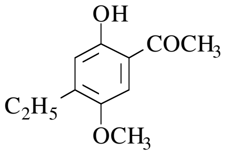
Synthesis

-Preparation by reaction of acetic acid on 4-ethyl-1,3-dihydroxy-2-methylbenzene with zinc chloride at 95-100° (Nencki reaction) (24%) [777].

crystalline product [777].

1-(4-Ethyl-2-hydroxy-5-methoxyphenyl)ethanone

$C_{11}H_{14}O_3$ mol.wt. 194.23



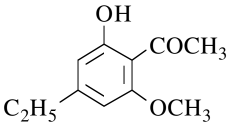
Syntheses

-Preparation from 2-ethylhydroquinone dimethyl ether,
*by reaction with acetic acid in the presence of boron trifluoride (55%) [1459];
*by reaction with acetyl chloride in the presence of aluminium chloride in boiling ethyl ether (27%) [1461].
-Preparation by partial methylation of 4-ethyl-2,5-hydroxyacetophenone with dimethyl sulfate in the presence of potassium carbonate in boiling acetone (47%) [1461].
-Also obtained (poor yield) by partial demethylation of 4-ethyl-2,5-dimethoxyacetophenone with 6% aqueous hydrobromic acid in acetic acid at r.t. (9%) [1459].

m.p. 60°4-61° [1459], 60° [1461]; UV [1459].

1-(4-Ethyl-2-hydroxy-6-methoxyphenyl)ethanone

[128546-82-7] $C_{11}H_{14}O_3$ mol.wt. 194.23



Syntheses

-Refer to: [1254] [1255] [1256] [1763] [1765] [1766] (Japanese papers) and [1253].

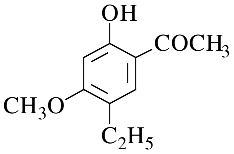
Isolation from natural sources

-From *Juniperus semiglobosa* Regel (Cupressaceae) [11].

m.p. 85° [11]; ^{1}H NMR [11], IR [11], UV [11], MS [11].

1-(5-Ethyl-2-hydroxy-4-methoxyphenyl)ethanone

[4223-85-2] $C_{11}H_{14}O_3$ mol.wt. 194.23



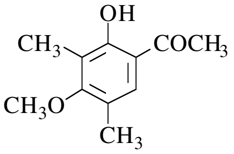
Syntheses

-Preparation by reaction of dimethyl sulfate [930] or methyl iodide [313] on 5-ethyl-2,4-dihydroxyacetophenone with potassium carbonate in refluxing acetone.
-Preparation by chromic acid degradation of 5-ethyl-6-methoxy-2,3-dimethylbenzofuran (21%) [1521].

m.p. 49-50° [313], 48° [1521]; b.p.$_{20}$ 165-167° [1521].

1-(2-Hydroxy-4-methoxy-3,5-dimethylphenyl)ethanone

$C_{11}H_{14}O_3$ mol.wt. 194.23



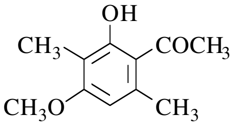
Synthesis

-Preparation by treating 2,4-dihydroxy-3,5-dimethylacetophenone with diazomethane or with dimethyl sulfate and sodium hydroxide [755].

m.p. 35-36° [755]; b.p.$_{0.6}$ 90° [755].

1-(2-Hydroxy-4-methoxy-3,6-dimethylphenyl)ethanone

$C_{11}H_{14}O_3$ mol.wt. 194.23



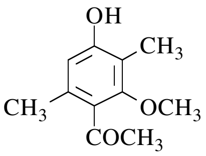
Synthesis

-Obtained by reaction of methyl iodide with 2,4-dihydroxy-6-methylacetophenone in the presence of potassium hydroxide (15%) [448].

m.p. 90-91° [448].

1-(4-Hydroxy-2-methoxy-3,6-dimethylphenyl)ethanone

[97761-88-1] $C_{11}H_{14}O_3$ mol.wt. 194.23

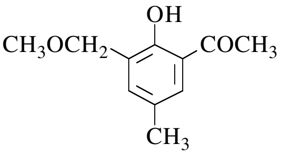


Synthesis

N.B.: Mentioned in the Chem. Abstr. **103**, 85031d (1985). However, this compound does not appear in the original paper [1563] which concerns only some ketones derived of phloroglucinol.

1-[2-Hydroxy-3-(methoxymethyl)-5-methylphenyl]ethanone

[87165-63-7] $C_{11}H_{14}O_3$ mol.wt. 194.23



Syntheses

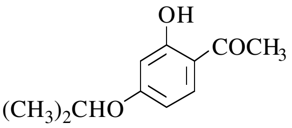
-Preparation from 3-chloromethyl-2-hydroxy-5-methylacetophenone (b.p.$_{0.4}$ 110-116°) [289] by reaction with methanol in the presence of concentrated hydrochloric acid and iron powder at reflux for 3.5 to 4.5 h (82%) [30], (49%) [289].

-Also refer to: [31].

m.p. 36-38° [30]; b.p.$_{0.6}$ 95-103° [289], b.p.$_{20}$ 160-165° [30]; ^{1}H NMR [30] [289], ^{13}C NMR [30], IR [30] [289].

1-[2-Hydroxy-4-(1-methylethoxy)phenyl]ethanone

[73473-62-8] $C_{11}H_{14}O_3$ mol.wt. 194.23

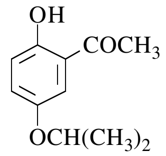


Synthesis

-Refer to: [409] (Chinese reference) and [1770] (Japanese patent).

1-[2-Hydroxy-5-(1-methylethoxy)phenyl]ethanone

[152810-05-4] $C_{11}H_{14}O_3$ mol.wt. 194.23



Syntheses

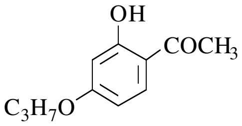
-Preparation by reaction of 2-bromopropane with quinacetophenone in the presence of sodium iodide and potassium carbonate in DMF at 60° for 24 h (51%) [856].

-Also refer to: [855] [1666].

oil [856]; ^{1}H NMR [856].

1-(2-Hydroxy-4-propoxyphenyl)ethanone

[55329-63-0] $C_{11}H_{14}O_3$ mol.wt. 194.23



Syntheses

-Preparation by reaction of propyl iodide [313] [364] [578] or propyl bromide [578] on resacetophenone,
*with potassium hydroxide in boiling ethanol [364] [578];
*with potassium carbonate in boiling acetone [313].

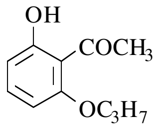
-Also refer to: [43] [44].

N.B.: Pr indicates the *propyl* group -C_3H_7 in Chem. Abstr., **92**, 6368x (1980) and **98**, 54239b (1983), an usual abbreviation. However, in the two references [43] [44], Pr represented the *prenyl* group -$CH_2CH=C(CH_3)_2$. Therefore they concern the 2-hydroxy-4-prenyloxyacetophenone and not the above mentioned 2-hydroxy-4-propyloxyacetophenone.

m.p. 25° [578]; b.p.$_{3-4}$ 136° [364].

1-(2-Hydroxy-6-propoxyphenyl)ethanone

[14718-38-8] $C_{11}H_{14}O_3$ mol.wt. 194.23



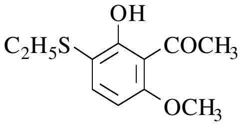
Synthesis

-Preparation by reaction of propyl iodide on 2,6-dihydroxyacetophenone with potassium carbonate in refluxing acetone (66%) [1567].

m.p. 70-71° [1567].

1-[3-(Ethylthio)-2-hydroxy-6-methoxyphenyl]ethanone

[126405-82-1] $C_{11}H_{14}O_3S$ mol.wt. 226.30



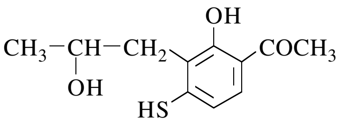
Synthesis

-Preparation by adding 2-hydroxy-3-iodo-6-methoxyacetophenone and cuprous oxide to a solution of sodium ethyl sulfhydrate, previously prepared from ethanethiol and sodium hydride in DMF [1873].

m.p. 57° [1873]; ^{1}H NMR [1873], IR [1873].

1-[2-Hydroxy-3-(2-hydroxypropyl)-4-mercaptophenyl]ethanone

[167211-59-8] $C_{11}H_{14}O_3S$ mol.wt. 226.30

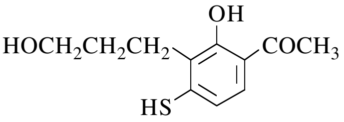


Synthesis

-Preparation in six steps from 3-allyl-2,4-dihydroxyacetophenone [1367] (Japanese patent).

1-[2-Hydroxy-3-(3-hydroxypropyl)-4-mercaptophenyl]ethanone

[167211-71-4] $C_{11}H_{14}O_3S$ mol.wt. 226.30

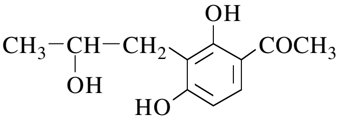


Synthesis

-Refer to: [1367] (Japanese patent).

1-[2,4-Dihydroxy-3-(2-hydroxypropyl)phenyl]ethanone

[167211-56-5] $C_{11}H_{14}O_4$ mol.wt. 210.23

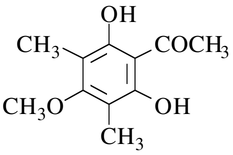


Synthesis

-Refer to: [1367] (Japanese patent).

1-(2,6-Dihydroxy-4-methoxy-3,5-dimethylphenyl)ethanone *(Mallophenone)*

[129399-54-8] $C_{11}H_{14}O_4$ mol.wt. 210.23



Syntheses

-Obtained by degradation of 5-hydroxy-7-methoxy-6,8-dimethylchromone (Leptorumol monomethyl ether) with 2 N potassium hydroxide (30%) [645].
-Also refer to: [1322] [1323].

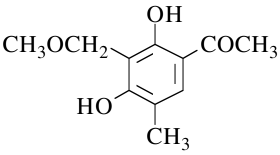
Isolation from natural sources

-From the pericarps of *Mallotus japonicus* Muell. Arg. (Euphorbiaceae) [77].

m.p. 132° [645], 131-132° [77];
^{1}H NMR [77] [645], ^{13}C NMR [77], IR [77] [645], UV [77] [645] [1322], MS [77].

1-[2,4-Dihydroxy-3-(methoxymethyl)-5-methylphenyl]ethanone

[333763-54-5] $C_{11}H_{14}O_4$ mol.wt. 210.23

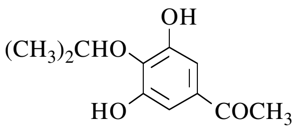


Isolation from natural sources

-From the culture filtrate of chilean strain of *Trichoderma pseudokoningii* [90].

1-[3,5-Dihydroxy-4-(1-methylethoxy)phenyl]ethanone

[192625-58-4] $C_{11}H_{14}O_4$ mol.wt. 210.23



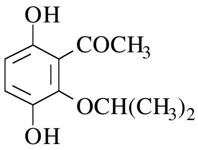
Synthesis

-Preparation by total demethylation of 3',5'-dimethoxy-4'-isopropoxyacetophenone in two steps *via* formation of dimethyl acetal (80%) [1076].

^{1}H NMR [1076], MS [1076]; TLC [1076].

1-[3,6-Dihydroxy-2-(1-methylethoxy)phenyl]ethanone

[33539-22-9] $C_{11}H_{14}O_4$ mol.wt. 210.23



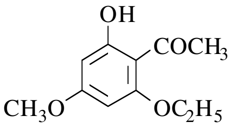
Syntheses

-Easy preparation by reduction of 2-acetyl-3-isopropoxy-1,4-benzoquinone using conventional methods [587].
-Also obtained (low yield) by reaction of 2-acetyl-1,4-benzoquinone with an excess of isopropanol at r.t., with exclusion of light [587].

m.p. 90-92° [587]; ^{1}H NMR [587], IR [587].

1-(2-Ethoxy-6-hydroxy-4-methoxyphenyl)ethanone

[76554-79-5] $C_{11}H_{14}O_4$ mol.wt. 210.23



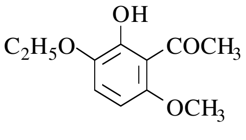
Syntheses

-Preparation by reaction of dimethyl sulfate on 6-ethoxy-2,4-dihydroxyacetophenone with potassium carbonate in boiling acetone (81%) [73].
-Preparation by reaction of diethyl sulfate on 2,6-dihydroxy-4-methoxyacetophenone with potassium carbonate in boiling acetone [73].
-Preparation by reaction of diazoethane on 2,6-dihydroxy-4-methoxyacetophenone [1675].

m.p. 134° [73], 133-134° [1675].

1-(3-Ethoxy-2-hydroxy-6-methoxyphenyl)ethanone

[126405-76-3] $C_{11}H_{14}O_4$ mol.wt. 210.23



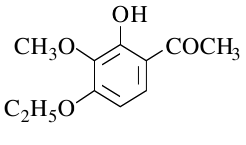
Synthesis

-Preparation by adding 2-hydroxy-3-iodo-6-methoxyacetophenone and cuprous iodide to a solution of sodium ethoxide, previously prepared from ethyl alcohol and sodium hydride in DMF [1873].

m.p. 70° [1873]; ^{1}H NMR [1873], IR [1873].

1-(4-Ethoxy-2-hydroxy-3-methoxyphenyl)ethanone

[69616-59-7] $C_{11}H_{14}O_4$ mol.wt. 210.23



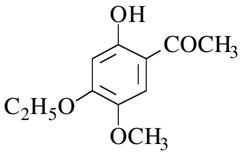
Synthesis

-Preparation by reaction of ethyl iodide with 2,4-dihydroxy-3-methoxyacetophenone in the presence of potassium carbonate in refluxing acetone (64%) [1360].

m.p. 76-77° [1360]; ^{1}H NMR [1360], IR [1360].

1-(4-Ethoxy-2-hydroxy-5-methoxyphenyl)ethanone

[75672-62-7] $C_{11}H_{14}O_4$ mol.wt. 210.23



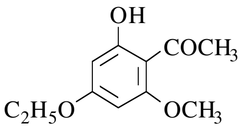
Synthesis

-Preparation by reaction of dimethyl sulfate with 4-ethoxy-2,5-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone (82%) [212].

m.p. 94-95° [212].

1-(4-Ethoxy-2-hydroxy-6-methoxyphenyl)ethanone

[76554-80-8] $C_{11}H_{14}O_4$ mol.wt. 210.23



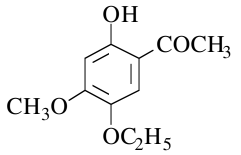
Syntheses

-Preparation by reaction of diazoethane on 2,4-dihydroxy-6-methoxyacetophenone [1675].
-Also refer to: [639].

m.p. 56-57° [1675].

1-(5-Ethoxy-2-hydroxy-4-methoxyphenyl)ethanone

[75672-59-2] $C_{11}H_{14}O_4$ mol.wt. 210.23



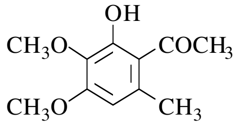
Synthesis

-Preparation by reaction of diethyl sulfate with 2,5-dihydroxy-4-methoxyacetophenone in the presence of potassium carbonate in refluxing acetone (71%) [212].

m.p. 101-102° [212].

1-(2-Hydroxy-3,4-dimethoxy-6-methylphenyl)ethanone

[63542-37-0] $C_{11}H_{14}O_4$ mol.wt. 210.23



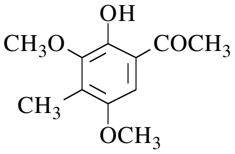
Syntheses

-Preparation by reaction of acetyl chloride on 3,4,5-trimethoxytoluene with aluminium chloride,
*in ethyl ether at r.t. [133] [1449], (50%) [133];
*in refluxing methylene chloride (67%) [1782].

m.p. 94° [1449], 92° [133], 77-78° [1782];
^{1}H NMR [1782], ^{13}C NMR [1782], IR [1782], MS [1782].

1-(2-Hydroxy-3,5-dimethoxy-4-methylphenyl)ethanone

[134255-78-0] $C_{11}H_{14}O_4$ mol.wt. 210.23



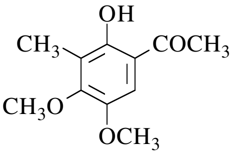
Synthesis

-Obtained by Fries rearrangement of 3-acetoxy-2,6-dimethoxytoluene (oil) with boron trifluoride etherate at 95° for 3 h (63%) [274].

m.p. 73°5-75° [274]; TLC [274];
^{1}H NMR [274], IR [274], MS [274].

1-(2-Hydroxy-4,5-dimethoxy-3-methylphenyl)ethanone

[134255-79-1] $C_{11}H_{14}O_4$ mol.wt. 210.23



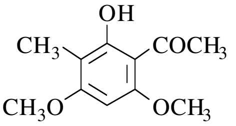
Synthesis

-Obtained by selective demethylation of 3-methyl-2,4,5-trimethoxyacetophenone (pale yellow oil) with boron trichloride in methylene chloride at 0° for 80 min (85%) [274].

m.p. 86-87° [274]; ^{1}H NMR [274], MS [274].

1-(2-Hydroxy-4,6-dimethoxy-3-methylphenyl)ethanone

[23121-32-6] $C_{11}H_{14}O_4$ mol.wt. 210.23



Syntheses

-Preparation by reaction of acetonitrile on 3,5-dimethoxy-2-methylphenol (Hoesch reaction) (68%) [469].
-Preparation by reaction of methyl iodide, in the presence of potassium carbonate in boiling acetone,
*on 2,4-dihydroxy-6-methoxy-3-methylacetophenone [1500];
*on 2,6-dihydroxy-4-methoxy-3-methylacetophenone [470];
*on phloroacetophenone [145] [469] [706] [736] [1297] [1434] [1564] [1735], (37-42%) [706] [1735], (21-28%) [469] [1297] [1564].
-Also obtained (by-product) by reaction of methyl iodide with phloroacetophenone in 10% methanolic potassium hydroxide (< 3%) [875].
-Preparation by partial methylation of 2,4,6-trihydroxy-3-methylacetophenone,
*with diazomethane in ethyl ether-methanol mixture at 0° (good yield) [1564];
*with dimethyl sulfate in the presence of potassium carbonate in boiling acetone [883] [1297], (71%) [1297];
*with methyl iodide, in the presence of potassium carbonate in boiling acetone [469] [1297] [1490].
-Preparation by partial demethylation of 2,4,6-trimethoxy-3-methylacetophenone with aluminium chloride in acetonitrile at 30° for 6 h (90%) [962].
-Preparation by reaction of acetyl chloride,
*with 2,4,6-trimethoxytoluene in the presence of aluminium chloride in ethyl ether at r.t. (51%) [962];
*with 2-hydroxy-4,6-dimethoxytoluene in the presence of aluminium chloride in nitrobenzene at r.t. [1184] according to [1299].

-Preparation by reaction of acetic anhydride and acetic acid,
*on 3,5-dimethoxy-2-methylphenol with boron trifluoride at 20-30° (60%) [494];
*on 2,4,6-trimethoxytoluene with boron trifluoride at 20-30° or at 100° [494].
-Also obtained on deacylation of 2,4-diacetyl-3,5-dimethoxy-6-methylphenol acetate with 10% hydrochloric acid in ethanol [494].

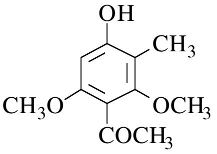
Isolation from natural sources

-From the leaves and bark of *Acradenia franklinii* (Kippist) (Rutaceae) [145].
-From the stem wood of *Euphorbia quinquecostata* Volk. (Euphorbiaceae) [1209].
-From *Euphorbia portulacoides* (Euphorbiaceae) [1261].

m.p. 145° [494], 144-145° [1564], 144° [1297], 143-144° [469], 143° [145], 142-143° [1735], 142° [1490], 141°5-143° [962], 141-143° [706], 141-142° [383] [470] [1500], 140-141° [875], 130-131° [1209];
^{1}H NMR [883] [1209] [1261], ^{13}C NMR [736] [1209], IR [145] [1209], UV [145] [1209], MS [1209].

1-(4-Hydroxy-2,6-dimethoxy-3-methylphenyl)ethanone

$C_{11}H_{14}O_4$ mol.wt. 210.23



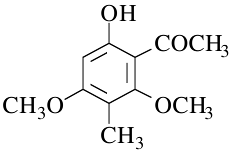
Synthesis

-Preparation by catalytic hydrogenolysis of 4-(benzyloxy)-2,6-dimethoxy-3-methylacetophenone with Pd/C in acetic acid (quantitative yield) [1883].

m.p. 121° [1883].

1-(6-Hydroxy-2,4-dimethoxy-3-methylphenyl)ethanone *(Bancroftinone)*

[14964-98-8] $C_{11}H_{14}O_4$ mol.wt. 210.23



Syntheses

-Preparation by hydrolysis of 6-(benzoyloxy)-2,4-dimethoxy-3-methylacetophenone with 3 N aqueous-methanolic potassium hydroxide at r.t. (75%) [1883].
-Preparation by Fries rearrangement of 3,5-dimethoxy-4-methylphenyl acetate with aluminium chloride in nitrobenzene (75-77%) [224] [1106].
-Preparation by reaction of methyl iodide with 4,6-dihydroxy-2-methoxy-3-methylacetophenone in the presence of potassium carbonate in refluxing acetone (93%) [1186].
-Preparation by reaction of acetyl chloride on 3,5-dimethoxy-4-methylphenol with aluminium chloride in ethyl ether first at 0°, then at r.t. [75] [883] [1454], (40%) [883].

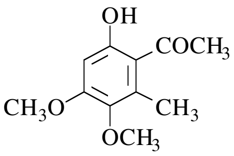
Isolation from natural sources

-From the leaf oils of *Backhousia bancroftii* F. M. Bailey & Muell. (Myrtaceae) as a major constituent [294].
-The ketone was present to the extent of 35% in clove oil [837].
-Swertisin was isolated from the whole herb of *Swertia japonica* Makino (Gentianaceae). Further, hydrolytic decomposition of its dimethyl ether with aqueous barium hydroxide gave a degradation product, the 3-C-β-D-glucopyranosyl-6-hydroxy-2,4-dimethoxyacetophenone. This one, by treatment with an excess of aqueous periodic acid followed by Clemmensen reduction gave 6-hydroxy-2,4-dimethoxy-3-methylacetophenone [1147].

m.p. 44-45° [837], 38-39° [1106], 35° [1883];
oil [1186]; b.p.$_{0.2}$ 110-112° [224], b.p.$_2$ 120-122° [883], b.p.$_1$ 128-131° [1106];
GC [294], GC/MS [294];
^{1}H NMR [75] [294] [837], ^{13}C NMR [294], IR [837], UV [837], MS [294] [837].

1-(6-Hydroxy-3,4-dimethoxy-2-methylphenyl)ethanone

[62615-64-9] $C_{11}H_{14}O_4$ mol.wt. 210.23



Syntheses

-Obtained by partial methylation of 2,5-dihydroxy-4-methoxy-6-methylacetophenone with dimethyl sulfate in acetone, in the presence of potassium carbonate (20%) [16].
-Preparation by partial demethylation of 2,4,5-trimethoxy-6-methylacetophenone with boron trichloride in methylene chloride at 0° (85%) [1449].

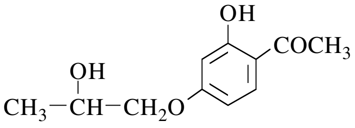
Isolation from natural sources

-By hydrolysis of 4,6,7-trimethoxy-5-methylcoumarin, isolated from *Leonotis nepetaefolia* [1449].

m.p. 77° [1449], 76-77° [16]; ^{1}H NMR [1449], IR [1449], UV [1449].

1-[2-Hydroxy-4-(2-hydroxypropoxy)phenyl]ethanone

[149454-57-9] $C_{11}H_{14}O_4$ mol.wt. 210.23



Synthesis

-Obtained by reaction of resacetophenone with propylene oxide in the presence of sodium hydroxide in ethanol [185].

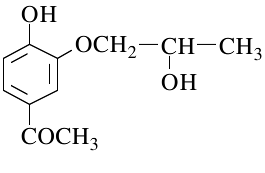
Isolation from natural sources

-From the aerial parts of *Urolepis hecatantha*, flowers and leaves of *Chromolaena arnottiana* (compound 11) [493].

^{1}H NMR [493], MS [493].

1-[4-Hydroxy-3-(2-hydroxypropoxy)phenyl]ethanone

[63437-94-5] $C_{11}H_{14}O_4$ mol.wt. 210.23



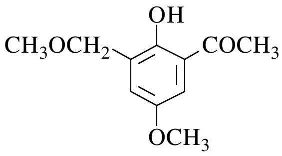
Synthesis

-Preparation by hydrogenolysis of 4-(benzyloxy)-3-(2-hydroxypropoxy)acetophenone in ethanol under hydrogen atmosphere in the presence of 5% Pd/C for 45 min (81%) [486].

m.p. 143° [486].

1-[2-Hydroxy-5-methoxy-3-(methoxymethyl)phenyl]ethanone

[87165-71-7] $C_{11}H_{14}O_4$ mol.wt. 210.23



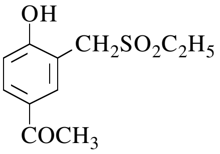
Synthesis

-Preparation from 3-chloromethyl-2-hydroxy-5-methoxyacetophenone (m.p. 71°) by reaction with methanol in the presence of concentrated hydrochloric acid and iron powder at reflux for 3.5 to 4 h (69%) [289].

b.p.$_{0.3}$ 110-114° [289]; ^{1}H NMR [289], IR [289].

1-[3-[(Ethylsulfonyl)methyl]-4-hydroxyphenyl]ethanone

[56490-62-1] $C_{11}H_{14}O_4S$ mol.wt. 242.30



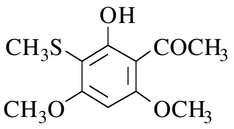
Synthesis

-Obtained by reaction of 3'-chloromethyl-4'-hydroxyacetophenone with magnesium ethylsulfinate in refluxing aqueous methanol for 18 h (30%) [935].

m.p. 137-141° [935].

1-[2-Hydroxy-4,6-dimethoxy-3-(methylthio)phenyl]ethanone

[154389-63-6] $C_{11}H_{14}O_4S$ mol.wt. 242.30



Syntheses

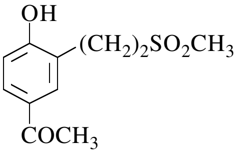
-Preparation by partial demethylation of 2,4,6-trimethoxy-3-methylthioacetophenone with aluminium chloride in acetonitrile for 1 h at 30° (95%) [962].

-Also obtained by reaction of acetyl chloride with 2,4,6-trimethoxy-1-(methylthio)benzene in the presence of aluminium chloride in ethyl ether at 0° (24%) [962].

m.p. 143-145° [962].

1-[4-Hydroxy-3-[2-(methylsulfonyl)ethyl]phenyl]ethanone

[56490-44-9] $C_{11}H_{14}O_4S$ mol.wt. 242.30



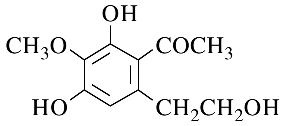
Synthesis

-Obtained by Fries rearrangement of 2-(methylsulfonylethyl)phenyl acetate (m.p. 80-82°) with aluminium chloride in nitrobenzene, first at r.t. for 1 h, then at 50-60° for 1.5 h (53%) [935].

m.p. 176-178° [935].

1-[2,4-Dihydroxy-6-(2-hydroxyethyl)-3-methoxyphenyl]ethanone

[165186-29-8] $C_{11}H_{14}O_5$ mol.wt. 226.23

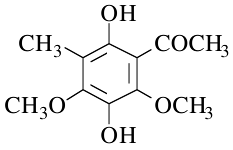


Isolation from natural sources

-One of seven metabolites produced by *Ophiosphaerella herpotricha* in liquid culture [1846].

1-(2,5-Dihydroxy-4,6-dimethoxy-3-methylphenyl)ethanone

$C_{11}H_{14}O_5$ mol.wt. 226.23



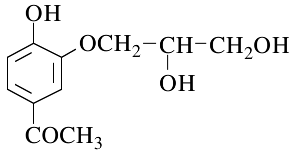
Syntheses

-Preparation by reaction of potassium persulfate on 2-hydroxy-4,6-dimethoxy-3-methylacetophenone in aqueous pyridine solution in the presence of potassium hydroxide [1282] or sodium hydroxide [1434] [1490], (27-35%) [1282] [1490], (10%) [1434].

m.p. 122-123° [1490], 121-122° [1434], 119-120° [1282]; ^{1}H NMR [1434], UV [1490], MS [1434].

1-[3-(2,3-Dihydroxypropoxy)-4-hydroxyphenyl]ethanone

[70064-44-7] $C_{11}H_{14}O_5$ mol.wt. 226.23



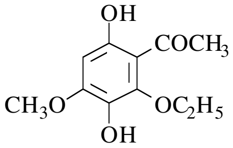
Synthesis

-Preparation by hydrogenolysis of 4-(benzyloxy)-3-(2,3-dihydroxypropoxy)acetophenone in ethanol under hydrogen atmosphere in the presence of 5% Pd/C for 45 min (99%) [486].

m.p. 136° [486].

1-(2-Ethoxy-3,6-dihydroxy-4-methoxyphenyl)ethanone

$C_{11}H_{14}O_5$ mol.wt. 226.23



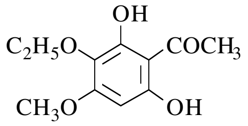
Synthesis

-Preparation by reaction of potassium persulfate on 2-ethoxy-6-hydroxy-4-methoxyacetophenone in dilute aqueous sodium hydroxide solution at 15-20° (25%) [73].

m.p. 145° [73].

1-(3-Ethoxy-2,6-dihydroxy-4-methoxyphenyl)ethanone

[105342-70-9] $C_{11}H_{14}O_5$ mol.wt. 226.23



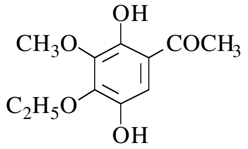
Synthesis

-Obtained (by-product) by reaction of hydrobromic acid with 3-ethoxy-2-hydroxy-4,6-dimethoxyacetophenone in acetic acid at r.t. [198].

m.p. 108°5-110° [198];
^{1}H NMR [198], IR [198], MS [198].

1-(4-Ethoxy-2,5-dihydroxy-3-methoxyphenyl)ethanone

$C_{11}H_{14}O_5$ mol.wt. 226.23

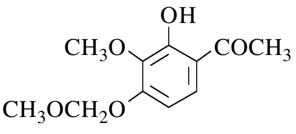


Synthesis

-Preparation from 4-ethoxy-2-hydroxy-3-methoxyacetophenone by persulfate oxidation in 10% aqueous sodium hydroxide (Elbs reaction) [1360].

1-[2-Hydroxy-3-methoxy-4-(methoxymethoxy)phenyl]ethanone

[220504-99-4] $C_{11}H_{14}O_5$ mol.wt. 226.23



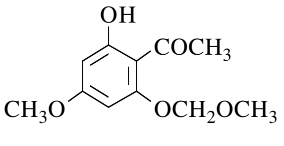
Synthesis

-Preparation in two steps: first, reaction of acetic acid with a mixture (*ca.* 1:1) of 1-O- and 2-O-methylpyrogallol in the presence of zinc chloride at reflux for 6 h (Nencki reaction); then, methoxymethylation of the obtained product (31%) [945].

^{1}H NMR [945]; MS [945].

1-[2-Hydroxy-4-methoxy-6-(methoxymethoxy)phenyl]ethanone

[186693-85-6] $C_{11}H_{14}O_5$ mol.wt. 226.23



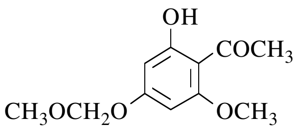
Synthesis

-Obtained by treatment of 2,6-dihydroxy-4-methoxyacetophenone with methoxymethyl chloride [1946] in the presence of potassium carbonate in refluxing acetone for 2 h (86%) [824].

m.p. 59-61°5 [824]; ^{1}H NMR [824], IR [824], EIMS [824].

1-[2-Hydroxy-6-methoxy-4-(methoxymethoxy)phenyl]ethanone

[404597-93-9] $C_{11}H_{14}O_5$ mol.wt. 226.23

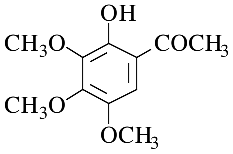


Synthesis

-Obtained by treatment of 2,4-di(methoxymethoxy)-6-methoxyacetophenone with silica gel in mild acetic medium (97%) [553].

1-(2-Hydroxy-3,4,5-trimethoxyphenyl)ethanone

[30225-96-8] $C_{11}H_{14}O_5$ mol.wt. 226.23



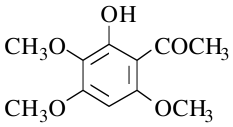
Syntheses

-Preparation by reaction of dimethyl sulfate on 2,5-dihydroxy-3,4-dimethoxyacetophenone with potassium carbonate in refluxing benzene (73%) [135].
-Preparation by reaction of acetyl chloride on 1,2,3,4-tetramethoxybenzene with aluminium chloride in refluxing carbon disulfide (70%) [165] [831] [1355] or in boiling ethyl ether [1355] [1357], (76%) [1357].

m.p. 88° [165] [1355] [1357], 86° [135] [831]; ^{1}H NMR [831].

1-(2-Hydroxy-3,4,6-trimethoxyphenyl)ethanone *(Xanthoxylone)*

[7507-98-4] $C_{11}H_{14}O_5$ mol.wt. 226.23



Syntheses

-Preparation by reaction of diazomethane on 2,4-dihydroxy-3,6-dimethoxyacetophenone in ethyl ether [757] [758].
-Preparation by reaction of dimethyl sulfate,
*on 2,6-dihydroxy-3,4-dimethoxyacetophenone disodium salt (95%) [1328];
*on 2,4-dihydroxy-3,6-dimethoxyacetophenone with potassium carbonate in boiling acetone (75%) [1552];
*on 2,3,6-trihydroxy-4-methoxyacetophenone in the presence of potassium carbonate in refluxing acetone [1845];
*on 2,3,4,6-tetrahydroxyacetophenone [166] [1328].
-Also obtained by partial methylation of 2,4-dihydroxy-3,6-dimethoxyacetophenone [1379], according to [1552].
-Also obtained by Friedel-Crafts acylation of 1,2,3,5-tetramethoxybenzene [1616].
-Preparation by reaction of acetyl chloride on 1,2,3,5-tetramethoxybenzene with aluminium chloride,
*in ethyl ether [135] [198] [808] [1263] [1357] [1358] [1452] [1496], (81%) [1357], (64-70%) [135] [1263] [1496], (53%) [198], (35-36%) [361] [1452];
*in carbon disulfide [160] [161] [166] [167] [375] [1358], (51%) [166];
*without solvent at 70° (44%) [1881].
-Preparation by reaction of acetic acid with 1,2,3,5-tetramethoxybenzene in the presence of boron trifluoride at 30° (81%) [815].
-Also obtained by partial demethylation of 2,3,4,6-tetramethoxyacetophenone in the presence of aluminium chloride [759] [962] in acetonitrile at 30° for 1 h (95%) [962].
-Also refer to: [805] [1617] [1687] [1929].

Isolation from natural sources

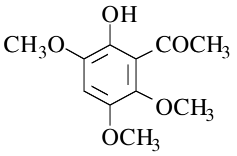
-From the New Zealand liverwort, *Plagiochila fasciculata* [1113].
-From *Croton aff. nepetifolius* Bail (Euphorbiaceae) [450].
-From hydrolysis of Wogonin (5,7-dihydroxy-8-methoxyflavone). Wogonin was isolated in small amounts in the roots of *Scutellaria baicalensis* Georgi (Labiatae) [759].
-From the fresh leaves of *Fagara okinawensis* Nakai (Rutaceae) [1263].

m.p. 125-126° [1328], 113-115° [1452], 113-114° [1552], 113° [1845], 112-114° [198], 112-113° [166] [167] [759] [1263] [1357] [1358], 111°5-113°5 [361], 111-112° [375], 110-112° [1379], 110-111° [757] [758], 109-114° [815], 109°5-111°5 [1496], 109-111° [1881], 105-107° [160] [161] [162], 103-105° [135] [801];

^{1}H NMR [198] [361] [450] [757] [758] [1113] [1263] [1379] [1496], ^{13}C NMR [1379], IR [198] [361] [450] [757] [758] [1113] [1263] [1379] [1496], UV [1113] [1263], MS [450] [1379].

1-(2-Hydroxy-3,5,6-trimethoxyphenyl)ethanone

[72424-28-3] $C_{11}H_{14}O_5$ mol.wt. 226.23



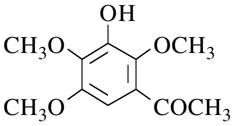
Synthesis

-Preparation by partial demethylation of 2,3,5,6-tetramethoxyacetophenone with aluminium chloride in ethyl ether in an ice bath (55%) [808] or in acetonitrile for 6 h at 45° (25%) [962].

m.p. 62-63°5 [808]; ^{1}H NMR [808].

1-(3-Hydroxy-2,4,5-trimethoxyphenyl)ethanone

[97565-35-0] $C_{11}H_{14}O_5$ mol.wt. 226.23



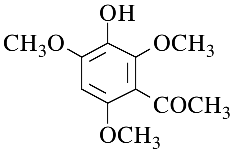
Isolation from natural sources

-Obtained by alkaline degradation of two octasubstituted flavones with 50% potassium hydroxide in refluxing ethanol under nitrogen atmosphere for 15 h. These flavones were isolated from the aerial parts of *Ageratum houstonianum* Mill (Asteraceae) (Eupatorieae) [1450],
*From *agehoustin C* (3'-hydroxy-5,6,7,8,2',4',5'-heptamethoxyflavone) (m.p. 145°);
*From *agehoustin D* (5,3'-dihydroxy-6,7,8,2',4',5'-hexamethoxyflavone) (m.p. 168-169°).

m.p. 98-100° [1450]; ^{1}H NMR [1450], IR [1450], UV [1450], MS [1450].

1-(3-Hydroxy-2,4,6-trimethoxyphenyl)ethanone

[103777-45-3] $C_{11}H_{14}O_5$ mol.wt. 226.23



Syntheses

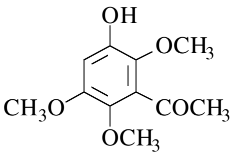
-Obtained by treatment of polygoacetophenoside with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 24 h. Then, the formed oil was hydrolyzed with 10% sulfuric acid on a water bath for 3 h [1929].

-Also obtained (by-product) by reaction of dimethyl sulfate on 3,6-dihydroxy-2,4-dimethoxyacetophenone in aqueous sodium hydroxide solution at r.t. (3%) [1452].

m.p. 128-129° [1929], 113-117° [1452];
^{1}H NMR [1929], ^{13}C NMR [1929], IR [1929], MS [1929].

1-(3-Hydroxy-2,5,6-trimethoxyphenyl)ethanone

[73034-32-9] $C_{11}H_{14}O_5$ mol.wt. 226.23



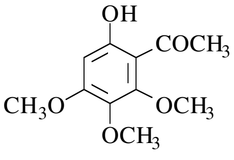
Synthesis

-Preparation by hydrolysis of 3-acetoxy-2,5,6-trimethoxyacetophenone with 10% sodium hydroxide in methanol [198] [808].

m.p. 71-72° [198]; b.p.$_{0.1}$ 150-160° [198];
^{1}H NMR [198], IR [198].

1-(6-Hydroxy-2,3,4-trimethoxyphenyl)ethanone

[22248-14-2] $C_{11}H_{14}O_5$ mol.wt. 226.23



Syntheses

-Preparation by Fries rearrangement of antiarol acetate (3,4,5-trimethoxyphenyl acetate) with aluminium chloride in nitrobenzene at r.t. (54%) [1354], (45%) [1452].
-Preparation by reaction of antiarol (3,4,5-trimethoxyphenol) with boron trifluoride-acetic acid complex at 28-30° (50%) [1146].
-Also obtained by reaction of acetyl chloride,
*on antiarol benzyl ether with aluminium chloride in ethyl ether, followed by subsequent debenzylation of the keto compound obtained (22%) [1354];
*on 1,2,3,5-tetramethoxybenzene with aluminium chloride in carbon disulfide at r.t. (9%) [162].
-Also obtained by reaction of dimethyl sulfate,
*on 3,6-dihydroxy-2,4-dimethoxyacetophenone,
    -with potassium carbonate in refluxing benzene [135] [1354] [1452], (15-18%) [135] [1452] or in refluxing acetone-benzene mixture [808] [1055] [1551], (70%) [1551], (36%) [1055];
    -with aqueous sodium hydroxide solution at r.t. (52%) [1452].
*on 2,3,4,6-tetrahydroxyacetophenone [1328];
*on 2,6-dihydroxy-3,4-dimethoxyacetophenone disodium salt, followed by acidification (< 5%) [1328].
-Also obtained by alkaline degradation of 3',4',5,6,7-pentamethoxyflavone with potassium hydroxide in refluxing aqueous ethanol [73].
-Also refer to: [1187] [1311].

Isolation from natural sources

-From 5,6,7-trimethoxyflavone by alkaline hydrolysis in refluxing 50% methanolic potassium hydroxide. The 5,6,7-trimethoxyflavone is one of major constituents of the leaves of *Zeyhera tuberculosa* Bur. ex. Verlot (Bignoniaceae) [1055].

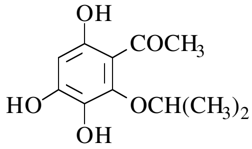
yellow oil [73] [1055] [1551];
m.p. 164-165° [1328], 105-107° [162], 41-42° [1354], 32° [1146], 30°5-31°5 [1452].
There is a discrepancy between the different melting points indicated in literature.

b.p.$_{0.35}$ 121-122° [1452], b.p.$_1$ 140° [1146], b.p.$_{20}$ 180-185° [1354], b.p.$_{14}$ 182-185° [1452], b.p.$_{27}$ 184-186° [135];

^{1}H NMR [1055], ^{13}C NMR [1396], IR [1055], UV [1055], MS [1055].

1-[3,4,6-Trihydroxy-2-(1-methylethoxy)phenyl]ethanone

[60840-21-3] $C_{11}H_{14}O_5$ mol.wt. 226.23



Synthesis

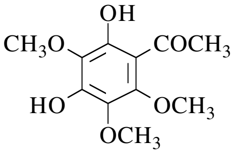
-Preparation by catalytic hydrogenolysis of 3,4,6-tris-(benzyloxy)-2-isopropoxyacetophenone in the presence of 5% Pd/C in ethanol at r.t. (94%) [757] [758].

m.p. 137° [757] [758];

^{1}H NMR [757] [758], IR [757] [758], MS [757] [758].

1-(2,4-Dihydroxy-3,5,6-trimethoxyphenyl)ethanone

$C_{11}H_{14}O_6$ mol.wt. 242.23



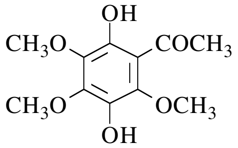
Synthesis

-Obtained by hydrolysis of 1-(2,4-diacetoxy-3,5,6-trimethoxyphenyl)ethanone (SM) with aqueous 10% sodium hydroxide at r.t. for 10-15 min. SM was obtained by Friedel-Crafts acylation of 2,3,5,6-tetramethoxyphenyl acetate (m.p. 97-98°) with acetic anhydride/acetic acid in the presence of excess boron trifluoride at 50-60° for 5 h (65%, m.p. 82-84°) [797].

N.B.: This ketone was not obtained by Friedel-Crafts reaction of 2,3,5,6-tetramethoxyphenol, and its acetate or benzyl ether with acetyl chloride and aluminium chloride in ethyl ether [797] [802].

1-(2,5-Dihydroxy-3,4,6-trimethoxyphenyl)ethanone

[55742-65-9] $C_{11}H_{14}O_6$ mol.wt. 242.23



Syntheses

-Obtained by persulfate oxidation of 2-hydroxy-3,4,6-trimethoxyacetophenone (Elbs reaction) [1617], (33%) [1616], (29%) [135], (9%) [1609].

-Also obtained by reduction of 2-acetyl-3,5,6-trimethoxy-1,4-benzoquinone with zinc dust in acetic anhydride, followed by hydrolysis of the acetic ester formed with dilute sulfuric acid [1328].

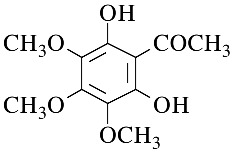
-Also refer to: [795] [796] [800] [1465].

m.p. 174-176° [1328], 116-117° [135], 115-117° [1616] [1617].

One of the reported melting points is obviously wrong.

1-(2,6-Dihydroxy-3,4,5-trimethoxyphenyl)ethanone

$C_{11}H_{14}O_6$ mol.wt. 242.23



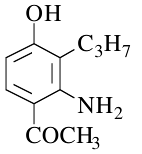
Synthesis

-Obtained by acylation of pentamethoxybenzene with acetyl chloride in the presence of aluminium chloride in ethyl ether, first for 14 h at r.t., then for 2 h at reflux (17%) [1695].

m.p. 86-88° [1695];
^{1}H NMR [1695], IR [1695], UV [1695].

1-(2-Amino-4-hydroxy-3-propylphenyl)ethanone

[87472-78-4] $C_{11}H_{15}NO_2$ mol.wt. 193.25



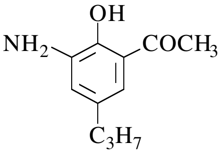
Synthesis

-Preparation by hydrogenation of 3-allyl-2-amino-4-hydroxyacetophenone in the presence of 5% Pd/C in ethanol (quantitative yield) [297].

viscous oil [297]; ^{1}H NMR [297].

1-(3-Amino-2-hydroxy-5-propylphenyl)ethanone

[70978-22-2] $C_{11}H_{15}NO_2$ mol.wt. 193.25



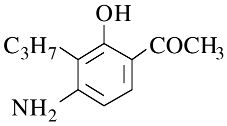
Synthesis

-Preparation by catalytic hydrogenation of 2-hydroxy-3-nitro-5-propylacetophenone in the presence of 5% Pd/C in ethanol at 25° [620] [1463], (77%) [620].

m.p. 43-45° [1463], 42-43° [620].

1-(4-Amino-2-hydroxy-3-propylphenyl)ethanone

[75452-54-9] $C_{11}H_{15}NO_2$ mol.wt. 193.25



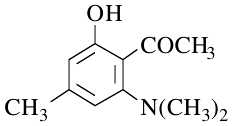
Synthesis

-Preparation by hydrolysis of 4-acetamido-2-hydroxy-3-propylacetophenone with 6 N hydrochloric acid in refluxing ethanol (95%) [297].

yellow oil [297]; b.p.$_{0.15}$ 120-122° [297]; ^{1}H NMR [297].

1-[2-(Dimethylamino)-6-hydroxy-4-methylphenyl]ethanone

[97066-06-3] $C_{11}H_{15}NO_2$ mol.wt. 193.25



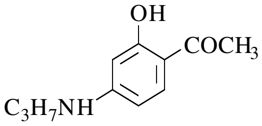
Synthesis

-Preparation by reaction of potassium hydroxide with 2-acetyl-3-dimethylamino-5-hydroxy-5-methyl-2-cyclohexenone in ethanol at 40° (41%) [562].

yellow oil [562]; m.p. -5° [562];
^{1}H NMR [562], IR [562], UV [562], MS [562].

1-[2-Hydroxy-4-(propylamino)phenyl]ethanone

[118684-26-7] $C_{11}H_{15}NO_2$ mol.wt. 193.25



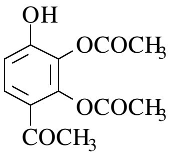
Synthesis

-A solution of 4-amino-2-hydroxyacetophenone and propionaldehyde in methanol was stored over 3 Å molecular sieves for 3 days. The solution of "2-hydroxy-4-propyliminoacetophenone" so obtained was then treated with hydrogen in the presence of 10% Pd/C (50%) [297].

m.p. 73-75° [297]; ^{1}H NMR [297].

1-[2,3-Bis(acetyloxy)-4-hydroxyphenyl]ethanone

[144152-31-8] $C_{12}H_{12}O_6$ mol.wt. 252.22



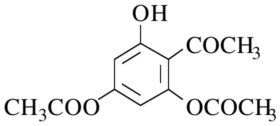
Synthesis

-Obtained by enzymatic deacylation of 2,3,4-triacetoxyacetophenone with porcine pancreas lipase in tetrahydrofuran at 42-45° (55%) [1381] [1383].

pale yellow viscous oil [1383]; ^{1}H NMR [1383].

1-[2,4-Bis(acetyloxy)-6-hydroxyphenyl]ethanone

[17820-33-6] $C_{12}H_{12}O_6$ mol.wt. 252.22



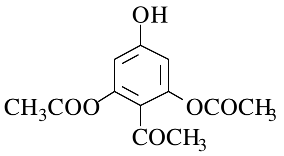
Syntheses

-Obtained (by-product) by reaction of acetic anhydride on phloroacetophenone with pyridine at r.t. (7%) [5].
-Also obtained by photo-Fries rearrangement of 1,3,5-triacetoxybenzene in methanol (15%) [1614].

m.p. 86-87° [311], 79-80° [1614];
^{1}H NMR [311] [1614], ^{13}C NMR [5], IR [1614].

1-[2,6-Bis(acetyloxy)-4-hydroxyphenyl]ethanone

[17820-32-5] $C_{12}H_{12}O_6$ mol.wt. 252.22



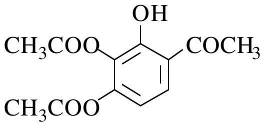
Syntheses

-Preparation by reaction of acetic anhydride with phloroacetophenone between 110 to 165° (40%) [311].
-Also obtained by enzymatic deacylation of 2,4,6-triacetoxyacetophenone with porcine pancreatic lipase in tetrahydrofuran at 42-45° (78%) [1381] [1382] [1383].

m.p. 154-155° [311], 112° [1383]. One of the reported melting points is obviously wrong.
^{1}H NMR [311] [1383].

1-[3,4-Bis(acetyloxy)-2-hydroxyphenyl]ethanone

[27865-58-3] $C_{12}H_{12}O_6$ mol.wt. 252.22



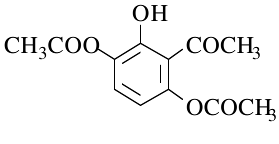
Syntheses

-Obtained by UV light irradiation of pyrogallol triacetate in methanol (15%) [1614].
-Also obtained by partial Fries rearrangement of pyrogallol triacetate with zinc chloride at 130-135° [770].
-Also obtained by reaction of acetic anhydride on gallacetophenone with pyridine [1637].
-Also refer to: [1264].

m.p. 217-219° [770], 110-112° [1614], 78-81° [1637];
^{1}H NMR [1614], IR [1614].

1-[3,6-Bis(acetyloxy)-2-hydroxyphenyl]ethanone

[104654-33-3] $C_{12}H_{12}O_6$ mol.wt. 252.22



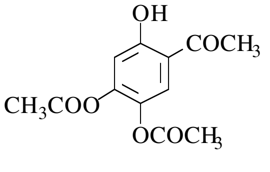
Synthesis

-Obtained by photo-Fries rearrangement of 1,2,4-triacetoxybenzene in methanol (15%) [1614].

m.p. 116-118° [1614]; ^{1}H NMR [1614], IR [1614].

1-[4,5-Bis(acetyloxy)-2-hydroxyphenyl]ethanone

[42059-51-8] $C_{12}H_{12}O_6$ mol.wt. 252.22



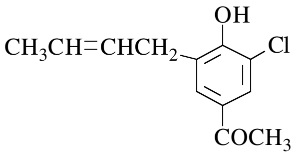
Syntheses

-Obtained by partial Fries rearrangement of 1,2,4-triacetoxybenzene with zinc chloride in acetic acid at 140° (21%) [159] [168], (8%) [1335].
-Preparation by reaction of acetic anhydride with 2,4,5-trihydroxyacetophenone in the presence of pyridine at 35° (52%) [1335].

m.p. 165-166° [159] [168], 100-102° [1335]; ^{1}H NMR [1335], IR [1335].

1-[3-(2-Butenyl)-5-chloro-4-hydroxyphenyl]ethanone

$C_{12}H_{13}ClO_2$ mol.wt. 224.69

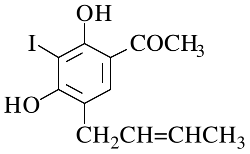


Synthesis

-Obtained by heating 4-(2-butenyloxy)-3-chloroacetophenone for 3 h under nitrogen atmosphere (Claisen rearrangement) [950].

1-[5-(2-Butenyl)-2,4-dihydroxy-3-iodophenyl]ethanone

[91664-19-6] $C_{12}H_{13}IO_3$ mol.wt. 332.14



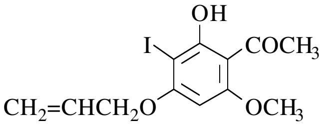
Synthesis

-Preparation by condensation of 2,4-dihydroxy-3-iodo-acetophenone with 1,3-butadiene in the presence of 85% orthophosphoric acid in xylene at 30-35° (75%) [19].

m.p. 100-101° [19]; ^{1}H NMR [19].

1-[2-Hydroxy-3-iodo-6-methoxy-4-(2-propenyloxy)phenyl]ethanone

[74047-33-9] $C_{12}H_{13}IO_4$ mol.wt. 348.14



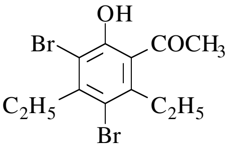
Synthesis

-Preparation by reaction of allyl bromide with 2,4-dihydroxy-3-iodo-6-methoxyacetophenone in the presence of potassium carbonate in refluxing acetone (58%) [15].

m.p. 162-164° [15]; ^{1}H NMR [15].

1-(3,5-Dibromo-2,4-diethyl-6-hydroxyphenyl)ethanone

$C_{12}H_{14}Br_2O_2$ mol.wt. 350.05



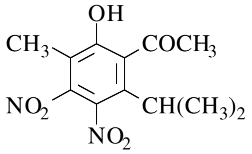
Synthesis

-Preparation by reaction of potassium bromate and bromide on 2,4-diethyl-6-hydroxyacetophenone in solution of acetic acid-carbon tetrachloride mixture (quantitative yield) [123].

m.p. 81° [123].

1-[2-Hydroxy-3-methyl-6-(1-methylethyl)-4,5-dinitrophenyl]ethanone

$C_{12}H_{14}N_2O_6$ mol.wt. 282.26



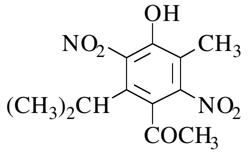
Synthesis

-Preparation by reaction of nitric acid (d = 1.4) on 2-hydroxy-3-methyl-5-nitro-6-isopropylacetophenone in acetic acid, between -5° and 0° (53%) [903].

m.p. 119° [903].

1-[4-Hydroxy-3-methyl-6-(1-methylethyl)-2,5-dinitrophenyl]ethanone

$C_{12}H_{14}N_2O_6$ mol.wt. 282.26



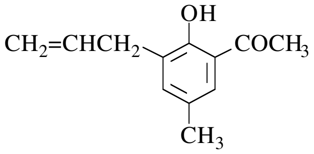
Synthesis

-Preparation by reaction of nitric acid (d = 1.4) on 4-hydroxy-5-methyl-3-nitro-2-isopropylacetophenone in acetic acid (59%) [902].

m.p. 55° [902].

1-[2-Hydroxy-5-methyl-3-(2-propenyl)phenyl]ethanone

[108293-73-8] $C_{12}H_{14}O_2$ mol.wt. 190.24



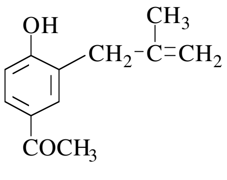
Synthesis

-Preparation by thermal Claisen rearrangement of 2-(allyloxy)-5-methylacetophenone without solvent at 190° (95%) [527] or at 260-270° (84%) [1747].

yellow oil [527];
b.p.$_{0.15}$ 94-96° [527], b.p.$_5$ 103-105° [1747];
^{1}H NMR [527], ^{13}C NMR [527], IR [527], MS [527].

1-[4-Hydroxy-3-(2-methyl-2-propenyl)phenyl]ethanone

[57899-03-3] $C_{12}H_{14}O_2$ mol.wt. 190.24



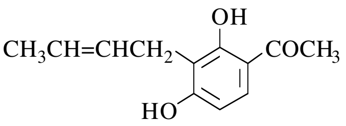
Synthesis

-Preparation by thermal Claisen rearrangement of 4-(β-methallyloxy)acetophenone in boiling N,N-dimethylaniline [333].

m.p. 86° [333]; b.p.$_{16}$ 196° [333].

1-[3-(2-Butenyl)-2,4-dihydroxyphenyl]ethanone

[91664-16-3] $C_{12}H_{14}O_3$ mol.wt. 206.24



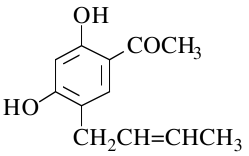
Synthesis

-Preparation by condensation of resacetophenone with 1,3-butadiene in the presence of 85% orthophosphoric acid in xylene at 30-35° (38%) [19].

m.p. 164-165° [19]; ^{1}H NMR [19].

1-[5-(2-Butenyl)-2,4-dihydroxyphenyl]ethanone

[91664-17-4] $C_{12}H_{14}O_3$ mol.wt. 206.24



Syntheses

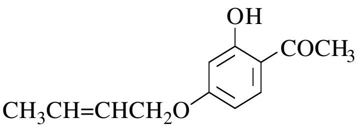
-Preparation by condensation of resacetophenone with 1,3-butadiene in the presence of 85% orthophosphoric acid in xylene at 30-35° (42%) [19].

-Also obtained from 5-(2-butenyl)-2,4-dihydroxy-3-iodoacetophenone by heating with zinc dust and concentrated hydrochloric acid in refluxing ethanol (80%) [19].

m.p. 103-104° [19]; ^{1}H NMR [19], IR [19].

1-[4-(2-Butenyloxy)-2-hydroxyphenyl]ethanone

[79557-72-5] $C_{12}H_{14}O_3$ mol.wt. 206.24



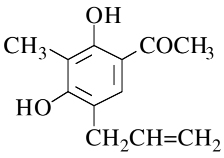
Synthesis

-Preparation by reaction of 3-chloro-1-butene with resacetophenone in the presence of potassium carbonate and sodium iodide in refluxing butanone (44%) [1372].

oil [1372]; b.p.$_{0.1}$ 162-175° [1372].

1-[2,4-Dihydroxy-3-methyl-5-(2-propenyl)phenyl]ethanone

[77869-01-3] $C_{12}H_{14}O_3$ mol.wt. 206.24



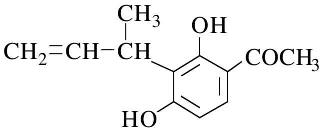
Synthesis

-Preparation by thermal Claisen rearrangement of 4-(allyloxy)-2-hydroxy-3-methylacetophenone in boiling N,N-dimethylaniline [1393].

m.p. 139° [1393]; IR [1393].

1-[2,4-Dihydroxy-3-(1-methyl-2-propenyl)phenyl]ethanone

[79557-73-6] $C_{12}H_{14}O_3$ mol.wt. 206.24



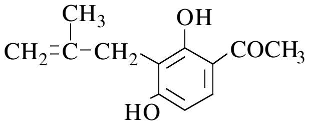
Syntheses

-Preparation by thermal Claisen rearrangement of 4-(2-butenyloxy)-2-hydroxyacetophenone without solvent at 180-190° under nitrogen (40%) [1372].
-Also obtained (by-product) by condensation of resacetophenone with 1,3-butadiene in the presence of 85% orthophosphoric acid in xylene at 30-35° (3%) [19].

m.p. 147-149° [19], 146-147° [1372]; ^{1}H NMR [19].

1-[2,4-Dihydroxy-3-(2-methyl-2-propenyl)phenyl]ethanone

[118683-89-9] $C_{12}H_{14}O_3$ mol.wt. 206.24



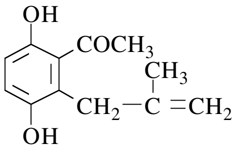
Synthesis

-Preparation by thermal Claisen rearrangement of 2-hydroxy-4-(2-methylprop-2-enoxy)acetophenone without solvent at 210° (24%) [297].

white solid [297]; ^{1}H NMR [297].

1-[3,6-Dihydroxy-2-(2-methyl-2-propenyl)phenyl]ethanone

[127870-07-9] $C_{12}H_{14}O_3$ mol.wt. 206.24



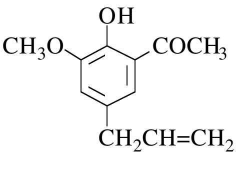
Synthesis

-Obtained by thermal reaction of 2-acetyl-1,4-benzoquinone (1 mol) with (2-methallyl)trimethylstannane (2 mol) in benzene or acetonitrile under argon atmosphere (77%) [1171].

m.p. 78-80° [1171]; ^{1}H NMR [1171], MS [1171].

1-[2-Hydroxy-3-methoxy-5-(2-propenyl)phenyl]ethanone

[23343-04-6] $C_{12}H_{14}O_3$ mol.wt. 206.24



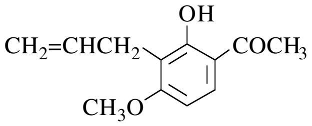
Synthesis

-Preparation by thermal Claisen rearrangement of 2-(allyloxy)-3-methoxyacetophenone [1212] without solvent at 210° [1417], (77%) [1417], (38%) [1212].

m.p. 43-44° [1417], 42-43° [1212];
^{1}H NMR [1212], IR [1212], UV [1212].

1-[2-Hydroxy-4-methoxy-3-(2-propenyl)phenyl]ethanone

[117156-86-2] $C_{12}H_{14}O_3$ mol.wt. 206.24



Syntheses

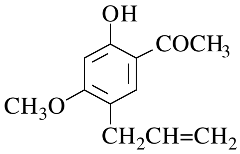
-Preparation by thermal Claisen rearrangement of 2'-(allyloxy)-4'-methoxyacetophenone in boiling N,N-dimethylaniline (80%) [61].

-Preparation by reaction of dimethyl sulfate on 3-allylresacetophenone in 10% aqueous potassium hydroxide at 30° [132].

m.p. 61° [132], 59° [61]; ^1H NMR [61], IR [61], UV [61].

1-[2-Hydroxy-4-methoxy-5-(2-propenyl)phenyl]ethanone

[117713-79-8] $C_{12}H_{14}O_3$ mol.wt. 206.24

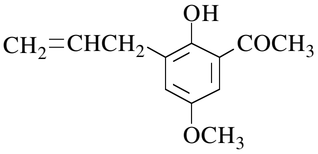


Synthesis

-Preparation by reaction of methyl bromide on 5-allyl-2,4-dihydroxyacetophenone with potassium carbonate and potassium iodide (41%) [256] [257].

1-[2-Hydroxy-5-methoxy-3-(2-propenyl)phenyl]ethanone

[186956-47-8] $C_{12}H_{14}O_3$ mol.wt. 206.24



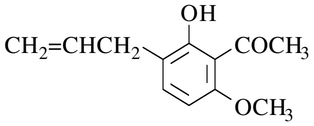
Synthesis

-Obtained by Claisen rearrangement of 2-(allyloxy)-5-methoxyacetophenone in refluxing N,N-diethylaniline at 220° for 4 h [1476].

colourless oil [1476]; b.p.$_{0.1}$ 145° [1476]; ^1H NMR [1476], IR [1476].

1-[2-Hydroxy-6-methoxy-3-(2-propenyl)phenyl]ethanone

[17488-68-5] $C_{12}H_{14}O_3$ mol.wt. 206.24



Syntheses

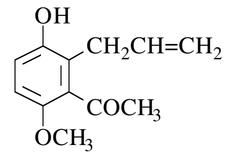
-Preparation by reaction of dimethyl sulfate on 3-allyl-2,6-dihydroxyacetophenone with potassium carbonate in benzene in a water bath (89%) [1648].

-Also obtained by thermal Claisen rearrangement of 2-(allyloxy)-6-methoxyacetophenone at 215-220°, in a sealed tube (35%) [1648].

b.p.$_2$ 122-124° [1648], b.p.$_3$ 127° [1648]; d^{20} = 1.0283 [1648]; n_D^{20} = 1.5602 and 1.5598 [1648].

1-[3-Hydroxy-6-methoxy-2-(2-propenyl)phenyl]ethanone

$C_{12}H_{14}O_3$ mol.wt. 206.24



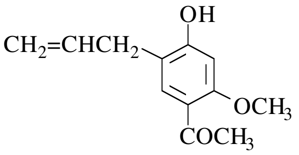
Synthesis

-Preparation by thermal Claisen rearrangement of 5-(allyloxy)-2-methoxyacetophenone at 230° (74%) [131].

m.p. 104° [131].

1-[4-Hydroxy-2-methoxy-5-(2-propenyl)phenyl]ethanone

[117705-59-6] $C_{12}H_{14}O_3$ mol.wt. 206.24



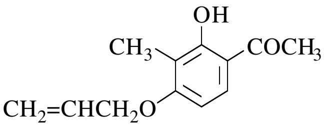
Synthesis

-Preparation by Claisen rearrangement of 4-(allyloxy)-2-methoxyacetophenone at 210-215° (60%) [132], (24%) [256] [257] [777].

m.p. 136° [132], < 25° [777]; ^{1}H NMR [256] [257].

1-[2-Hydroxy-3-methyl-4-(2-propenyloxy)phenyl]ethanone

[77036-77-2] $C_{12}H_{14}O_3$ mol.wt. 206.24

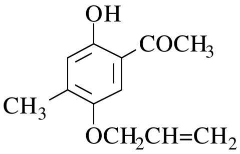


Synthesis

-Preparation by reaction of allyl bromide on 2,4-dihydroxy-3-methylacetophenone with potassium carbonate in refluxing acetone [523].

1-[2-Hydroxy-4-methyl-5-(2-propenyloxy)phenyl]ethanone

[76267-82-8] $C_{12}H_{14}O_3$ mol.wt. 206.24



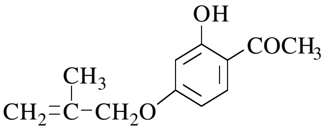
Synthesis

-Preparation by reaction of allyl bromide with 2,5-dihydroxy-4-methylacetophenone in the presence of potassium carbonate in refluxing acetone [1392].

greenish yellow liquid [1392].

1-[2-Hydroxy-4-[(2-methyl-2-propenyl)oxy]phenyl]ethanone

[118683-88-8] $C_{12}H_{14}O_3$ mol.wt. 206.24



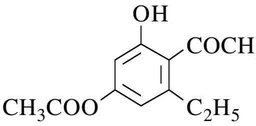
Synthesis

-Preparation by reaction of 3-chloro-2-methylpropene with resacetophenone in the presence of potassium carbonate in refluxing acetone (75%) [297].

white solid [297]; ¹H NMR [297].

1-[4-(Acetyloxy)-2-ethyl-6-hydroxyphenyl]ethanone

[57600-88-1] $C_{12}H_{14}O_4$ mol.wt. 222.24

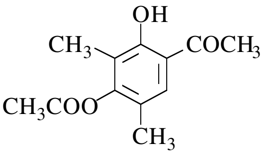


Synthesis

-Preparation by treatment of a mixture of alkylated resorcinols with acetic anhydride and acetic acid in the presence of zinc chloride at 140-145°, followed by suitable separation [936].

1-[4-(Acetyloxy)-2-hydroxy-3,5-dimethylphenyl]ethanone

$C_{12}H_{14}O_4$ mol.wt. 222.24



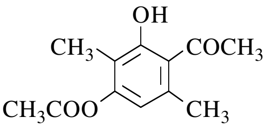
Synthesis

-Preparation by reaction of acetic anhydride with 2,4-dihydroxy-3,5-dimethylacetophenone in the presence of pyridine [755].

m.p. 95-96° [755].

1-[4-(Acetyloxy)-2-hydroxy-3,6-dimethylphenyl]ethanone

[57600-89-2] $C_{12}H_{14}O_4$ mol.wt. 222.24

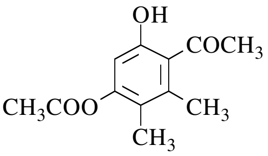


Synthesis

-Preparation by treatment of a mixture of alkylated resorcinols with acetic anhydride and acetic acid in the presence of zinc chloride at 140-145°, followed by suitable separation [936].

1-[4-(Acetyloxy)-6-hydroxy-2,3-dimethylpheny]ethanone

[57600-90-5] $C_{12}H_{14}O_4$ mol.wt. 222.24

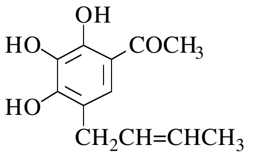


Synthesis

-Preparation by treatment of a mixture of alkylated resorcinols with acetic anhydride and acetic acid in the presence of zinc chloride at 140-145°, followed by suitable separation [936].

1-[5-(2-Butenyl)-2,3,4-trihydroxyphenyl]ethanone

[91664-14-1] $C_{12}H_{14}O_4$ mol.wt. 222.24



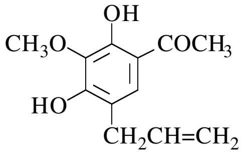
Synthesis

-Preparation by condensation of gallacetophenone with 1,3-butadiene in the presence of 85% orthophosphoric acid in xylene at 30-35° (60%) [19].

m.p. 93-94° [19]; ^{1}H NMR [19].

1-[2,4-Dihydroxy-3-methoxy-5-(2-propenyl)phenyl]ethanone

$C_{12}H_{14}O_4$ mol.wt. 222.24



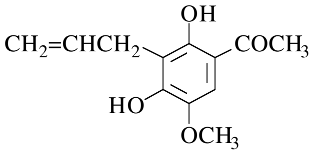
Synthesis

-Preparation by heating 4-(allyloxy)-2-hydroxy-3-methoxyacetophenone at 220° under reduced pressure (Claisen rearrangement) (70%) [972].

m.p. 94° [972].

1-[2,4-Dihydroxy-5-methoxy-3-(2-propenyl)phenyl]ethanone

$C_{12}H_{14}O_4$ mol.wt. 222.24



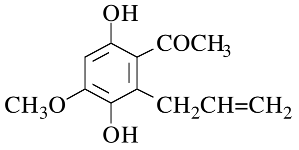
Synthesis

-Preparation by thermal Claisen rearrangement of 4-(allyloxy)-2-hydroxy-5-methoxyacetophenone without solvent at 180° (85%) [60].

m.p. 118° [60].

1-[3,6-Dihydroxy-4-methoxy-2-(2-propenyl)phenyl]ethanone

$C_{12}H_{14}O_4$ mol.wt. 222.24



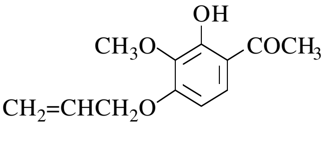
Synthesis

-Preparation by heating 5-(allyloxy)-2-hydroxy-4-methoxyacetophenone in glycerol at 200° (Claisen rearrangement) (81%) [498].

m.p. 114° [498].

1-[2-Hydroxy-3-methoxy-4-(2-propenyloxy)phenyl]ethanone

$C_{12}H_{14}O_4$ mol.wt. 222.24



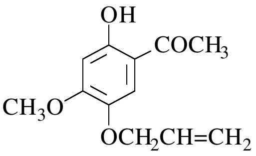
Syntheses

-Preparation by reaction of allyl bromide on 2,4-dihydroxy-3-methoxyacetophenone with potassium carbonate in boiling acetone (70%) [972].
-Preparation by reaction of dimethyl sulfate on 4-(allyloxy)-2,3-dihydroxyacetophenone with potassium carbonate in boiling acetone (80%) [972].

m.p. 63-64° [972].

1-[2-Hydroxy-4-methoxy-5-(2-propenyloxy)phenyl]ethanone

$C_{12}H_{14}O_4$ mol.wt. 222.24



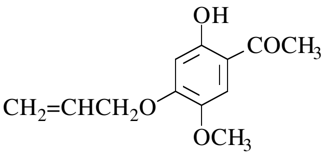
Synthesis

-Preparation by reaction of allyl bromide on 2,5-dihydroxy-4-methoxyacetophenone with potassium carbonate in boiling acetone (82%) [498].

m.p. 80° [498].

1-[2-Hydroxy-5-methoxy-4-(2-propenyloxy)phenyl]ethanone

[91497-16-4] $C_{12}H_{14}O_4$ mol.wt. 222.24



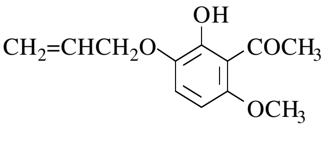
Syntheses

-Preparation by partial methylation of 4-(allyloxy)-2,5-dihydroxyacetophenone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone (90%) [82].
-Preparation by reaction of allyl bromide with 2,4-dihydroxy-5-methoxyacetophenone in the presence of potassium carbonate in boiling acetone (60%) [60].

m.p. 50-51° [82], 50° [60].

1-[2-Hydroxy-6-methoxy-3-(2-propenyloxy)phenyl]ethanone

[126405-78-5] $C_{12}H_{14}O_4$ mol.wt. 222.24



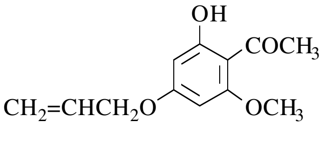
Synthesis

-Preparation by adding 2-hydroxy-3-iodo-6-methoxyacetophenone and cuprous iodide to a solution of sodium allyloxide, previously prepared from allyl alcohol and sodium hydride in DMF (45%) [1873].

oil [1873]; ^{1}H NMR [1873], IR [1873].

1-[2-Hydroxy-6-methoxy-4-(2-propenyloxy)phenyl]ethanone

[74047-37-3] $C_{12}H_{14}O_4$ mol.wt. 222.24



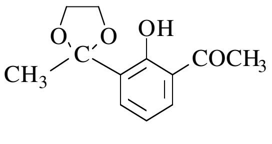
Syntheses

-Preparation by reaction of allyl bromide with 2,4-dihydroxy-6-methoxyacetophenone in the presence of potassium carbonate in refluxing acetone (61%) [18].
-Also refer to: [1624].

m.p. 74-76° [18]; ^{1}H NMR [18].

1-[2-Hydroxy-3-(2-methyl-1,3-dioxolan-2-yl)phenyl]ethanone

[103867-84-1] $C_{12}H_{14}O_4$ mol.wt. 222.24



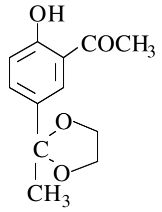
Syntheses

-Preparation by UV light irradiation of ethylene acetal of 2-acetoxyacetophenone in hexane,
*with potassium carbonate (76%) [659];
*without potassium carbonate (10%) [658] [659].

oil [658]; ^{1}H NMR [658], IR [658], UV [658].

1-[2-Hydroxy-5-(2-methyl-1,3-dioxolan-2-yl)phenyl]ethanone

[103867-87-4] $C_{12}H_{14}O_4$ mol.wt. 222.24



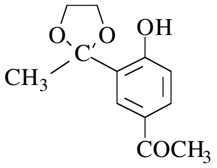
Syntheses

-Preparation by UV light irradiation of ethylene acetal of the 4-acetoxyacetophenone in hexane,
*with potassium carbonate (82%) [659];
*without potassium carbonate (21%) [658] [659].

m.p. 56-57° [658];
^{1}H NMR [658], IR [658], UV [658].

1-[4-Hydroxy-3-(2-methyl-1,3-dioxolan-2-yl)phenyl]ethanone

[103867-88-5] $C_{12}H_{14}O_4$ mol.wt. 222.24



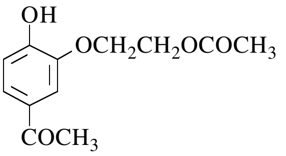
Synthesis

-Obtained (by-product) by UV light irradiation of ethylene acetal of 2-acetoxyacetophenone in hexane, with or without potassium carbonate (8-9%) [658] [659].

m.p. 78-80° [658];
^{1}H NMR [658], IR [658], UV [658].

1-[3-[2-(Acetyloxy)ethoxy]-4-hydroxyphenyl]ethanone

[63437-82-1] $C_{12}H_{14}O_5$ mol.wt. 238.24



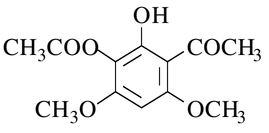
Syntheses

-Preparation by Fries rearrangement of 2-(2-acetoxyethoxy)phenyl acetate (m.p. 142-146°) with aluminium chloride in nitrobenzene for 48 h at 20° (55%) [486].
-Also refer to: [485].

m.p. 103-104° [486].

1-[3-(Acetyloxy)-2-hydroxy-4,6-dimethoxyphenyl]ethanone

[21919-65-3] $C_{12}H_{14}O_6$ mol.wt. 254.24



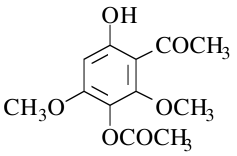
Syntheses

-Preparation by reaction of acetic anhydride with 2,3-dihydroxy-4,6-dimethoxyacetophenone in the presence of sodium acetate at 60° (80%) [1303].
-Preparation by reaction of aluminium chloride with 3-acetoxy-2,4,6-trimethoxyacetophenone in nitrobenzene at 100° [1303] [1309], (52%) [1303].

m.p. 180° [1303].

1-[3-(Acetyloxy)-6-hydroxy-2,4-dimethoxyphenyl]ethanone

[21919-63-1] $C_{12}H_{14}O_6$ mol.wt. 254.24



Syntheses

-Preparation by reaction of acetic anhydride with 3,6-dihydroxy-2,4-dimethoxyacetophenone in the presence of sodium acetate at 60° [1303] [1309], (80%) [1303].
-Preparation by Fries rearrangement of 2,6-dimethoxyhydroquinone diacetate with aluminium chloride at 120-125° (80%) [1055].

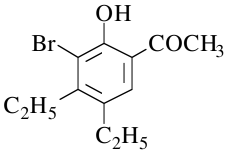
Isolation from natural sources

-From *Euphorbia portulacoides* (Euphorbiaceae) [231].

m.p. 112° [1303], 109-110° [1055];
^1H NMR [1055], IR [1055], UV [1055], MS [1055].

1-(3-Bromo-4,5-diethyl-2-hydroxyphenyl)ethanone

$C_{12}H_{15}BrO_2$ mol.wt. 271.15



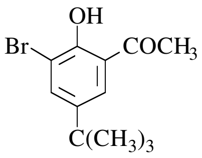
Synthesis

-Preparation by reaction of potassium bromate and bromide on 4,5-diethyl-2-hydroxyacetophenone (quantitative yield) [123].

m.p. 59° [123].

1-[3-Bromo-5-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone

[105340-27-0] $C_{12}H_{15}BrO_2$ mol.wt. 271.15



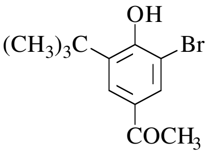
Synthesis

-Preparation by Fries rearrangement of 2-bromo-4-tert-butylphenyl acetate with aluminium chloride without solvent at 110° (54%) [1797].

b.p.$_3$ 142° [1797].

1-[3-Bromo-5-(1,1-dimethylethyl)-4-hydroxyphenyl]ethanone

[153356-10-6] $C_{12}H_{15}BrO_2$ mol.wt. 271.15

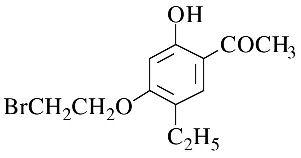


Synthesis

-Refer to: [1916] (Japanese patent).

1-[4-(2-Bromoethoxy)-5-ethyl-2-hydroxyphenyl]ethanone

[117706-54-4] $C_{12}H_{15}BrO_3$ mol.wt. 287.15



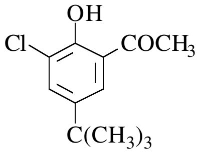
Synthesis

-Preparation by reaction of 2-bromoethyl bromide on 5-ethyl-2,4-dihydroxyacetophenone with potassium carbonate and potassium iodide at reflux (43%) [256] [257].

m.p. 58-59° [256] [257]; ^{1}H NMR [256] [257].

1-[3-Chloro-5-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone

$C_{12}H_{15}ClO_2$ mol.wt. 226.70



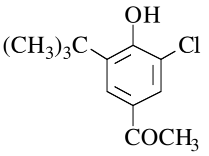
Synthesis

-Preparation by Fries rearrangement of 4-tert-butyl-2-chlorophenyl acetate with aluminium chloride at 110-130° (82-85%) [1785] [1801].

b.p.$_{33}$ 142° [1801].

1-[3-Chloro-5-(1,1-dimethylethyl)-4-hydroxyphenyl]ethanone

[153356-01-5] $C_{12}H_{15}ClO_2$ mol.wt. 226.70

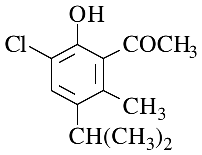


Synthesis

-Refer to: [1916] (Japanese patent).

1-[3-Chloro-2-hydroxy-6-methyl-5-(1-methylethyl)phenyl]ethanone

$C_{12}H_{15}ClO_2$ mol.wt. 226.70



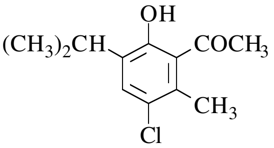
Synthesis

-Preparation by reaction of acetyl chloride on 2-chloro-5-methyl-4-isopropylanisole with aluminium chloride in carbon disulfide at r.t. (35%) [1526].

colourless oil [1526]; b.p.$_{12}$ 142° [1526].

1-[3-Chloro-6-hydroxy-2-methyl-5-(1-methylethyl)phenyl]ethanone

$C_{12}H_{15}ClO_2$ mol.wt. 226.70



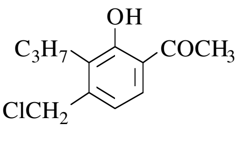
Syntheses

-Preparation by Fries rearrangement of 4-chloro-5-methyl-2-isopropylphenyl acetate with aluminium chloride at 155° [991].
-Also obtained by reaction of acetyl chloride on 4-chloro-5-methyl-2-isopropylanisole with aluminium chloride in carbon disulfide at r.t. (17%) [1524].

b.p.$_3$ 127-135° [991], b.p.$_{21}$ 151-152° [1524].

1-[4-(Chloromethyl)-2-hydroxy-3-propylphenyl]ethanone

[97582-36-0] $C_{12}H_{15}ClO_2$ mol.wt. 226.70



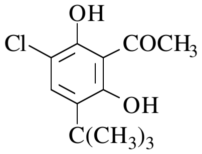
Syntheses

-Preparation by reaction of ethyl chloroformate with 4-(dimethylaminomethyl)-2-hydroxy-3-propylacetophenone in toluene (68-82%) [529] [530].
-Also refer to: [1173] [1174].

m.p. 55-57° [530]; b.p.$_{0.2}$ 105-125° [529]; ^{1}H NMR [529], IR [529].

1-[3-Chloro-5-(1,1-dimethylethyl)-2,6-dihydroxyphenyl]ethanone

[120034-10-8] $C_{12}H_{15}ClO_3$ mol.wt. 242.70

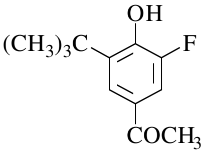


Synthesis

-Preparation by reaction of tert-butyl chloride with 3-chloro-2,6-dihydroxyacetophenone in the presence of sulfuric acid [93] [1067].

1-[3-(1,1-Dimethylethyl)-5-fluoro-4-hydroxyphenyl]ethanone

[153356-03-7] $C_{12}H_{15}FO_2$ mol.wt. 210.25

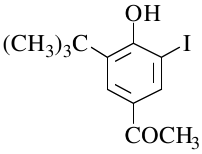


Synthesis

-Refer to: [1916] (Japanese patent).

1-[3-(1,1-Dimethylethyl)-4-hydroxy-5-iodophenyl]ethanone

[153356-02-6] $C_{12}H_{15}IO_2$ mol.wt. 318.15

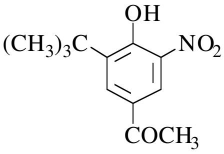


Synthesis

-Refer to: [1916] (Japanese patent).

1-[3-(1,1-Dimethylethyl)-4-hydroxy-5-nitrophenyl]ethanone

[153356-04-8] $C_{12}H_{15}NO_4$ mol.wt. 237.26

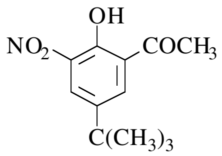


Synthesis

-Refer to: [1916] (Japanese patent).

1-[5-(1,1-Dimethylethyl)-2-hydroxy-3-nitrophenyl]ethanone

[100245-06-5] $C_{12}H_{15}NO_4$ mol.wt. 237.26



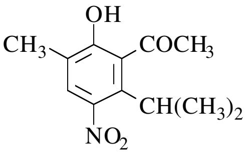
Synthesis

-Obtained (poor yield) by nitration of 5-tert-butyl-2-hydroxyacetophenone at -20° using standard reagents (2%) [620].

m.p. 80-81° [620].

1-[2-Hydroxy-3-methyl-6-(1-methylethyl)-5-nitrophenyl]ethanone

$C_{12}H_{15}NO_4$ mol.wt. 237.26



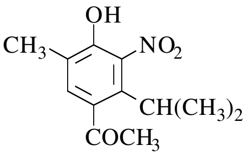
Synthesis

-Preparation by reaction of nitric acid (d = 1.4) on 2-hydroxy-3-methyl-6-isopropylacetophenone in acetic acid between -5° and 0° (67%) [903].

m.p. 151° [903].

1-[4-Hydroxy-5-methyl-2-(1-methylethyl)-3-nitrophenyl]ethanone

$C_{12}H_{15}NO_4$ mol.wt. 237.26



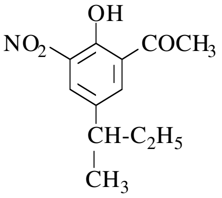
Synthesis

-Preparation by reaction of nitric acid (d = 1.4) on 4-hydroxy-5-methyl-2-isopropylacetophenone in acetic acid at -5° (69%) [902].

m.p. 157° [902].

1-[2-Hydroxy-5-(1-methylpropyl)-3-nitrophenyl]ethanone

[84942-36-9] $C_{12}H_{15}NO_4$ mol.wt. 237.26



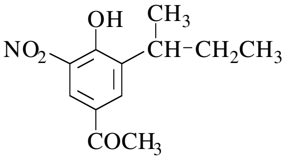
Synthesis

-Preparation by reaction of 100% nitric acid on 5-sec-butyl-2-hydroxyacetophenone in acetic acid at r.t. (89%) [318].

b.p.$_{0.05}$ 137-139° [318].

1-[4-Hydroxy-3-(1-methylpropyl)-5-nitrophenyl]ethanone

[150313-75-0] $C_{12}H_{15}NO_4$ mol.wt. 237.26

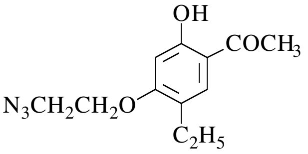


Synthesis

-Refer to: [1243].

1-[4-(2-Azidoethoxy)-5-ethyl-2-hydroxyphenyl]ethanone

[117706-27-1] $C_{12}H_{15}N_3O_3$ mol.wt. 249.27



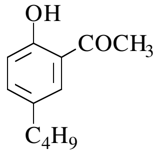
Synthesis

-Preparation by reaction of sodium azide with 4-(2-bromoethoxy)-5-ethyl-2-hydroxyacetophenone in N,N-dimethylformamide at r.t. [256] [257].

^{1}H NMR [256] [257], MS [256] [257].

1-(5-Butyl-2-hydroxyphenyl)ethanone

[50743-14-1] $C_{12}H_{16}O_2$ mol.wt. 192.26



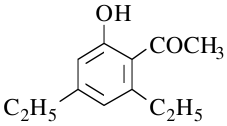
Syntheses

-Preparation by Fries rearrangement of p-butylphenyl acetate with aluminium chloride at 130° (80%) [1335].
-Preparation by reaction of acetyl chloride on 4-butylphenol with aluminium chloride in ethylene dichloride at 110-120° (63%) [1033].

oil [1335]; b.p.$_{1.5}$ 105-109° [1335], b.p.$_4$ 119-123° [1033].

1-(2,4-Diethyl-6-hydroxyphenyl)ethanone

$C_{12}H_{16}O_2$ mol.wt. 192.26



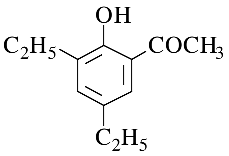
Synthesis

-Preparation by Fries rearrangement of 3,5-diethylphenyl acetate with aluminium chloride [102], between 120° and 150° (quantitative yield) [123].

b.p.$_{12}$ 140° [102].

1-(3,5-Diethyl-2-hydroxyphenyl)ethanone

$C_{12}H_{16}O_2$ mol.wt. 192.26



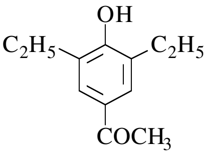
Synthesis

-Preparation by Fries rearrangement of 2,4-diethylphenyl acetate with aluminium chloride (67%) [102].

b.p.$_{12}$ 138-140° [102].

1-(3,5-Diethyl-4-hydroxyphenyl)ethanone

$C_{12}H_{16}O_2$ mol.wt. 192.26



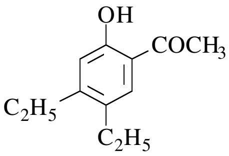
Synthesis

-Preparation by Fries rearrangement of 2,6-diethylphenyl acetate with aluminium chloride (60%) [102].

m.p. 92-92°5 [102].

1-(4,5-Diethyl-2-hydroxyphenyl)ethanone

[56394-40-2] $C_{12}H_{16}O_2$ mol.wt. 192.26



Syntheses

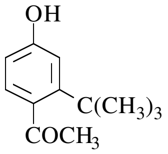
-Preparation by Fries rearrangement of 3,4-diethylphenyl acetate with aluminium chloride without solvent at 120-150° (90 to 100%) [123] [970].

-Also obtained by isomerization of 2,4-diethyl-6-hydroxyacetophenone by heating with aluminium chloride without solvent between 140-180° (quantitative yield) [123].

b.p.$_{0.75}$ 134-137° [970].

1-[2-(1,1-Dimethylethyl)-4-hydroxyphenyl]ethanone

[155982-91-5] $C_{12}H_{16}O_2$ mol.wt. 192.26



Syntheses

-Preparation from 4-hydroxyacetophenone by reaction,

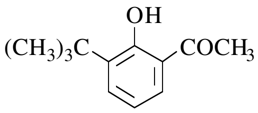
*with isobutylene in the presence of sulfuric acid in autoclave at 65° [1279];

*with tert-butyl chloride in the presence of aluminium chloride [1279].

crystalline compound [1279].

1-[3-(1,1-Dimethylethyl)-2-hydroxyphenyl]ethanone

[24242-55-5] $C_{12}H_{16}O_2$ mol.wt. 192.26



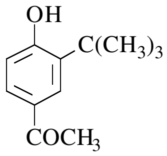
Syntheses

-Obtained by UV light irradiation of 2-tert-butylphenyl acetate in benzene (26%) [1188] [1189].
-Also obtained (by-product) by reaction of acetyl chloride on bromomagnesium 2-tert-butylphenolate in toluene at r.t. (< 3%) [1549].

pale yellow oil [1188] [1189] [1549]; b.p.$_5$ 87° [1189];
^{1}H NMR [1189] [1549], IR [1189] [1549], MS [1549].

1-[3-(1,1-Dimethylethyl)-4-hydroxyphenyl]ethanone

[16928-01-1] $C_{12}H_{16}O_2$ mol.wt. 192.26



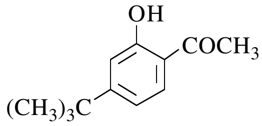
Syntheses

-Obtained by UV light irradiation of,
*3,5-di-tert-butyl-4-hydroxyacetophenone in cyclohexane solution (photochemical partial dealkylation) (> 95%) [1188] [1189];
*2-tert-butylphenyl acetate in benzene solution (photo-Fries rearrangement) (24%) [1188] [1189].

m.p. 175-176° [1188] [1189]; ^{1}H NMR [1188] [1189], IR [1189].

1-[4-(1,1-Dimethylethyl)-2-hydroxyphenyl]ethanone

[113027-08-0] $C_{12}H_{16}O_2$ mol.wt. 192.26

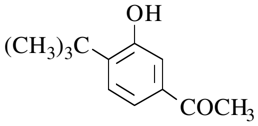


Syntheses

-Obtained by Fries rearrangement of 3-tert-butylphenyl acetate,
*in the presence of hafnium triflate in 12 M lithium perchlorate in nitromethane at 50° (60%) [1002];
*in the presence of aluminium chloride without solvent at 145° (68%) [1634].
-Also obtained by Friedel-Crafts acylation of 3-tert-butylphenol with acetyl chloride in the presence of hafnium triflate in 12 M lithium perchlorate in nitromethane (76%) [1002].
-Also obtained by acylation of 3-tert-butylphenol with acetic acid in the presence of hafnium triflate in 12 M lithium perchlorate in nitromethane at 50° (66%) [1003].
-Also refer to: [1310] (Japanese patent).

1-[4-(1,1-Dimethylethyl)-3-hydroxyphenyl]ethanone

[18606-87-6] $C_{12}H_{16}O_2$ mol.wt. 192.26



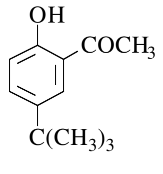
Synthesis

-Preparation by diazotization of 3-amino-4-tert-butylacetophenone, followed by hydrolysis of the diazonium salt obtained [1223].

m.p. 127° [1223].

1-[5-(1,1-Dimethylethyl)-2-hydroxyphenyl]ethanone

[57373-81-6] $C_{12}H_{16}O_2$ mol.wt. 192.26



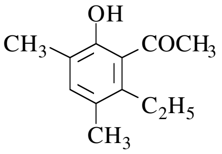
Syntheses

-Preparation by reaction of acetyl chloride on 4-tert-butylanisole with aluminium chloride,
*in methylene chloride, first at 0°, then at r.t. (55%) [863];
*in ethylene dichloride, followed by demethylation of the acylanisole obtained with 4% hydrobromic acid in refluxing acetic acid (47-52%) [1906].
-Also obtained by Friedel-Crafts acylation of 4-tert-butylphenol with acetic anhydride in nitrobenzene in the presence of aluminium chloride at 60° (30%) [653].
-Preparation by Fries rearrangement of 4-tert-butylphenyl acetate with aluminium chloride [789] [1583] [1842] [1906],
*without solvent at 120° (57%) [1583];
*in 1,2,3-trichloropropane at 120° (60%) [1842] or in boiling nitroethane (22%) [789].
-Preparation by Fries rearrangement of 4-tert-butylphenyl acetate in methylene chloride in the presence of zirconium chloride at r.t. for 48 h (52%). The same reaction performed in a simple ultrasound cleaning bath at r.t. for 10 h leads to 78% yield [748].
-Also obtained *via* an intermolecular photo-Fries rearrangement, by irradiation of a solution of pinacolone and 4-tert-butylphenol in benzene for 5 h (42%) [898].
-Also obtained by reaction of aluminium chloride on 4-(1,1,3,3-tetramethylbutyl)phenyl acetate at 120°, in 1,2,3-trichloropropane (60%) [1842] or in 1,1,2,2-tetrachloroethane (36%) [1842].

m.p. 26° [653];
b.p.$_2$ 105-106° [789], b.p.$_5$ 122-123° [789], b.p.$_{12}$ 130° [1583];
^{1}H NMR [863], IR [863].

1-(2-Ethyl-6-hydroxy-3,5-dimethylphenyl)ethanone

$C_{12}H_{16}O_2$ mol.wt. 192.26

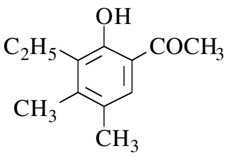


Synthesis

-Obtained (by-product) by Fries rearrangement of 5-ethyl-2,4-dimethylphenyl acetate with aluminium chloride at 130-140° [102].

1-(3-Ethyl-2-hydroxy-4,5-dimethylphenyl)ethanone

$C_{12}H_{16}O_2$ mol.wt. 192.26

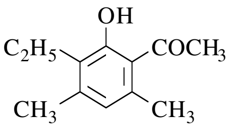


Synthesis

-Obtained (by-product) by heating some esters with aluminium chloride. There is simultaneously displacement and rearrangement of alkyl groups during the Fries reaction from 2-ethyl-4,6-dimethylphenyl acetate or from 2-ethyl-4,5-dimethylphenyl acetate [102].

1-(3-Ethyl-2-hydroxy-4,6-dimethylphenyl)ethanone

[69051-59-8] $C_{12}H_{16}O_2$ mol.wt. 192.26

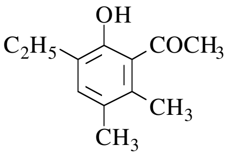


Synthesis

-Preparation by Fries rearrangement of 2-ethyl-3,5-dimethylphenyl acetate [255].

1-(3-Ethyl-2-hydroxy-5,6-dimethylphenyl)ethanone

$C_{12}H_{16}O_2$ mol.wt. 192.26



Syntheses

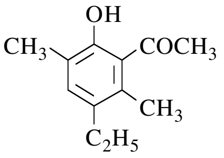
-Preparation by reaction of acetyl chloride on 2-ethyl-4,5-dimethylanisole with aluminium chloride in boiling carbon disulfide (50%) [102].

-Preparation by heating 2-ethyl-4,5-dimethylphenyl acetate with aluminium chloride (major product) [102].

b.p.$_{11}$ 143-145° [102], b.p.$_{12}$ 145-147° [102].

1-(3-Ethyl-6-hydroxy-2,5-dimethylphenyl)ethanone

$C_{12}H_{16}O_2$ mol.wt. 192.26



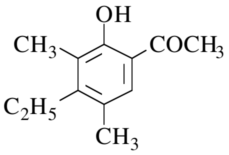
Synthesis

-Obtained by Fries rearrangement of 4-ethyl-2,5-dimethylphenyl acetate with aluminium chloride at 130° for 30 min (57%) [1527].

pale yellow oil [1527]; b.p.$_{16}$ 156-158° [1527]; n_D^{22} = 1.5410 [1527]; IR [1527].

1-(4-Ethyl-2-hydroxy-3,5-dimethylphenyl)ethanone

$C_{12}H_{16}O_2$ mol.wt. 192.26



Syntheses

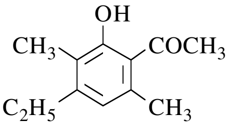
-Obtained by heating some esters* with aluminium chloride. There is simultaneously displacement and rearrangement of alkyl groups during the Fries reaction,

*2-ethyl-4,6-dimethylphenyl acetate (major product) [102];
*4-ethyl-2,5-dimethylphenyl acetate (75%) [101];
*4-ethyl-2,6-dimethylphenyl acetate (by-product) [102];
*5-ethyl-2,4-dimethylphenyl acetate (major product) [102].

m.p. 52-53° [102];
b.p.$_{12}$ 145-147° [102], b.p.$_{12}$ 146-152° [101], b.p.$_{11}$ 153-155° [102].

1-(4-Ethyl-2-hydroxy-3,6-dimethylphenyl)ethanone

$C_{12}H_{16}O_2$ mol.wt. 192.26



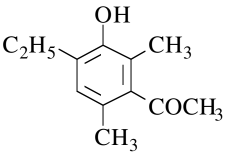
Synthesis

-Obtained by oxidation of 6-ethyl-2,3,4,7-tetramethylbenzofuran with chromium trioxide in acetic acid at 50° for 30 min, followed by saponification of the resulting keto ester with potassium hydroxide in boiling aqueous ethanol for 2 h (40%) [1527].

b.p.$_{20}$ 165-167° [1527]; n_D^{22} = 1.562 [1527]; IR [1527].

1-(4-Ethyl-3-hydroxy-2,6-dimethylphenyl)ethanone

$C_{12}H_{16}O_2$ mol.wt. 192.26



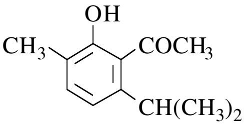
Synthesis

-Obtained by reaction of acetyl chloride on 6-ethyl-2,4-dimethylanisole with aluminium chloride in boiling carbon disulfide [102].

b.p.$_{15}$ 178-182° [102].

1-[2-Hydroxy-3-methyl-6-(1-methylethyl)phenyl]ethanone

[162853-19-2] $C_{12}H_{16}O_2$ mol.wt. 192.26



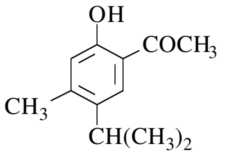
Syntheses

-Preparation by Fries rearrangement of carvacryl acetate,
*without solvent at 120°, with aluminium chloride (80-86%) [1584] [1585], with titanium tetrachloride (86%) [1585], with stannic chloride (80%) [1585] or with zinc chloride (60%) [1585];
*with aluminium chloride in nitrobenzene at 60° (67%) [1584], in toluene or xylene at 100° (58-61%) [1584].
-Preparation by reaction of acetyl chloride on carvacrol with aluminium chloride,
*in nitrobenzene at r.t. (49%) [903];
*in nitrobenzene in the presence of phosphorous oxychloride and magnesium chloride at r.t. (17%) [903].
-Also obtained by UV irradiation of a carvacryl acetate solution in methanol/water (2:1) at 254 nm at r.t. under nitrogen atmosphere (51%) [1703].

viscous oil [1703]; m.p. 100-101° [903];
^{1}H NMR [1703], ^{13}C NMR [1703], IR [1703], MS [1703].

1-[2-Hydroxy-4-methyl-5-(1-methylethyl)phenyl]ethanone

[52774-08-0] $C_{12}H_{16}O_2$ mol.wt. 192.26



Syntheses

-Preparation by Fries rearrangement of 3-methyl-4-isopropylphenyl acetate, with titanium tetrachloride in nitromethane at 20° (95%) [1162] or with aluminium chloride at 125° (11%) [1525] [1526].

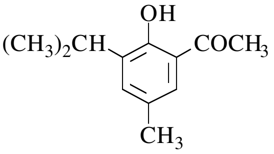
-Preparation by reaction of acetic anhydride on 3-methyl-4-isopropylphenol (p-thymol) with 70% perchloric acid at 125-135° (32%) [548].

N.B.: All the results of references [548] [1525] [1526] were erroneous. Only the Fries rearrangement using titanium tetrachloride leads to the expected ketone and with a good yield [1162]. The ^1H NMR spectra confirms the above structure [1162]. In addition, the reported melting point (29°) [1162] is in good agreement with those generally measured for o-hydroxyketones (below 80°) compared to those of p-hydroxyketones which are considerably higher (usually 120-200°).

m.p. 122°5 [1525] [1526], 110-115° [548], 29° [1162];
b.p.$_{17}$ 153° [1162], b.p.$_{15}$ 188-192° [1526];
^1H NMR [1162], (Sadtler: standard n° 52738 M);
IR [1162] [1526], (Sadtler: standard n° 79797 K); UV [1162], MS [1162].

1-[2-Hydroxy-5-methyl-3-(1-methylethyl)phenyl]ethanone

[35158-31-7] $C_{12}H_{16}O_2$ mol.wt. 192.26



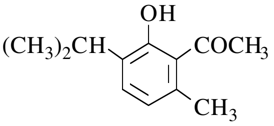
Synthesis

-Preparation by reaction of ethyl acetoacetate with 2,5-dimethyl-2-hexenal in the presence of pyridine and piperidine as catalysts in refluxing benzene [940] [941] [942].

yellow oil [940] [941] [942]; b.p.$_{1-2}$ 70-80° [940] [941] [942];
IR [940] [941] [942], UV [940] [941] [942], MS [940] [941] [942].

1-[2-Hydroxy-6-methyl-3-(1-methylethyl)phenyl]ethanone

[105337-34-6] $C_{12}H_{16}O_2$ mol.wt. 192.26



Syntheses

-Preparation by reaction of acetic acid on thymol with aluminium chloride at reflux (80%) [1699].

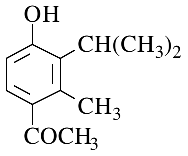
-Preparation by Fries rearrangement of thymyl acetate,
*without solvent at 120° with titanium tetrachloride (90%) [1585], with aluminium chloride (84-86%) [1584] [1585], with stannic chloride (84%) [1585] or with zinc chloride (62%) [1585];
*with aluminium chloride in nitrobenzene (68%) [1584], in toluene or xylene (59-60%) [1584].

-Also obtained by photo-Fries rearrangement of thymyl acetate in dilute methanol under nitrogen atmosphere at r.t. (48%) [1703].

viscous oil [1703]; b.p.$_{12}$ 119° [1699];
^1H NMR [1703], ^{13}C NMR [1703], IR [1703], MS [1703].

1-[4-Hydroxy-2-methyl-3-(1-methylethyl)phenyl]ethanone

$C_{12}H_{16}O_2$ mol.wt. 192.26



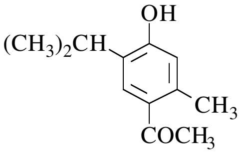
Syntheses

-Preparation by demethylation of 4-methoxy-2-methyl-3-isopropylacetophenone with boiling pyridinium chloride (33%) [967].
-Also obtained by Fries rearrangement of 3-methyl-2-isopropylphenyl acetate with aluminium chloride in nitrobenzene at r.t. (10%) [967].

m.p. 128° [967].

1-[4-hydroxy-2-methyl-5-(1-methylethyl)phenyl]ethanone

[37847-35-1] $C_{12}H_{16}O_2$ mol.wt. 192.26



Syntheses

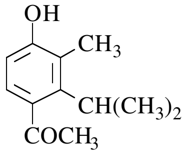
-Preparation by reaction of acetyl chloride on thymol, with aluminium chloride, in nitrobenzene [187] [188] [459] [1218] [1219] [1513], (97-100%) [187] [188] [459], (75%) [1512] or with zinc chloride [579] [580].
-Preparation by Fries rearrangement of thymyl acetate in nitrobenzene,
*with aluminium chloride, at 40-47° (87-95%) [648] [675] [1462] [1512] [1725], (65-75%) [1727], (51-55%) [676] or at 20-25° (80-87%) [1512] [1585];
*at 25°, with titanium tetrachloride (88%), stannic chloride (78%) or zinc chloride (58%) [1585].
-Preparation from 4-methoxy-2-methyl-5-isopropylacetophenone by demethylation with pyridinium chloride at reflux (73-75%) [1517] [1520] [1524].
-Also obtained (by-product) by reaction of aluminium chloride on p-thymyl acetate without solvent at 140° (15%) [1523].
-Also obtained by UV light irradiation of thymyl acetate in methanol at 25° (41%) [1389].
-Also obtained (by-product) by reaction of acetyl chloride on 5-methyl-2-isopropylanisole with aluminium chloride in carbon disulfide at r.t. (6%) [1520].
-Also obtained by irradiation of thymyl acetate in methanol at 254 nm under nitrogen atmosphere at r.t. (24%) [1703].

m.p. 152-154° [1703], 135° [1389], 125° [459] [675] [676] [1512] [1513] [1517] [1520], 122°5-125° [648] [1725], 122°5 [1523], 122° [1462]. There is a discrepancy between the different melting points indicated in literature.

b.p.$_{18}$ 204-207° [1517], b.p.$_{0.8}$ 204-207° [1520]; ^{1}H NMR [1389] [1462] [1703], ^{13}C NMR [1703], IR [1389] [1462] [1703], MS [1462] [1703].

1-[4-Hydroxy-3-methyl-2-(1-methylethyl)phenyl]ethanone

[61405-65-0] $C_{12}H_{16}O_2$ mol.wt. 192.26

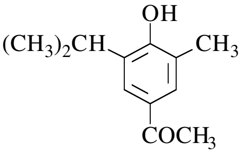


Synthesis

-Refer to: [1239] (Japanese patent).

1-[4-Hydroxy-3-methyl-5-(1-methylethyl)phenyl]ethanone

[713-23-5] $C_{12}H_{16}O_2$ mol.wt. 192.26

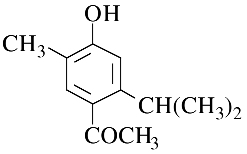


Synthesis

-Refer to: [1781] (Japanese patent).

1-[4-Hydroxy-5-methyl-2-(1-methylethyl)phenyl]ethanone

[37847-37-3] $C_{12}H_{16}O_2$ mol.wt. 192.26



Syntheses

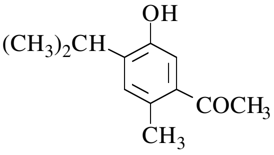
-Preparation by reaction of acetyl chloride on carvacrol with aluminium chloride in nitrobenzene,
*at r.t. [459] [899] [900] [902] [967], (71%) [459], (52%) [900] and (31-39%) [899] [902];
*at 50° (80-90%) [1508].

-Preparation by Fries rearrangement of 2-methyl-5-isopropylphenyl acetate in nitrobenzene at r.t.,
*with aluminium chloride (84-90%) [1512] [1585], (20%) [902];
*with stannic chloride or titanium tetrachloride (86%) [1585];
*with zinc chloride (58%) [1585].
-Preparation by reaction of pyridinium chloride on 4-methoxy-5-methyl-2-isopropylacetophenone [967].
-Also obtained by irradiation of carvacryl acetate in methanol at 254 nm under nitrogen atmosphere at r.t. (15%) [1703].

m.p. 127° [902], 120° [1508] [1512], 101° [459] [899], 86-88° [1703].
There is a discrepancy between the different melting points indicated in literature.
^{1}H NMR [1703], ^{13}C NMR [1703], IR [1703], MS [1703].

1-[5-Hydroxy-2-methyl-4-(1-methylethyl)phenyl]ethanone

[126570-37-4] $C_{12}H_{16}O_2$ mol.wt. 192.26



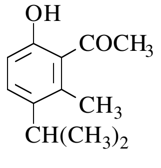
Synthesis

-Preparation by reaction of acetyl chloride with isothymol methyl ether in the presence of aluminium chloride in nitrobenzene at r.t. [1462].

m.p. 106-107° [1462]; ^{1}H NMR [1462], IR [1462].

1-[6-Hydroxy-2-methyl-3-(1-methylethyl)phenyl]ethanone

[105337-35-7] $C_{12}H_{16}O_2$ mol.wt. 192.26



Syntheses

-Preparation by reaction of aluminium chloride on 3-tert-butyl-2-hydroxy-6-methyl-5-isopropylacetophenone in nitromethane at 20° (84%) [1162].

-Claimed to be prepared,

*by Fries rearrangement of 3-methyl-4-isopropylphenyl acetate with aluminium chloride, without solvent at 90° (85%) [1523] or at 125° (43%) [1526] and in nitrobenzene at 90° (> 50%) [1523];

*by reaction of acetyl chloride on 3-methyl-4-isopropylanisole with aluminium chloride in boiling carbon disulfide (41%) [1525];

*by reaction of acetyl chloride on 3-methyl-4-isopropylphenetole with aluminium chloride in carbon disulfide at r.t. (37%) [1526];

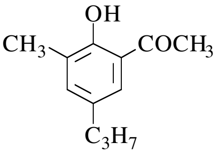
*by heating 6-methoxy-2-methyl-3-isopropylacetophenone with pyridinium chloride at reflux [1525].

N.B.: All the results of references [1523] [1525] [1526] were erroneous. Only the first route was correct. The ^1H NMR spectra confirms the above structure [1162].

m.p. 70° [1162]; amber-coloured liquid [1525] [1526];
b.p.$_{14}$ 150° [1526], b.p.$_{19}$ 153-154° [1525]; $n_D^{20} = 1.5410$ [1525] [1526];
^1H NMR [1162], (Sadtler: standard n° 52739 M);
IR [1162] [1526], (Sadtler: standard n° 79798 K);
UV [1162], MS [1162].

1-(2-Hydroxy-3-methyl-5-propylphenyl)ethanone

$C_{12}H_{16}O_2$ mol.wt. 192.26



Syntheses

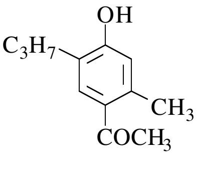
-Preparation by Fries rearrangement of 2-methyl-4-propylphenyl acetate with aluminium chloride without solvent at 100-110° [100].

-Also obtained by reaction of aluminium chloride on 2-ethyl-6-methyl-4-propylphenyl acetate, with elimination of ethyl group (8%) [100].

b.p.$_{12}$ 136° [100].

1-(4-Hydroxy-2-methyl-5-propylphenyl)ethanone

$C_{12}H_{16}O_2$ mol.wt. 192.26



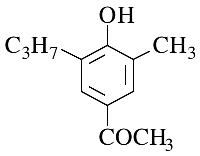
Synthesis

-Preparation by Fries rearrangement of 5-methyl-2-propylphenyl acetate with aluminium chloride in nitrobenzene at 20° (83%) [1512].

m.p. 113° [1512]; b.p.$_{18}$ 194° [1512].

1-(4-Hydroxy-3-methyl-5-propylphenyl)ethanone

$C_{12}H_{16}O_2$ mol.wt. 192.26



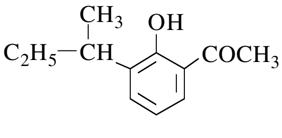
Syntheses

-Preparation by Fries rearrangement of 2-methyl-6-propylphenyl acetate with aluminium chloride without solvent at 130-140° [100].
-Also obtained by reaction of aluminium chloride on 4-ethyl-2-methyl-6-propylphenyl acetate, with elimination of ethyl group (12%) [100].

m.p. 101° [100].

1-[2-Hydroxy-3-(1-methylpropyl)phenyl]ethanone

$C_{12}H_{16}O_2$ mol.wt. 192.26



Synthesis

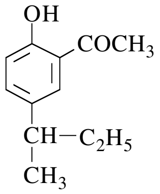
-Obtained (poor yield) by reaction of acetyl chloride with a suspension of aluminium o-sec-butylphenoxide in benzene in the presence of aluminium chloride, first at r.t. for 12 h, then on a water bath for 2 h (11%) [1018].

m.p. 121° [1018].

N.B.: This o-hydroxyketone should be liquid. The authors probably intended to write b.p.$_3$ 121° instead of m.p. 121°. This b.p. would be in agreement with those of the other homologous o-hydroxyketones, that have been prepared by the authors [1018].

1-[2-Hydroxy-5-(1-methylpropyl)phenyl]ethanone

[84942-39-2] $C_{12}H_{16}O_2$ mol.wt. 192.26



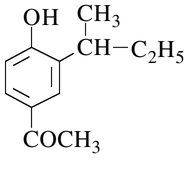
Syntheses

-Preparation by reaction of acetyl chloride with a suspension of aluminium p-sec-butylphenoxide in benzene in the presence of aluminium chloride, first at r.t. for 12 h, then on a water bath for 2 h (75%) [1018].
-Preparation by Fries rearrangement of 4-sec-butylphenyl acetate with aluminium chloride at 120° (84%) [318].

b.p.$_{0.15}$ 86-87° [318], b.p.$_3$ 115-119° [1018].

1-[4-Hydroxy-3-(1-methylpropyl)phenyl]ethanone

$C_{12}H_{16}O_2$ mol.wt. 192.26



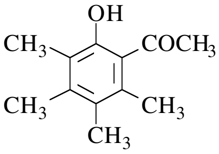
Synthesis

-Obtained (poor yield) by reaction of acetyl chloride with a suspension of aluminium o-sec-butylphenoxide in benzene in the presence of aluminium chloride, first at r.t. for 12 h, then on a water bath for 2 h (8%) [1018].

m.p. 123° [1018].

1-(2-Hydroxy-3,4,5,6-tetramethylphenyl)ethanone

[118078-21-0] $C_{12}H_{16}O_2$ mol.wt. 192.26

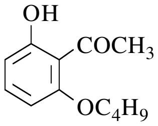


Synthesis

-Preparation by acetylation of 2,3,4,5-tetramethylphenol [1927] according to [1891].

1-(2-Butoxy-6-hydroxyphenyl)ethanone

[63438-68-6] $C_{12}H_{16}O_3$ mol.wt. 208.26



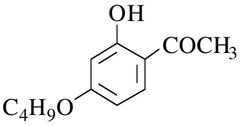
Synthesis

-Obtained by reaction of n-butyl iodide with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone (40%) [237].

m.p. 59-60° [237].

1-(4-Butoxy-2-hydroxyphenyl)ethanone

[57221-60-0] $C_{12}H_{16}O_3$ mol.wt. 208.26



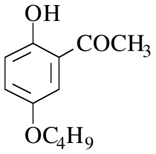
Synthesis

-Preparation by reaction of butyl iodide on resacetophenone with potassium hydroxide in boiling ethanol [364] [578], (14%) [364].

m.p. 43° [364], 42° [578].

1-(5-Butoxy-2-hydroxyphenyl)ethanone

[152810-06-5] $C_{12}H_{16}O_3$ mol.wt. 208.26

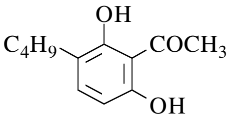


Synthesis

-Refer to: [1666].

1-(3-Butyl-2,6-dihydroxyphenyl)ethanone

[63411-82-5] $C_{12}H_{16}O_3$ mol.wt. 208.26



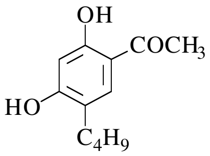
Synthesis

-Preparation from 2,6-dihydroxyacetophenone according to the method [1532], (70%) [237].

m.p. 72-73° [237].

1-(5-Butyl-2,4-dihydroxyphenyl)ethanone

[81468-73-7] $C_{12}H_{16}O_3$ mol.wt. 208.26



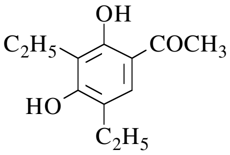
Syntheses

-Preparation by reaction of acetonitrile on 4-n-butylresorcinol (Hoesch reaction) (80%) [1277].
-Preparation from 5-n-butyl-2,4-dimethoxyacetophenone by demethylation with boron tribromide in methylene chloride at r.t. (64%) [256] [257] [777].
-Preparation by reaction of acetic acid on 4-n-butylresorcinol with zinc chloride (Nencki reaction) [506] [930].

m.p. 95-96° [1277], 95° [506].

1-(3,5-Diethyl-2,4-dihydroxyphenyl)ethanone

$C_{12}H_{16}O_3$ mol.wt. 208.26



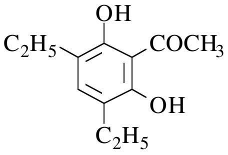
Synthesis

-Obtained by reaction of acetic acid with 2,4-diethylresorcinol in the presence of zinc chloride at 140° for 15 min (Nencki reaction) [1095].

m.p. 115° [1095].

1-(3,5-Diethyl-2,6-dihydroxyphenyl)ethanone

[37467-65-5] $C_{12}H_{16}O_3$ mol.wt. 208.26



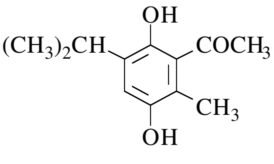
Synthesis

-Preparation by reaction of acetic anhydride with 4,6-diethylresorcinol in the presence of boron trifluoride-acetic acid complex for 2 h at 100° [343].

m.p. 76-77° [343].

1-[2,5-Dihydroxy-6-methyl-3-(1-methylethyl)phenyl]ethanone

$C_{12}H_{16}O_3$ mol.wt. 208.26



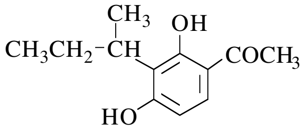
Synthesis

-Obtained by reaction of acetyl chloride on 2-methyl-5-isopropylhydroquinone dimethyl ether with aluminium chloride in carbon disulfide at 35-40° (6%) [1524].

b.p.$_{17}$ 148-149° [1524].

1-[2,4-Dihydroxy-3-(1-methylpropyl)phenyl]ethanone

[79557-74-7] $C_{12}H_{16}O_3$ mol.wt. 208.26



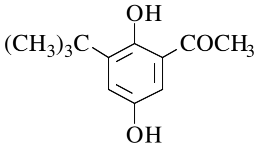
Synthesis

-Preparation by hydrogenation of 2,4-dihydroxy-3-(1-methyl-2-propenyl)acetophenone in ethanol using 5% Pd/C as catalyst [1372].

m.p. 174-175° [1372].

1-[3-(1,1-Dimethylethyl)-2,5-dihydroxyphenyl]ethanone

[35205-23-3] $C_{12}H_{16}O_3$ mol.wt. 208.26



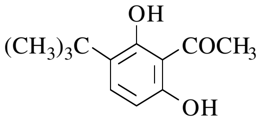
Synthesis

-Obtained (trace) by reaction of di-tert-butyl diperoxyoxalate with tert-butyl-1,4-benzoquinone in acetaldehyde; the solution was kept in the dark at r.t. (< 1%) [300].

m.p. 141-142° [300];
^{1}H NMR [300], IR [300], UV [300].

1-[3-(1,1-Dimethylethyl)-2,6-dihydroxyphenyl]ethanone

[91124-33-3] $C_{12}H_{16}O_3$ mol.wt. 208.26



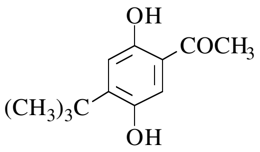
Synthesis

-Preparation by reaction of 2,6-dihydroxyacetophenone with tert-butanol in the presence of concentrated sulfuric acid in benzene at 55° in a sealed tube [1940].

m.p. 183-186° [1940]; ^{1}H NMR [1940].

1-[4-(1,1-Dimethylethyl)-2,5-dihydroxyphenyl]ethanone

[35205-24-4] $C_{12}H_{16}O_3$ mol.wt. 208.26



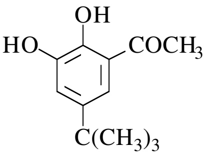
Syntheses

-Preparation by reaction of acetic acid with 2-tert-butylhydroquinone in the presence of boron trifluoride at 80-90° (65%) [1293].
-Preparation by demethylation of 4-tert-butyl-2,5-dimethoxyacetophenone with boron tribromide in methylene chloride at r.t. (58%) [22].
-Also obtained (trace) by reaction of di-tert-butyl diperoxyoxalate with tert-butyl-1,4-benzoquinone in acetaldehyde; the solution was kept in the dark at r.t. (< 1%) [300].
-Also refer to: [634] [1928].

m.p. 195-196°5 [300], 193°5-195°5 [22];
^{1}H NMR [22] [300], IR [22] [300], UV [300], MS [22].

1-[5-(1,1-Dimethylethyl)-2,3-dihydroxyphenyl]ethanone

[84296-64-0] $C_{12}H_{16}O_3$ mol.wt. 208.26



Syntheses

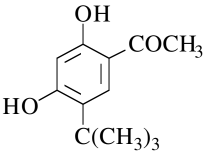
-Obtained by irradiation of a benzene solution of 4-tert-butyl-o-benzoquinone in the presence of a large excess of acetaldehyde (20%) [1758].

-Also obtained by treatment of a benzene solution of 4-tert-butyl-o-benzoquinone and acetaldehyde in the presence of di-tert-butyl diperoxyoxalate at 38° (26%) [1758].

m.p. 82-83° [1758]; ^{1}H NMR [1758], IR [1758].

1-[5-(1,1-Dimethylethyl)-2,4-dihydroxyphenyl]ethanone

[140660-31-7] $C_{12}H_{16}O_3$ mol.wt. 208.26



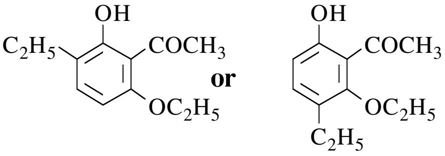
Synthesis

-Preparation by reaction of tert-butyl alcohol with resacetophenone in the presence of zinc chloride at 95° (53%) [777].

oil [777].

1-(6-Ethoxy-3-ethyl-2-hydroxyphenyl)ethanone or 1-(2-Ethoxy-3-ethyl-6-hydroxyphenyl)ethanone

$C_{12}H_{16}O_3$ mol.wt. 208.26



Syntheses

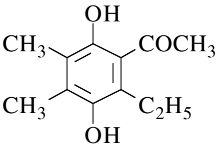
-Obtained by partial ethylation of 2-acetyl-4-ethylresorcinol with diethyl sulfate in refluxing 2 N sodium hydroxide for 30 min [1097].

-Also obtained by ethylation of 2-acetyl-resorcinol [1097].

m.p. 84° [1097].

1-(2-Ethyl-3,6-dihydroxy-4,5-dimethylphenyl)ethanone

[396639-83-1] $C_{12}H_{16}O_3$ mol.wt. 208.26



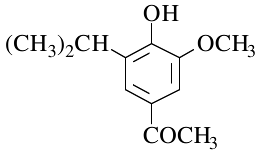
Synthesis

-Obtained by diethylcadmium alkylation of 5-acetyl-2,3-dimethylbenzoquinone (71%) [68].

m.p. 76° [68];
^{1}H NMR [68], ^{13}C NMR [68].

1-[4-Hydroxy-3-methoxy-5-(1-methylethyl)phenyl]ethanone

[133393-99-4] $C_{12}H_{16}O_3$ mol.wt. 208.26

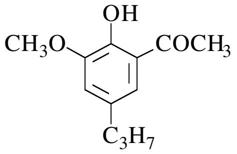


Synthesis

-Preparation from guaiacol by acetylation and isopropylation [1826].

1-(2-Hydroxy-3-methoxy-5-propylphenyl)ethanone

[23343-03-5] $C_{12}H_{16}O_3$ mol.wt. 208.26



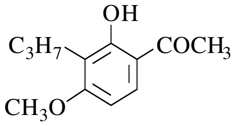
Syntheses

-Preparation by partial demethylation of 2,3-dimethoxy-5-propylacetophenone with aluminium chloride in refluxing methylene chloride (67%) [1216].
-Preparation by catalytic hydrogenation of 5-allyl-2-hydroxy-3-methoxyacetophenone [1212] [1417] in the presence of 5% palladium on barium sulfate (97%) [1417].

m.p. 18-19° [1417], 17-19° [1212]; b.p.$_{0.2}$ 105-120° [1216];
^{1}H NMR [1212] [1216], IR [1212], UV [1212].

1-(2-Hydroxy-4-methoxy-3-propylphenyl)ethanone

[72018-33-8] $C_{12}H_{16}O_3$ mol.wt. 208.26



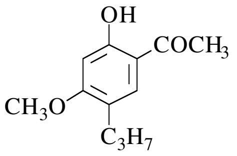
Synthesis not yet described

-Refer to: [43] [44].

N.B.: Pr indicates the *propyl* group -C_3H_7 in Chem. Abstr., **92**, 6368x (1980) and **98**, 54239b (1983), an usual abbreviation. However, in the two references [43] [44], Pr represented the *prenyl* group -$CH_2CH{=}C(CH_3)_2$. Therefore they concern the 2-hydroxy-4-methoxy-3-prenylacetophenone and not the above mentioned 2-hydroxy-4-methoxy-3-propylacetophenone.

1-(2-Hydroxy-4-methoxy-5-propylphenyl)ethanone

[72018-35-0] $C_{12}H_{16}O_3$ mol.wt. 208.26



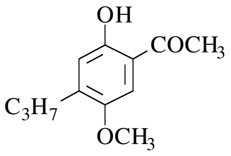
Syntheses

-Preparation by reaction of dimethyl sulfate on 2,4-dihydroxy-5-propylacetophenone with calcinated potassium carbonate in refluxing acetone [930].
-Also refer to: [43] [44].

N.B.: Pr indicates the *propyl* group -C_3H_7 in Chem. Abstr., **92**, 6368x (1980) and **98**, 54239b (1983), an usual abbreviation. However, in the two references [43] [44], Pr represented the *prenyl* group -$CH_2CH=C(CH_3)_2$. Therefore they concern the 2-hydroxy-4-methoxy-5-prenylacetophenone and not the above mentioned 2-hydroxy-4-methoxy-3-propylacetophenone.

1-(2-Hydroxy-5-methoxy-4-propylphenyl)ethanone

$C_{12}H_{16}O_3$ mol.wt. 208.26



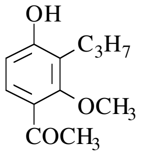
Synthesis

-Preparation by reaction of acetyl chloride on 2-propylhydroquinone dimethyl ether with aluminium chloride in boiling carbon disulfide (69%) [457].

b.p.$_1$ 150-155° [457].

1-(4-Hydroxy-2-methoxy-3-propylphenyl)ethanone

[151027-43-9] $C_{12}H_{16}O_3$ mol.wt. 208.26

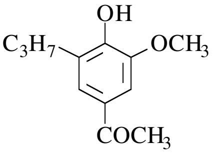


Synthesis

-Refer to: [52] [53].

1-(4-Hydroxy-3-methoxy-5-propylphenyl)ethanone

[54514-40-8] $C_{12}H_{16}O_3$ mol.wt. 208.26

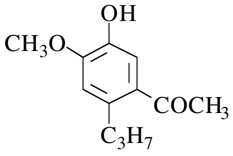


Synthesis

-Refer to: [960] [1783].

1-(5-Hydroxy-4-methoxy-2-propylphenyl)ethanone

[23343-08-0] $C_{12}H_{16}O_3$ mol.wt. 208.26



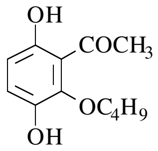
Syntheses

-Preparation by Fries rearrangement of dihydroeugenol acetate with aluminium chloride in nitrobenzene at 5° (13%) [1212].
-Also refer to: [848].

m.p. 68° [1212]; b.p.$_1$ 138° [1212]; ^{1}H NMR [1212], IR [1212], UV [1212].

1-(2-Butoxy-3,6-dihydroxyphenyl)ethanone

[33539-23-0] $C_{12}H_{16}O_4$ mol.wt. 224.26



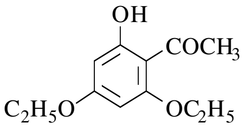
Syntheses

-Easy preparation by reduction of 2-acetyl-3-butoxy-1,4-benzoquinone using conventional methods [587].
-Also obtained in low yield by reaction of 2-acetyl-1,4-benzoquinone with an excess of butanol at r.t., with exclusion of light [587].

m.p. 62°5-63°5 [587]; ^{1}H NMR [587], IR [587].

1-(2,4-Diethoxy-6-hydroxyphenyl)ethanone

[26207-59-0] $C_{12}H_{16}O_4$ mol.wt. 224.26



Syntheses

-Obtained from phloroacetophenone triethyl ether by heating with aluminium chloride [1013].
-Also obtained by reaction of acetonitrile on phloroglucinol diethyl ether (Hoesch reaction) (18%) [494].
-Also obtained by reaction of ethyl iodide [1516] [1550] or diethyl sulfate [964] on phloroacetophenone with potassium carbonate in refluxing acetone (18%) [1516].

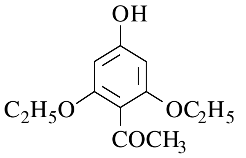
Isolation from natural sources

-By treatment of Sotetsuflavone pentaethyl ether with a methanolic barium hydroxide suspension [964]. Sotetsuflavone was extracted of the plants of Coniferae and allied orders.
-By reaction of Kayaflavone triethyl ether with barium hydroxide octahydrate in refluxing methanol (55%) [966]. Kayaflavone was isolated from dried leaves of *Torreya nucifera*.

m.p. 86-87° [1516], 85° [494] [1013], 83-84° [964], 81-83° [966].

1-(2,6-Diethoxy-4-hydroxyphenyl)ethanone

$C_{12}H_{16}O_4$ mol.wt. 224.26



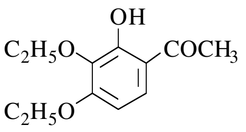
Synthesis

-Preparation by reaction of acetonitrile on phloroglucinol diethyl ether (Hoesch reaction) (29%) [494].

m.p. 186-187° [494].

1-(3,4-Diethoxy-2-hydroxyphenyl)ethanone

[6342-86-5] $C_{12}H_{16}O_4$ mol.wt. 224.26

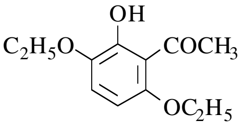


Syntheses

-Refer to: [211] [888] [1599].

1-(3,6-Diethoxy-2-hydroxyphenyl)ethanone

[88771-47-5] $C_{12}H_{16}O_4$ mol.wt. 224.26



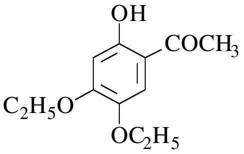
Synthesis

-Preparation by hydrogenolysis procedure on 2-(benzyloxy)-3,6-diethoxyacetophenone with 10% Pd/C as catalyst, and ethanol as solvent at 40° (99%) [502].

m.p. 64° [502]; ^{1}H NMR [502], IR [502].

1-(4,5-Diethoxy-2-hydroxyphenyl)ethanone

[80938-23-4] $C_{12}H_{16}O_4$ mol.wt. 224.26

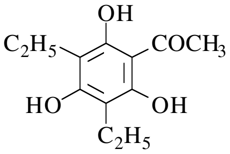


Syntheses

-Refer to: [211] [888].

1-(3,5-Diethyl-2,4,6-trihydroxyphenyl)ethanone

[19687-48-0] $C_{12}H_{16}O_4$ mol.wt. 224.26



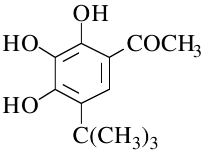
Syntheses

-Preparation by reaction of acetyl chloride with 2,4-diethylphloroglucinol in the presence of aluminium chloride in nitrobenzene (28%) [428].
-Preparation by reaction of acetonitrile on 2,4-diethylphloroglucinol (Hoesch reaction) (39%) [1618].

m.p. 106-109° [428], 102-105° [1618];
^{1}H NMR [428], UV [428] [1618], MS [428].

1-[5-(1,1-Dimethylethyl)-2,3,4-trihydroxyphenyl]ethanone

$C_{12}H_{16}O_4$ mol.wt. 224.26



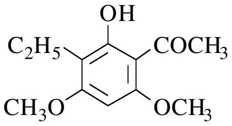
Synthesis

-Preparation by reaction of tert-butyl chloride with gallacetophenone in the presence of ferric chloride in acetic acid and heating on a steam bath (52%) [347].

m.p. 174° [347]; UV [347].

1-(3-Ethyl-2-hydroxy-4,6-dimethoxyphenyl)ethanone

$C_{12}H_{16}O_4$ mol.wt. 224.26



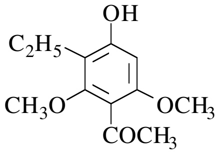
Synthesis

-Preparation by reaction of acetonitrile on 2-ethyl-3,5-dimethoxyphenol (Hoesch reaction) [495] [706], (55%) [706].

m.p. 111° [495], 66-68° [706].

1-(3-Ethyl-4-hydroxy-2,6-dimethoxyphenyl)ethanone

$C_{12}H_{16}O_4$ mol.wt. 224.26



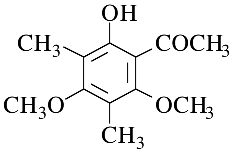
Synthesis

-Obtained (poor yield) by reaction of acetonitrile on 2-ethyl-3,5-dimethoxyphenol (Hoesch reaction) (7%) [706].

m.p. 184-186° [706].

1-(2-Hydroxy-4,6-dimethoxy-3,5-dimethylphenyl)ethanone

[21722-31-6] $C_{12}H_{16}O_4$ mol.wt. 224.26



Syntheses

-Preparation by adding of an ethereal solution of diazomethane to a methanolic solution of phloroacetophenone (25%) [645]; this compound was obtained from 3,5-dimethylphloroacetophenone or from 2,6-dihydroxy-4-methoxy-3,5-dimethylacetophenone in the same conditions [645].

-Also obtained (by-product) from phloroacetophenone by reaction with methyl iodide in the presence of potassium carbonate in refluxing acetone (6%) [1735].

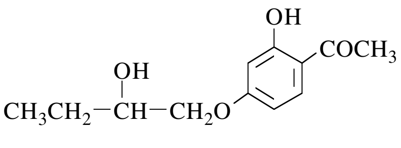
Isolation from natural sources

-By chromatography of Melaleuca cajeputi oil; this oil was obtained from the leaves of *Melaleuca cajeputi* Powell (Myrtaceae) (10%) [1118].

crystalline compound [1118]; m.p. 51-52° [1735], 51° [645];
^{1}H NMR [645] [1118], IR [645] [1118], UV [645] [1118], MS [1118].

1-[2-Hydroxy-4-(2-hydroxybutoxy)phenyl]ethanone

[149454-53-5] $C_{12}H_{16}O_4$ mol.wt. 224.26

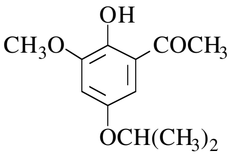


Synthesis

-Obtained by reaction of resacetophenone with 1,2-butylene oxide in the presence of sodium hydroxide in ethanol [185].

1-[2-Hydroxy-3-methoxy-5-(1-methylethoxy)phenyl]ethanone

$C_{12}H_{16}O_4$ mol.wt. 224.26



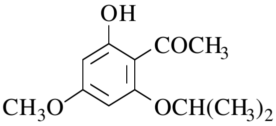
Synthesis

-Preparation by partial alkylation of 2,5-dihydroxy-3-methoxyacetophenone with isopropyl sulfate in alkaline medium (41%) [1643].

m.p. 70-72° [1643].

1-[2-Hydroxy-4-methoxy-6-(1-methylethoxy)phenyl]ethanone

[76554-78-4] $C_{12}H_{16}O_4$ mol.wt. 224.26



Syntheses

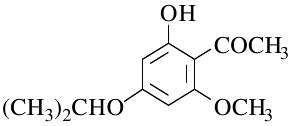
-Preparation by partial demethylation of 2,4-dimethoxy-6-isopropoxyacetophenone with aluminium bromide in acetonitrile at 0° (95%) [962].

-Also refer to: [639].

m.p. 65-66° [962].

1-[2-Hydroxy-6-methoxy-4-(1-methylethoxy)phenyl]ethanone

[119136-15-1] $C_{12}H_{16}O_4$ mol.wt. 224.26



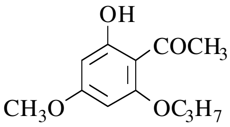
Synthesis

-Preparation by action of 2-bromopropane with 2,4-dihydroxy-6-methoxyacetophenone in the presence of potassium carbonate in DMF for 2 h at 100-110° (87%) [841].

m.p. 71-72° [841]; ^{1}H NMR [841], IR [841], MS [841].

1-(2-Hydroxy-4-methoxy-6-propoxyphenyl)ethanone

[76554-77-3] $C_{12}H_{16}O_4$ mol.wt. 224.26

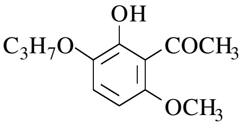


Synthesis

-Refer to: [639].

1-(2-Hydroxy-6-methoxy-3-propoxyphenyl)ethanone

[126405-77-4] $C_{12}H_{16}O_4$ mol.wt. 224.26



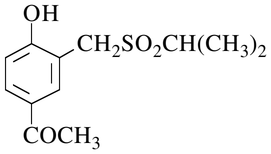
Synthesis

-Preparation by adding 2-hydroxy-3-iodo-6-methoxyacetophenone and cuprous iodide to a solution of sodium propoxide, previously prepared from propyl alcohol and sodium hydride in DMF [1873].

m.p. 90° [1873]; ^{1}H NMR [1873], IR [1873].

1-[4-Hydroxy-3-[[(1-methylethyl)sulfonyl]methyl]phenyl]ethanone

[56490-64-3] $C_{12}H_{16}O_4S$ mol.wt. 256.32



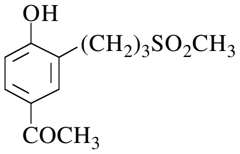
Synthesis

-Obtained by reaction of 3-chloromethyl-4-hydroxyacetophenone with magnesium isopropylsulfinate in refluxing dilute methanol for 18 h (83%) [935].

m.p. 96°5-100° [935].

1-[4-Hydroxy-3-[3-(methylsulfonyl)propyl]phenyl]ethanone

[56490-61-0] $C_{12}H_{16}O_4S$ mol.wt. 256.32



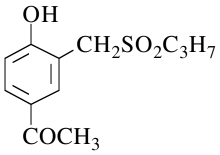
Synthesis

-Obtained by Fries rearrangement of 2-(methylsulfonylpropyl)phenyl acetate with aluminium chloride in nitrobenzene, first at r.t. for 1 h, then at 50-60° for 1.5 h (48%) [935].

m.p. 140-141° [935].

1-[4-Hydroxy-3-[(propylsulfonyl)methyl]phenyl]ethanone

[56490-63-2] $C_{12}H_{16}O_4S$ mol.wt. 256.32



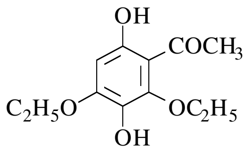
Synthesis

-Obtained by reaction of 3-chloromethyl-4-hydroxyacetophenone with magnesium propylsulfinate in refluxing aqueous methanol for 18 h (36%) [935].

m.p. 73°5-76° [935].

1-(2,4-Diethoxy-3,6-dihydroxyphenyl)ethanone

$C_{12}H_{16}O_5$ mol.wt. 240.26



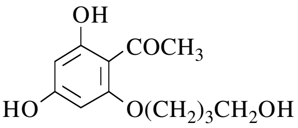
Synthesis

-Preparation from 2,4-diethoxy-6-hydroxyacetophenone by persulfate oxidation [73] [1516] [1550], (Elbs reaction) (21%) [1516].

m.p. 130-131° [1516].

1-[2,4-Dihydroxy-6-(4-hydroxybutoxy)phenyl]ethanone

[121379-45-1] $C_{12}H_{16}O_5$ mol.wt. 240.26

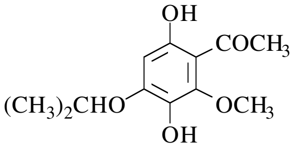


Isolation from natural sources

-From the bulbs of *Dioscorea bulbifera* [715].

1-[3,6-Dihydroxy-2-methoxy-4-(1-methylethoxy)phenyl]ethanone

[119136-16-2] $C_{12}H_{16}O_5$ mol.wt. 240.26



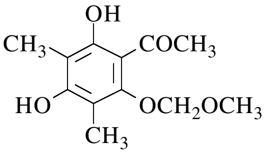
Synthesis

-Preparation from 4-(allyloxy)-2-hydroxy-6-methoxyacetophenone by persulfate oxidation (Elbs reaction) (20%) [841].

oil [841]; ^1H NMR [841], IR [841], MS [841].

1-[2,4-Dihydroxy-6-(methoxymethoxy)-3,5-dimethylphenyl]ethanone

[175465-97-1] $C_{12}H_{16}O_5$ mol.wt. 240.26

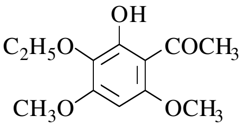


Synthesis

-Refer to: [1736] (Japanese patent).

1-(3-Ethoxy-2-hydroxy-4,6-dimethoxyphenyl)ethanone

[89880-47-7] $C_{12}H_{16}O_5$ mol.wt. 240.26



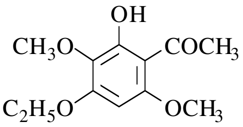
Synthesis

-Obtained (by-product) by reaction of acetyl chloride with 1,2,3,5-tetramethoxybenzene in the presence of aluminium chloride in ethyl ether (9-12%) [198] [1496].

m.p. 74-75° [198], 71°5-72°5 [1496];
^{1}H NMR [198] [1496], IR [198] [1496], MS [198].

1-(4-Ethoxy-2-hydroxy-3,6-dimethoxyphenyl)ethanone

$C_{12}H_{16}O_5$ mol.wt. 240.26



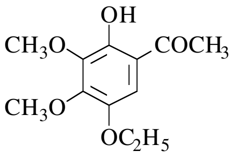
Synthesis

-Preparation by Friedel-Crafts acylation of 1,3-diethoxy-2,5-dimethoxybenzene with acetyl chloride in the presence of aluminium chloride in ether (81%) [801].

m.p. 106-107° [801].

1-(5-Ethoxy-2-hydroxy-3,4-dimethoxyphenyl)ethanone

[69616-62-2] $C_{12}H_{16}O_5$ mol.wt. 240.26



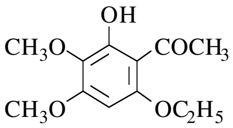
Synthesis

-Preparation by reaction of ethyl iodide with 2,5-dihydroxy-3,4-dimethoxyacetophenone in the presence of potassium carbonate in refluxing acetone (57%) [1360].

oil [1360]; b.p.$_{0.1}$ 120° [1360];
^{1}H NMR [1360], IR [1360].

1-(6-Ethoxy-2-hydroxy-3,4-dimethoxyphenyl)ethanone

$C_{12}H_{16}O_5$ mol.wt. 240.26



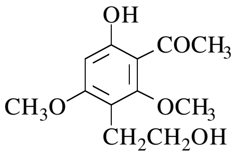
Synthesis

-Preparation by reaction of acetyl chloride on antiarol ethyl ether with aluminium chloride [760].

m.p. 97-98° [760].

1-[6-Hydroxy-3-(2-hydroxyethyl)-2,4-dimethoxyphenyl]ethanone

[34288-73-8] $C_{12}H_{16}O_5$ mol.wt. 240.26



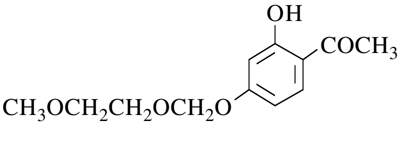
Synthesis

-Obtained from 6-(2'-hydroxyethyl)-5,7-dimethoxy-2-methylchromanone by degradation with potassium hydroxide in refluxing ethanol under nitrogen (32%) [1214].

m.p. 133-134° [1214]; ^{1}H NMR [1214], UV [1214].

1-[2-Hydroxy-4-[(2-methoxyethoxy)methoxy]phenyl]ethanone

[123253-31-6] $C_{12}H_{16}O_5$ mol.wt. 240.26



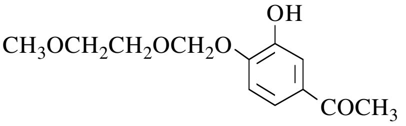
Syntheses

-Preparation by reaction of 2-methoxyethoxymethyl chloride with resacetophenone,
*in the presence of N,N-diisopropylethylamine, in DMF at 0° for 1.5 h (83%) [1338] or in methylene chloride at r.t. for 20 h (48%) [70]
*in the presence of potassium carbonate in acetone for 20 h at 20° (65-70%) [1720];
*also obtained in two steps: first, by adding sodium hydride (11 mmol) to a solution of resacetophenone (10 mmol) in DMF during 15-30 min at 20°; then, addition of methoxyethoxymethyl chloride (10 mmol) to the mixture between 0 to 5° (80-85%) [1720].

pasty solid [70]; TLC [1720];
^{1}H NMR [70] [1338] [1720], ^{13}C NMR [1338] [1720], IR [70] [1720], MS [1338] [1720].

1-[3-Hydroxy-4-[(2-methoxyethoxy)methoxy]phenyl]ethanone

[101140-09-4] $C_{12}H_{16}O_5$ mol.wt. 240.26



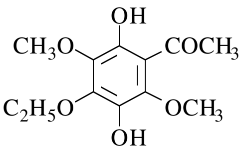
Synthesis

-Preparation by action of sodium methoxide with the crude 3-(benzoyloxy)-4-(2-methoxyethoxy)methoxyacetophenone (SM) in THF at r.t. in a nitrogen atmosphere for 30 min (92%). SM was previously prepared from 3-(benzoyloxy)-4-hydroxyacetophenone by etherification with 2-methoxyethoxymethyl chloride in the presence of N,N-diisopropylethylamine in methylene chloride at r.t. [1700].

colourless oil [1700]; ^{1}H NMR [1700], IR [1700], MS [1700].

1-(4-Ethoxy-2,5-dihydroxy-3,6-dimethoxyphenyl)ethanone

$C_{12}H_{16}O_6$ mol.wt. 256.26



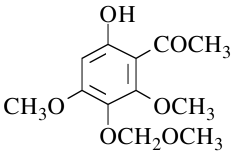
Synthesis

-Preparation from 2-hydroxy-4-ethoxy-3,6-dimethoxyacetophenone by persulfate oxidation (Elbs reaction) (31%) [801].

m.p. 73-74° [801].

1-[6-Hydroxy-2,4-dimethoxy-3-(methoxymethoxy)phenyl]ethanone

[104481-00-7] $C_{12}H_{16}O_6$ mol.wt. 256.26

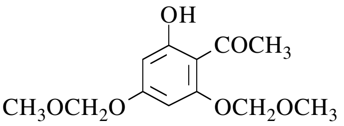


Synthesis

-Obtained from 3,6-dihydroxy-2,4-dimethoxyacetophenone by methoxymethylation with chloromethyl methyl ether in the presence of diisopropylamine in methylene chloride [798] [806].

1-[2-Hydroxy-4,6-bis(methoxymethoxy)phenyl]ethanone

[65490-09-7] $C_{12}H_{16}O_6$ mol.wt. 256.26



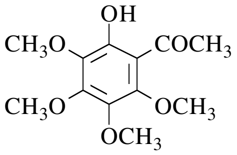
Syntheses

-Obtained by reaction of methoxymethyl chloride with phloroacetophenone in the presence of potassium carbonate,
*in acetone at r.t. for 2.5 h (47%) [1395];
*in refluxing acetone for 15 min (43%) [1620] or for 1 h (60%) [553].
-Also refer to: [404] [405] [722] [772] [1089] [1952] [1954].

m.p. 52° [1620], 45-46°5 [1395]; ^{1}H NMR [1395] [1620], IR [1395] [1620], UV [1620].

1-(2-Hydroxy-3,4,5,6-tetramethoxyphenyl)ethanone

[3162-28-5] $C_{12}H_{16}O_6$ mol.wt. 256.26



Syntheses

-Obtained by partial demethylation of 2,3,4,5,6-pentamethoxyacetophenone (**I**),
*with boron trifluoride etherate in acetic acid at 80°. (**I**) was obtained by metallation of pentamethoxybenzene, followed by treatment of the intermediate aryllithium compound with acetic anhydride at r.t. (85% yield) [1561];
*with aluminium chloride in ethyl ether at r.t. for 3 h (21%) [1609];
*with aluminium chloride in acetonitrile for 6 h at 30° (75%) [962].
-Also obtained by acylation of pentamethoxybenzene with acetyl chloride in the presence of aluminium chloride in ethyl ether [135] [1356] [1357] [1695], (25-34%) [135] [1357] or first for 14 h at r.t., then for 2 h at reflux (14%) [1695].
-Also obtained by adding a methanolic solution of 2,5-dihydroxy-3,4,6-trimethoxyacetophenone to an ethereal solution of diazomethane and keeping the mixture overnight in a refrigerator [1616] [1617], (80%) [1616].
-Also refer to: [207] [209] [213] [1246] [1380] [1769].

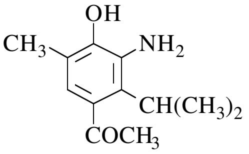
Isolation from natural sources

-By alkaline degradation of two substituted flavones with potassium hydroxide in boiling aqueous ethanol for 17-20 h under nitrogen,
a)-From *Lucidin dimethyl ether* (5,6,7,8-tetramethoxy-3',4'-methylenedioxyflavone) (m.p. 171-172°) (SM) (60% yield) [1072]. SM was obtained from two origins:
  -Isolation from ground root of *Lindera lucida* (Lauraceae);
  -Also prepared by methylation of *Lucidin* (5,7-dihydroxy-6,8-dimethoxy-3',4'-methylenedioxyflavone) (m.p. 255-257°), itself isolated from ground root of *Lindera lucida*.
b)-From 5,6,7,8-tetramethoxyflavone (m.p. 112-113°) (SM), [86], (53% yield) [1072]. SM was also isolated from the above mentioned plant.

yellow oil [1356] [1695], light orange oil [1072], oil [1561], liquid [1616] [1617];
b.p.$_{2}$ 115° [1616] [1617], b.p.$_{0.2}$ 130° [1072], b.p.$_{14}$ 183° [135], b.p.$_{15}$ 183° [1356];
^{1}H NMR [86] [1695], IR [86] [1695], UV [86] [1072] [1695].

1-[3-Amino-4-hydroxy-5-methyl-2-(1-methylethyl)phenyl]ethanone

$C_{12}H_{17}NO_2$ mol.wt. 207.27



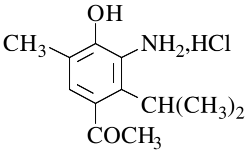
Syntheses

-Preparation by reduction of 4-hydroxy-5-methyl-3-nitro-2-isopropylacetophenone,
*with sodium hydrosulfite in aqueous sodium hydroxide solution at 80-90° (92%) [902];
*with tin in dilute hydrochloric acid (46%) [902].

m.p. 100° [902].

1-[3-Amino-4-hydroxy-5-methyl-2-(1-methylethyl)phenyl]ethanone *(Hydrochloride)*

$C_{12}H_{17}NO_2$, HCl mol.wt. 243.73



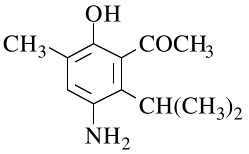
Synthesis

-Preparation by reaction of hydrochloric acid on 3-amino-4-hydroxy-5-methyl-2-isopropylacetophenone in ethyl ether [902].

m.p. 199-200° (d) [902].

1-[3-Amino-6-hydroxy-5-methyl-2-(1-methylethyl)phenyl]ethanone

$C_{12}H_{17}NO_2$ mol.wt. 207.27



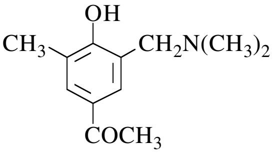
Syntheses

-Preparation by reduction of 2-hydroxy-3-methyl-5-nitro-6-isopropylacetophenone,
*with sodium hydrosulfite in aqueous sodium hydroxide solution (87%) [903];
*with tin in dilute hydrochloric acid (50%) [903].

m.p. 117° [903].

1-[3-[(Dimethylamino)methyl]-4-hydroxy-5-methylphenyl]ethanone

[82506-14-7] $C_{12}H_{17}NO_2$ mol.wt. 207.27



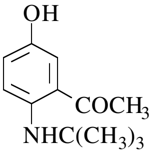
Synthesis

-Preparation by aminomethylation of 4-hydroxy-3-methyl-acetophenone with dimethylamine and formalin in water at 35-40° for 4 h (64%) [1040].

m.p. 44° [1040]; ^{1}H NMR [1040], IR [1040].

1-[2-[(1,1-Dimethylethyl)amino]-5-hydroxyphenyl]ethanone

[63609-62-1] $C_{12}H_{17}NO_2$ mol.wt. 207.27



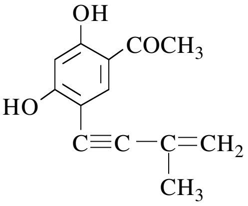
Synthesis

-Obtained by UV irradiation of a solution of 3-methyl-N-tert-butylanthranilium perchlorate (SM) in 10% aqueous acetonitrile (64%) [55]. SM was prepared according to [725].

yellow oil [55]; TLC [55];
^1H NMR [55], ^{13}C NMR [55], IR [55], MS [55].

1-[2,4-Dihydroxy-5-(3-methyl-3-buten-1-ynyl)phenyl]ethanone

[193333-25-4] $C_{13}H_{12}O_3$ mol.wt. 216.24



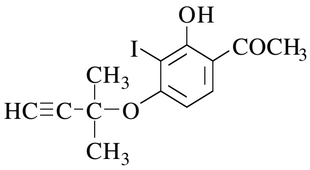
Synthesis

-Obtained (by-product) by reaction of boron tribromide (4 equiv.) with 2,4-bis(benzyloxy)-5-(3-hydroxy-3-methylbutynyl)acetophenone in methylene chloride for 5 min at 0° (14%) [1825].

m.p. 110-112° [1825]; ^1H NMR [1825].

1-[4-[(1,1-Dimethyl-2-propynyl)oxy]-2-hydroxy-3-iodophenyl]ethanone

[82538-73-6] $C_{13}H_{13}IO_3$ mol.wt. 344.15



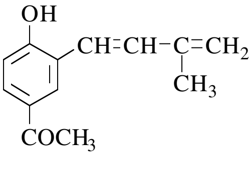
Synthesis

-Preparation by reaction of 3-chloro-3-methylbut-1-yne with 2,4-dihydroxy-3-iodoacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (65%) [15].

m.p. 100-101° [15]; ^1H NMR [15].

1-[4-Hydroxy-3-(3-methyl-1,3-butadienyl)phenyl]ethanone

$C_{13}H_{14}O_2$ mol.wt. 202.10



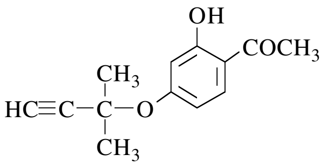
Isolation from natural sources

-From the roots of *Helianthella uniflora* (Heliantheae) [242].

m.p. 137-138° [242];
^1H NMR [242], IR [242], UV [242], MS [242].

1-[4-[(1,1-Dimethyl-2-propynyl)oxy]-2-hydroxyphenyl]ethanone

$C_{13}H_{14}O_3$ mol.wt. 218.25



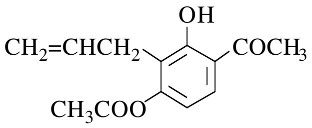
Synthesis

-Obtained by treatment of resacetophenone with 3-chloro-3-methylbutyne in DMF in the presence of potassium carbonate and potassium iodide for 12 h at 75° (29%) [245].

m.p. 62°5 [245]; ^{1}H NMR [245], IR [245].

1-[4-(Acetyloxy)-2-hydroxy-3-(2-propenyl)phenyl]ethanone

[149810-10-6] $C_{13}H_{14}O_4$ mol.wt. 234.25



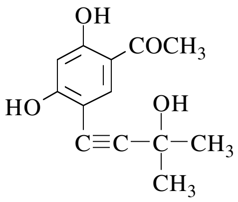
Synthesis

-Preparation by reaction of acetyl chloride with 3-allyl-2,4-dihydroxyacetophenone in the presence of triethylamine in methylene chloride for 1 h at 0° and at 10° for 30 min (62%) [1265].

m.p. 56-57° [1265]; ^{1}H NMR [1265], ^{13}C NMR [1265], IR [1265].

1-[2,4-Dihydroxy-5-(3-hydroxy-3-methyl-1-butynyl)phenyl]ethanone

[193333-24-3] $C_{13}H_{14}O_4$ mol.wt. 234.25



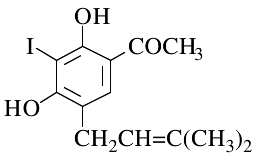
Synthesis

-Obtained (by-product) by reaction of boron tribromide (4 equiv.) with 2,4-bis(benzyloxy)-5-(3-hydroxy-3-methylbutynyl)acetophenone in methylene chloride for 5 min at 0° (18%) [1825].

m.p. 148-150° [1825]; ^{1}H NMR [1825].

1-[2,4-Dihydroxy-3-iodo-5-(3-methyl-2-butenyl)phenyl]ethanone

[82538-74-7] $C_{13}H_{15}IO_3$ mol.wt. 346.16



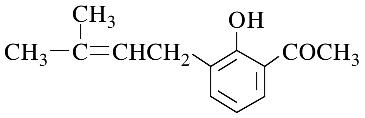
Synthesis

-Obtained by reaction of 2-methylbut-3-en-2-ol with 2,4-dihydroxy-3-iodoacetophenone in the presence of boron trifluoride etherate in dioxane at 35-40° (15%) [15].

m.p. 135-137° [15]; ^{1}H NMR [15].

1-[2-Hydroxy-3-(3-methyl-2-butenyl)phenyl]ethanone

[310402-63-2] $C_{13}H_{16}O_2$ mol.wt. 204.27

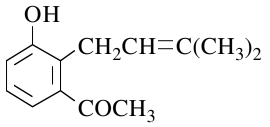


Synthesis

-Refer to: [1325] (compound 76).

1-[3-Hydroxy-2-(3-methyl-2-butenyl)phenyl]ethanone

[154520-54-4] $C_{13}H_{16}O_2$ mol.wt. 204.27

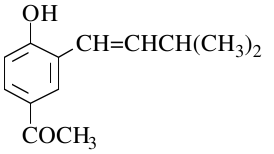


Isolation from natural sources

-From the aerial parts of *Helichrysum stoechas* (L.) grown in Libya [568].

1-[4-Hydroxy-3-(3-methyl-1-butenyl)phenyl]ethanone

[35816-89-8] $C_{13}H_{16}O_2$ mol.wt. 204.27



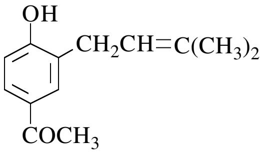
Synthesis

-Preparation by migration of a C=C double bond in 4-hydroxy-3-(2-isopentenyl)acetophenone by treatment with potassium hydroxide in triethylene glycol (Triglykol) at 150° (70%) [241] (allylic/propenylic rearrangement).

b.p.$_1$ 120° [241]; ^{1}H NMR [241].

1-[4-Hydroxy-3-(3-methyl-2-butenyl)phenyl]ethanone

[26932-05-8] $C_{13}H_{16}O_2$ mol.wt. 204.27



Syntheses

-Obtained by reaction of 2-methyl-3-buten-2-ol with 4-hydroxyacetophenone in the presence of boron trifluoride etherate [128] [246], (15%) [128].

-Preparation by thermal Claisen rearrangement of 4-(2,2-dimethylallyloxy)acetophenone in diethylaniline at 165° (79%) [241].

Isolation from natural sources

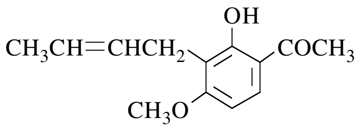
-From the aerial parts of *Ophryosporus chilca* (Compositae, tribe Eupatorieae) [251].
-From the roots of *Flourensia cernua* DC (Compositae) [244].
-From *Artemis campestris* silbsp. glutinosa (Compositae) [489].
-From *Senecio phylolleptus* Cuatr., *Senecio viridis* Phil. and *Senecio nutans* sch. Bip. (Asteraceae) native of northern Chile [1260].
-From *Senecio nutans* sch. Bip. [556].
-From the aerial parts of *Stevia hyssopifolia* Phil. var. hyssopifolia [1942].
-From the aerial parts of *Baccharis santelicis* Phil. (Compositae, tribe Cistereae, subtribe Baccharidinae) [242].

-From sliced yacon tubers after inoculation with the bacterium *Pseudomonas cichorii* and incubation at 20° for three days, then extraction with acetone. Yacon (*Polymnia sonchifolia*) (Compositae) is cultivated in South America and has recently been introduced into Japan [1749].
-From the aerial parts of *Helichrysum italicum* (Compositae) (major compound) [1807].
-From the aerial parts of *Helichrysum stoechas* (Compositae) [657], (trace amounts) [1807].
-From the aerial parts of *Werneria poposa* [1429].
-From the roots of *Helianthella uniflora* (Compositae) [242] [264].
-From the leaves of *Ageratina altissima* (L) K & K (Compositae) [249].
-Also refer to: [1324].

Amorphous [1749]; TLC [251];
m.p. 94-95° [128], 93-94° [241] [242], 92-93° [657], 90-91° [1260], 90° [489];
^{1}H NMR [128] [242] [489] [657] [1260] [1429] [1749] [1807],
^{13}C NMR [1260] [1429] [1749] [1807], IR [128] [242] [489] [657] [1260] [1749] [1807],
UV [128] [242] [489] [657] [1749] [1807],
MS [242] [489] [657] [1260] [1429] [1749] [1807].

1-[3-(2-Butenyl)-2-hydroxy-4-methoxyphenyl]ethanone

[91664-24-3] $C_{13}H_{16}O_3$ mol.wt. 220.27

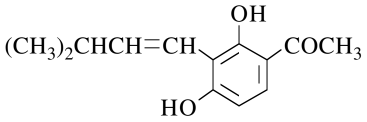


Synthesis

N.B.: In the paper [19], the formula of the compound **13** displayed page 131, which is the formula of the titled compound $C_{13}H_{16}O_3$, is incomplete and erroneous. It actually deals with another compound $C_{14}H_{18}O_4$, the 1-[3-(2-butenyl)-2-hydroxy-4,6-dimethoxyphenyl]ethanone, which is described in the experimental part. This is detailed just below the formula, page 131.

1-[2,4-Dihydroxy-3-(3-methyl-1-butenyl)phenyl]ethanone

[80190-95-0] $C_{13}H_{16}O_3$ mol.wt. 220.27

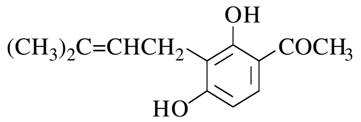


Syntheses

-Obtained by reaction of 2-methylbut-3-en-2-ol with resacetophenone in the presence of boron trifluoride etherate [915] according to the method [884].
-Also refer to: [1091] (Chinese paper).

1-[2,4-Dihydroxy-3-(3-methyl-2-butenyl)phenyl]ethanone

[19825-40-2] $C_{13}H_{16}O_3$ mol.wt. 220.27



Syntheses

-Preparation by reaction of prenyl bromide on resacetophenone with potassium hydroxide solution at r.t. [175] [882] [1056], (21-25%) [175] [882].
-Preparation by reaction of 2-methylbut-3-en-2-ol with resacetophenone in the presence of boron trifluoride etherate in dioxane at r.t. [43] [865] [884], (33%) [865], (13%) [884].
-Isoprenylation of resacetophenone with prenyl bromide by photochemical method in the presence of benzoyl peroxide in dry benzene for 8 h (40%) [175].
-Preparation from 6-acetyl-3-phenylthio-2,2-dimethylchroman-5-ol,

*by reaction with potassium naphthalenide in tetrahydrofuran at r.t. (59%) [1252] or by reaction with lithium naphthalenide in tetrahydrofuran at -32° for 30 min (38%) [1252];
*by electrolysis using a mercury cathode, and acetonitrile-tetraethylammonium bromide electrolyte (49%) [1252].
-Also obtained by reaction of potassium naphthalenide with 6-acetyl-2,2-dimethyl-3-phenylsulfonylchroman-5-ol in tetrahydrofuran at r.t. (25%) [1252].

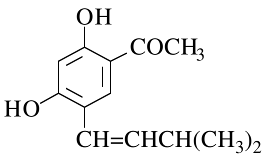
Isolation from natural sources

-By cleavage of isobavachin with alkali. The isobavachin is a flavonoid compound obtained from *Psoralea Corylifolia* Linn. [206].

m.p. 162° [1056], 157-158° [882], 155-156° [206] [884], 149-151° [1252], 148° [865];
^{1}H NMR [43] [44] [206] [865] [1056] [1252], IR [206] [865] [882] [1056], UV [43] [882], MS [1252].

1-[2,4-Dihydroxy-5-(3-methyl-1-butenyl)phenyl]ethanone

[41347-54-0] $C_{13}H_{16}O_3$ mol.wt. 220.27

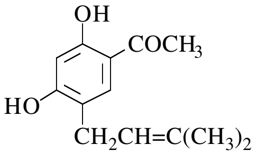


Synthesis

-Obtained by reaction of 2-methylbut-3-en-2-ol with resacetophenone in the presence of boron trifluoride etherate [915] according to the method [884].

1-[2,4-Dihydroxy-5-(3-methyl-2-butenyl)phenyl]ethanone

[28437-37-8] $C_{13}H_{16}O_3$ mol.wt. 220.27



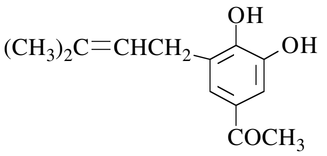
Syntheses

-Preparation by reaction of 2-methylbut-3-en-2-ol with resacetophenone in the presence of boron trifluoride etherate [43] [865] [884], (20-29%) [241] [884].
-Preparation from 2,4-dihydroxy-3-iodo-5-prenylacetophenone by elimination of iodine with zinc dust and concentrated hydrochloric acid in refluxing ethanol (79%) [15].
-Preparation by reaction of prenyl bromide with resacetophenone in potassium hydroxide solution at r.t. [1056].

m.p. 146° [1056], 144-145° [15] [884]; ^{1}H NMR [43] [44] [1056], IR [1056], UV [43].

1-[3,4-Dihydroxy-5-(3-methyl-2-butenyl)phenyl]ethanone

[186966-70-1] $C_{13}H_{16}O_3$ mol.wt. 220.27

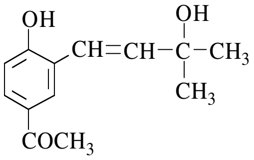


Synthesis

-Obtained (poor yield) by rearrangement of 4-(dimethylallyloxy)-3-hydroxyacetophenone in the presence of montmorillonite KSF (< 10%) [1814].

1-[4-Hydroxy-3-(3-hydroxy-3-methyl-1-butenyl)phenyl]ethanone

[35816-94-5]
[26931-61-3] *(E)* $C_{13}H_{16}O_3$ mol.wt. 220.27



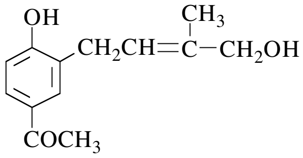
Isolation from natural sources

- -From the aerial parts of *Ophryosporus floribundus* (Compositae, tribe Eupatorieae) [1941].
- -From the leaves and the roots of *Ageratina altissima* (L.) K. et R. (Compositae) [249].
- -From the roots of *Helianthella uniflora* (tribe Heliantheae) [242].

^{1}H NMR [242], IR [242], UV [242], MS [242].

1-[4-Hydroxy-3-(4-hydroxy-3-methyl-2-butenyl)phenyl]ethanone

[68034-24-2] $C_{13}H_{16}O_3$ mol.wt. 220.27

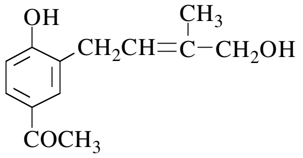


Isolation from natural sources

- -From the aerial parts of *Artemisia campestris*, L., subsp. glutinosa (Gay ex Besser), Batt (Compositae) [491].

1-[4-Hydroxy-3-(4-hydroxy-3-methyl-2-butenyl)phenyl]ethanone *(E)*

[73869-86-0] $C_{13}H_{16}O_3$ mol.wt. 220.27



Synthesis

- -Obtained by alkaline hydrolysis of 3-[4-acetoxyisopent-2(*E*)-enyl]-4-hydroxyacetophenone (SM) (viscous oil) with 10% potassium hydroxide in methanol (quantitative yield) [492]. SM was isolated from the *Artemisia campestris* L., subsp. glutinosa (Gay ex Besser), Batt.

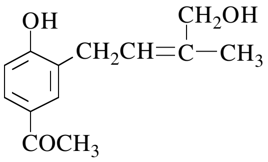
Isolation from natural sources

- -From the aerial parts of *Artemisia campestris* L., subsp. glutinosa (Gay ex Besser), Batt (Compositae), (1.1%) [488], (11.2%) [489].
- -From *Artemisia monosperma* [1].

m.p. 84-85° [488];
^{1}H NMR [488] [489], IR [488], UV [488], MS [488] [489].

1-[4-Hydroxy-3-(4-hydroxy-3-methyl-2-butenyl)phenyl]ethanone *(Z)*

[123614-13-1] $C_{13}H_{16}O_3$ mol.wt. 220.27



Synthesis

-Obtained by alkaline hydrolysis of 3-[4-acetoxyisopent-2(*Z*)-enyl]-4-hydroxyacetophenone (SM) (viscous oil) with 10% potassium hydroxide in methanol (quantitative yield) [492]. SM was isolated from the *Artemisia campestris* L., subsp. glutinosa (Gay ex Besser), Batt.

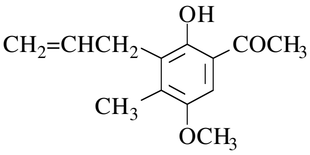
Isolation from natural sources

-From the aerial parts of *Artemisia campestris* L., subsp. glutinosa (Gay ex Besser), Batt (Compositae) [491], (44.8%) [489].
-From *Artemisia monosperma* [1].

viscid oil [489]; ^{1}H NMR [489], IR [489], UV [489], MS [489].

1-[2-Hydroxy-5-methoxy-4-methyl-3-(2-propenyl)phenyl]ethanone

[43037-66-7] $C_{13}H_{16}O_3$ mol.wt. 220.27

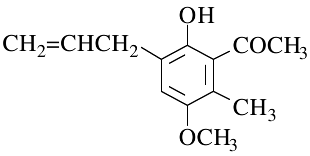


Synthesis

-Preparation by thermal Claisen rearrangement of 2-(allyloxy)-5-methoxy-4-methylacetophenone in N,N-dimethylaniline at 170° (42%) [581].

1-[2-Hydroxy-5-methoxy-6-methyl-3-(2-propenyl)phenyl]ethanone

[43037-68-9] $C_{13}H_{16}O_3$ mol.wt. 220.27

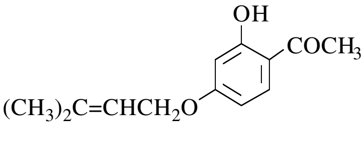


Synthesis

-Obtained by thermal Claisen rearrangement of 2-(allyloxy)-5-methoxy-4-methylacetophenone in N,N-dimethylaniline at 170°, with a [1,5] shift of the aromatic acetyl substituent (22%) [581].

1-[2-Hydroxy-4-[(3-methyl-2-butenyl)oxy]phenyl]ethanone

[24672-83-1] $C_{13}H_{16}O_3$ mol.wt. 220.27



Syntheses

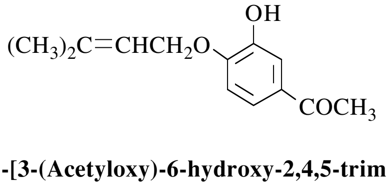
-Preparation by reaction of prenyl bromide on resacetophenone [1619],
*in the presence of potassium carbonate in refluxing acetone [43] [175] [882] [1390], (69%) [882], (40%) [175];

*in the presence of potassium hydroxide in methanol, at 0° (14%) or at r.t. (4%) [882];
*by photochemical method in the presence of benzoyl peroxide in dry benzene for 8 h (10%) [175].

m.p. 46-47° [882]; ^{1}H NMR [43] [44] [882], IR [882], UV [43] [882].

1-[3-Hydroxy-4-[(3-methyl-2-butenyl)oxy]phenyl]ethanone

[186966-69-8] $C_{13}H_{16}O_3$ mol.wt. 220.27

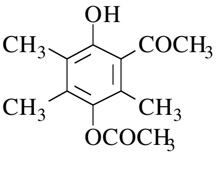


Synthesis

-Preparation by reaction of 3,3-dimethylallyl chloride (2.5 equiv.) with 4-acetylcatechol in the presence of sodium carbonate and catalytic amounts of TBAI in DMF at r.t. (73%) [1814].

1-[3-(Acetyloxy)-6-hydroxy-2,4,5-trimethylphenyl]ethanone

[66901-79-9] $C_{13}H_{16}O_4$ mol.wt. 236.27



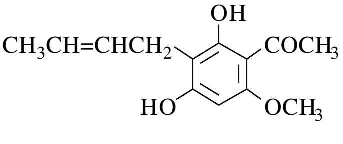
Syntheses

-Preparation by reaction of boron trifluoride-acetic acid complex,
*with trimethylhydroquinone [424] [1144], (90%) [424];
*with trimethylhydroquinone diacetate in ethylene dichloride *via* a Fries rearrangement (99%) [1872].
-Also refer to: [1928].

m.p. 75° [1144]; ^{13}C NMR [1872].

1-[3-(2-Butenyl)-2,4-dihydroxy-6-methoxyphenyl]ethanone

[91664-22-1] $C_{13}H_{16}O_4$ mol.wt. 236.27



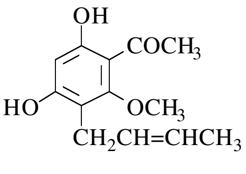
Synthesis

-Preparation by condensation of 2,4-dihydroxy-6-methoxyacetophenone with 1,3-butadiene in the presence of 85% orthophosphoric acid in xylene at 30-35° (37%) [19].

m.p. 134-135° [19]; ^{1}H NMR [19].

1-[3-(2-Butenyl)-4,6-dihydroxy-2-methoxyphenyl]ethanone

[91664-23-2] $C_{13}H_{16}O_4$ mol.wt. 236.27



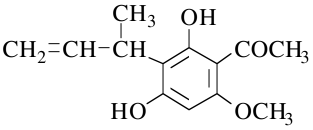
Synthesis

-Preparation by condensation of 2,4-dihydroxy-6-methoxyacetophenone with 1,3-butadiene in the presence of 85% orthophosphoric acid in xylene at 30-35° (41%) [19].

m.p. 128-129° [19]; ^{1}H NMR [19].

1-[2,4-Dihydroxy-6-methoxy-3-(1-methyl-2-propenyl)phenyl]ethanone

[91664-20-9] $C_{13}H_{16}O_4$ mol.wt. 236.27



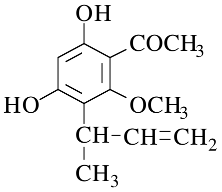
Synthesis

-Obtained, or else its isomer (see below), (by-product) by condensation of 2,4-dihydroxy-6-methoxyacetophenone with 1,3-butadiene in the presence of 85% orthophosphoric acid in xylene at 30-35° (7%) [19].

m.p. 130-140° [19]; ^{1}H NMR [19].

1-[4,6-Dihydroxy-2-methoxy-3-(1-methyl-2-propenyl)phenyl]ethanone

[91664-21-0] $C_{13}H_{16}O_4$ mol.wt. 236.27



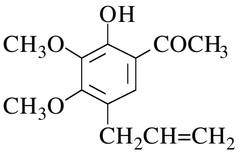
Synthesis

-Obtained, or else its isomer (see above), (by-product) by condensation of 2,4-dihydroxy-6-methoxyacetophenone with 1,3-butadiene in the presence of 85% orthophosphoric acid in xylene at 30-35° (7%) [19].

m.p. 130-140° [19]; ^{1}H NMR [19].

1-[2-Hydroxy-3,4-dimethoxy-5-(2-propenyl)phenyl]ethanone

[75254-93-2] $C_{13}H_{16}O_4$ mol.wt. 236.27

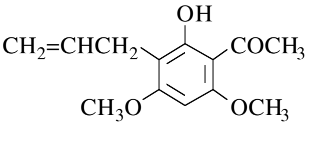


Synthesis

-Preparation by thermal Claisen rearrangement of 2-(allyloxy)-3,4-dimethoxyacetophenone without solvent at 190-200° [351].

1-[2-Hydroxy-4,6-dimethoxy-3-(2-propenyl)phenyl]ethanone

[35109-98-9] $C_{13}H_{16}O_4$ mol.wt. 236.27



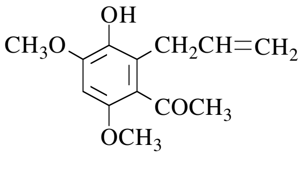
Synthesis

-Preparation by thermal Claisen rearrangement of 2-(allyloxy)-4,6-dimethoxyacetophenone in refluxing N,N-dimethylaniline (90%) [866].

m.p. 85-87° [866]; ^{1}H NMR [866], IR [866].

1-[3-Hydroxy-4,6-dimethoxy-2-(2-propenyl)phenyl]ethanone

[100612-87-1] $C_{13}H_{16}O_4$ mol.wt. 236.27



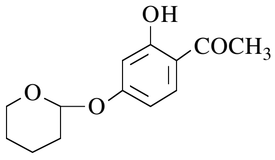
Syntheses

-Preparation by thermal Claisen rearrangement of 5-(allyloxy)-2,4-dimethoxyacetophenone,
*in boiling quinoline (65%) [498];
*in glycerol at 200° (87%) [498];
*by pyrolysis at 160° for 2 h under nitrogen [699].
-Preparation by reaction of methyl iodide on 2-allyl-3,6-dihydroxy-4-methoxyacetophenone with potassium carbonate in acetone (41%) [498].

m.p. 110° [498].

1-[2-Hydroxy-4-[(tetrahydro-2*H*-pyran-2-yl)oxy]phenyl]ethanone

[111841-07-7] $C_{13}H_{16}O_4$ mol.wt. 236.27



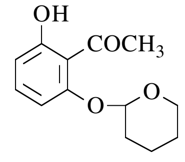
Syntheses

-Obtained by reaction of 2,3-dihydropyran with resacetophenone in the presence of concentrated hydrochloric acid (some drops) at r.t. overnight (33%) [671]. In later runs, p-toluenesulfonic acid was used as catalyst.
-Also refer to: [1348].

m.p. 76-78° [671].

1-[2-Hydroxy-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]phenyl]ethanone

[63854-17-1] $C_{13}H_{16}O_4$ mol.wt. 236.27



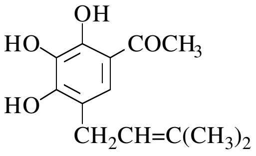
Syntheses

-Obtained by reaction of 2,3-dihydropyran with 2,6-dihydroxyacetophenone in the presence of p-toluenesulfonic acid in dioxane at r.t. for 3 h (64%) [1233] or for 20 h (69%) [5].
-Also refer to: [1348].

pale yellow crystals [1233];
^{1}H NMR [5] [1233], ^{13}C NMR [5] [1233], MS [1233].

1-[2,3,4-Trihydroxy-5-(3-methyl-2-butenyl)phenyl]ethanone

[35817-18-6] $C_{13}H_{16}O_4$ mol.wt. 236.27



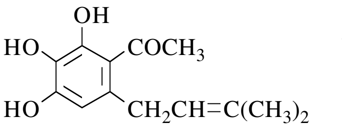
Synthesis

-Obtained by reaction of 2-methyl-3-buten-2-ol with gallacetophenone in the presence of boron trifluoride etherate in dioxane [128] [241] at 50-60° (21%) [128].

m.p. 74-75° [128]; ^{1}H NMR [128], IR [128], UV [128].

1-[2,3,4-Trihydroxy-6-(3-methyl-2-butenyl)phenyl]ethanone

[149876-26-6] $C_{13}H_{16}O_4$ mol.wt. 236.27

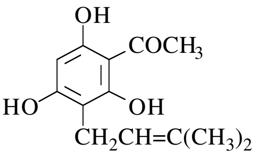


Synthesis

N.B.: The titled ketone is mentioned in Chem. Abstr. Vol. **119**, 1993-FORMULA INDEX, p. 1525F under the reference 172870a. However, the original publication [522] obtained from this reference doesn't include the expected ketone. This publication [522] concerns only an isomeric ketone, the 1-[2,3,4-trihydroxy-**5**-(3-methyl-2-butenyl)phenyl]ethanone [35817-18-6] already described [1166], p. 240.

1-[2,4,6-Trihydroxy-3-(3-methyl-2-butenyl)phenyl]ethanone

[27364-71-2] $C_{13}H_{16}O_4$ mol.wt. 236.27



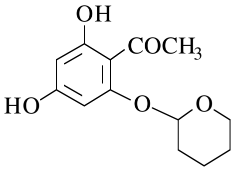
Syntheses

-Preparation from 2,4-dihydroxy-6-methoxy-5-isopentenylacetophenone *(Acronylin)* by demethylation with aluminium chloride in refluxing benzene [230].
-Also obtained by reaction of 2-methylbut-3-en-2-ol with phloroacetophenone in the presence of boron trifluoride etherate in dioxane at 20° (10%) [426].
-Also obtained by reaction of prenyl bromide with phloroacetophenone in solution of methanol in the presence of potassium hydroxide (26%) [1489] or sodium methoxide at r.t. (5%) [1491].

m.p. 182° [230], 172° [1489] [1491], 171-173° [426], 169-171° [350];
^{1}H NMR [230] [350], UV [426].

1-[2,4-Dihydroxy-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]phenyl]ethanone

[136257-86-8] $C_{13}H_{16}O_5$ mol.wt. 252.27



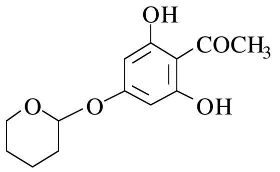
Syntheses

-Preparation by reaction of 3,4-dihydro-2*H*-pyran,
*on phloroacetophenone with p-toluenesulfonic acid in dioxane at r.t. (10%) [5];
*on 4-acetoxy-2,6-dihydroxyacetophenone with p-toluenesulfonic acid in dioxane (32-49%) [5].

white solid [5]; ^{1}H NMR [5], ^{13}C NMR [5].

1-[2,6-Dihydroxy-4-[(tetrahydro-2*H*-pyran-2-yl)oxy]phenyl]ethanone

[136257-85-7] $C_{13}H_{16}O_5$ mol.wt. 252.27



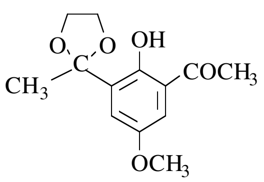
Syntheses

-Obtained by reaction of 3,4-dihydro-2*H*-pyran,
*on phloroacetophenone with p-toluenesulfonic acid in dioxane at r.t. (20%) [5];
*on 4-acetoxy-2,6-dihydroxyacetophenone with p-toluene sulfonic acid in dioxane (8-11%) [5].

white solid [5]; ^{1}H NMR [5], ^{13}C NMR [5].

1-[2-Hydroxy-5-methoxy-3-(2-methyl-1,3-dioxolan-2-yl)phenyl]ethanone

[103867-85-2] $C_{13}H_{16}O_5$ mol.wt. 252.27

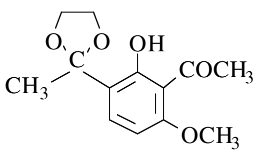


Synthesis

-Preparation by UV light irradiation of ethylene acetal of 2-acetoxy-5-methoxyacetophenone with potassium carbonate in hexane (85%) [659].

1-[2-Hydroxy-6-methoxy-3-(2-methyl-1,3-dioxolan-2-yl)phenyl]ethanone

[103867-86-3] $C_{13}H_{16}O_5$ mol.wt. 252.27



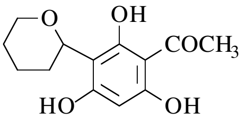
Synthesis

-Preparation by UV light irradiation of ethylene acetal of 2-acetoxy-4-methoxyacetophenone with potassium carbonate in hexane (52%) [659].

m.p. 120-123° [659]; ^1H NMR [659], IR [659].

1-[2,4,6-Trihydroxy-3-(tetrahydro-2*H*-pyran-2-yl)phenyl]ethanone

$C_{13}H_{16}O_5$ mol.wt. 252.27



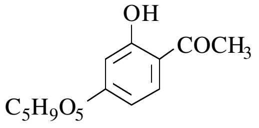
Synthesis

-Obtained by reaction of 3,4-dihydro-2*H*-pyran on phloroacetophenone with p-toluenesulfonic acid in dioxane at r.t. (21%) [5].

^1H NMR [5], ^{13}C NMR [5].

1-[2-Hydroxy-4-(β-D-xylopyranosyloxy)phenyl]ethanone

[54918-29-5] $C_{13}H_{16}O_7$ mol.wt. 284.14



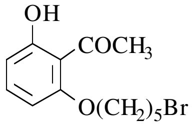
Synthesis

-Preparation by reaction of sodium on 2',4'-dihydroxy-acetophenone-4'-β-tri-O-acetyl-D-xylopyranoside in methanol (66%) [1480].

m.p. 204-205° [1480]; $(\alpha)_D^{17} = -70°$ (0.4%, THF) [1480].

1-[2-[(5-Bromopentyl)oxy]-6-hydroxyphenyl]ethanone

[28862-10-4] $C_{13}H_{17}BrO_3$ mol.wt. 301.18



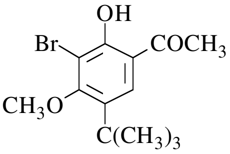
Synthesis

-Preparation by reaction of 1,5-dibromopentane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone [71].

m.p. 35-36° [71].

1-[3-Bromo-5-(1,1-dimethylethyl)-2-hydroxy-4-methoxyphenyl]ethanone

[127371-47-5] $C_{13}H_{17}BrO_3$ mol.wt. 301.18

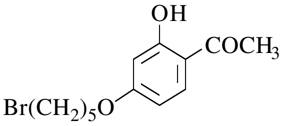


Synthesis

-Refer to: [1576] (patent).

1-[4-[(5-Bromopentyl)oxy]-2-hydroxyphenyl]ethanone

[40785-72-6] $C_{13}H_{17}BrO_3$ mol.wt. 301.18



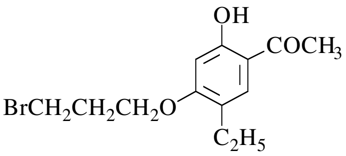
Synthesis

-Preparation by reaction of 1,5-dibromopentane with resacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (34%) [71].

m.p. 64-66° [71].

1-[4-(3-Bromopropoxy)-5-ethyl-2-hydroxyphenyl]ethanone

[117706-55-5] $C_{13}H_{17}BrO_3$ mol.wt. 301.18



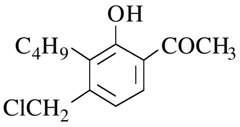
Synthesis

-Preparation by reaction of 3-bromopropyl bromide on 5-ethyl-2,4-dihydroxyacetophenone with potassium carbonate and potassium iodide, at reflux (80%) [256] [257].

m.p. 126-127° [256] [257]; ^{1}H NMR [256] [257].

1-[3-Butyl-4-(chloromethyl)-2-hydroxyphenyl]ethanone

[107223-43-8] $C_{13}H_{17}ClO_2$ mol.wt. 240.73



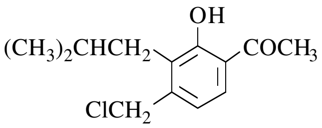
Synthesis

-Preparation by reaction of ethyl chloroformate with 3-n-butyl-4-(dimethylaminomethyl)-2-hydroxyacetophenone in toluene (78%) [530].

m.p. 42-44° [530].

1-[4-(Chloromethyl)-2-hydroxy-3-(2-methylpropyl)phenyl]ethanone

[97582-41-7] $C_{13}H_{17}ClO_2$ mol.wt. 240.73



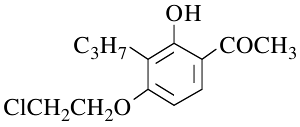
Synthesis

-Preparation by reaction of ethyl chloroformate with 3-isobutyl-4-(dimethylaminomethyl)-2-hydroxyacetophenone in toluene [529] [530], (42%) [530].

oil [530]; ^{1}H NMR [529], IR [529].

1-[4-(2-Chloroethoxy)-2-hydroxy-3-propylphenyl]ethanone

[104074-07-9] $C_{13}H_{17}ClO_3$ mol.wt. 256.73



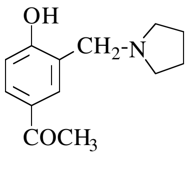
Synthesis

-Preparation by action of 2-chloroethyl p-toluenesulfonate with 2,4-dihydroxy-3-propylacetophenone in the presence of potassium carbonate and potassium iodide in boiling acetone for 16 h (36%) [1035].

m.p. 72-73°5 [1035]; ^{1}H NMR [1035].

1-[4-Hydroxy-3-(1-pyrrolidinylmethyl)phenyl]ethanone

$C_{13}H_{17}NO_2$ mol.wt. 219.28



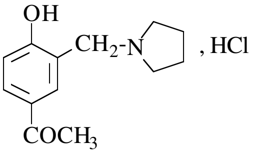
Synthesis

-Preparation by reaction of 4-hydroxyacetophenone with formaldehyde and pyrrolidine in 75% ethanol at r.t. (60%) [669] (Mannich reaction).

m.p. 97-98° [669].

1-[4-Hydroxy-3-(1-pyrrolidinylmethyl)phenyl]ethanone *(Hydrochloride)*

$C_{13}H_{17}NO_2$, HCl mol.wt. 255.74



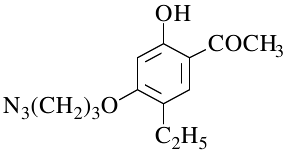
Synthesis

-Preparation from 4-hydroxy-3-(1-pyrrolidinylmethyl)-acetophenone [669].

m.p. 202-203° [669].

1-[4-(3-Azidopropoxy)-5-ethyl-2-hydroxyphenyl]ethanone

[117706-26-0] $C_{13}H_{17}N_3O_3$ mol.wt. 263.30



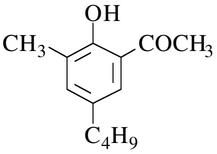
Synthesis

-Preparation by reaction of sodium azide with 4-(3-bromopropoxy)-5-ethyl-2-hydroxyacetophenone in DMF at r.t. [256] [257].

^1H NMR [256] [257], MS [256] [257].

1-(5-Butyl-2-hydroxy-3-methylphenyl)ethanone

$C_{13}H_{18}O_2$ mol.wt. 206.28



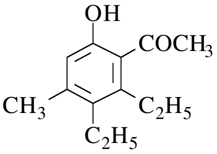
Synthesis

-Preparation by Fries rearrangement of 4-butyl-2-methylphenyl acetate with aluminium chloride without solvent at 100-110° (64%) [100].

b.p.$_{12}$ 152-154° [100].

1-(2,3-Diethyl-6-hydroxy-4-methylphenyl)ethanone

[27193-00-6] $C_{13}H_{18}O_2$ mol.wt. 206.28



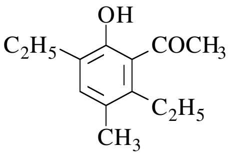
Synthesis

-Obtained *via* pyrolysis of 7,8-diethyl-1,3-dimethyl-2-oxabicyclo [4.2.0] octa-3,7-dien-5-one (2,6-dimethyl-4-pyrone - Hexyne-3 - Adduct) in refluxing o-dichlorobenzene [733].

IR [733], UV [733], MS [733].

1-(2,5-Diethyl-6-hydroxy-3-methylphenyl)ethanone

$C_{13}H_{18}O_2$ mol.wt. 206.28

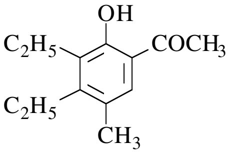


Synthesis

-Obtained (small amounts) by Fries rearrangement of 2,5-diethyl-4-methylphenyl acetate with aluminium chloride without solvent at 130° [101].

1-(3,4-Diethyl-2-hydroxy-5-methylphenyl)ethanone

$C_{13}H_{18}O_2$ mol.wt. 206.28



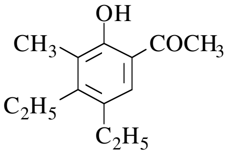
Syntheses

-Obtained by heating some esters* with aluminium chloride. There is simultaneously displacement and rearrangement of alkyl groups during the Fries reaction,
*2,4-diethyl-5-methylphenyl acetate (65%) [102];
*2,5-diethyl-4-methylphenyl acetate (at 130°) (60%) [101];
*2,6-diethyl-4-methylphenyl acetate (60%) [102].

b.p.$_{12}$ 136-137° [102], b.p.$_{11}$ 143-145° [102], b.p.$_{15}$ 154-162° [101].

1-(4,5-Diethyl-2-hydroxy-3-methylphenyl)ethanone

$C_{13}H_{18}O_2$ mol.wt. 206.28



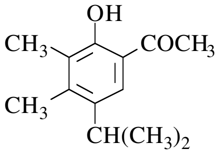
Synthesis

-Obtained by heating 2,4-diethyl-6-methylphenyl acetate with aluminium chloride at high temperature. In this reaction, a migration of an ethyl group occurs [102].

m.p. 50-51° [102].

1-[3,4-Dimethyl-2-hydroxy-5-(1-methylethyl)phenyl]ethanone

$C_{13}H_{18}O_2$ mol.wt. 206.28



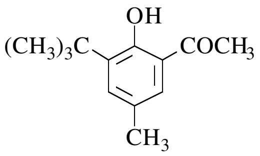
Synthesis

-Preparation by Fries rearrangement of 2,3-dimethyl-4-isopropylphenyl acetate with aluminium chloride at 140-150° (37%) [1523].

m.p. 132° [1523]; b.p.$_{22}$ 176-180° [1523].

1-[3-(1,1-Dimethylethyl)-2-hydroxy-5-methylphenyl]ethanone

[14813-18-4] $C_{13}H_{18}O_2$ mol.wt. 206.28



Syntheses

-Preparation by Fries rearrangement of 2-tert-butyl-4-methylphenyl acetate in the presence of aluminium chloride in cyclohexane at < 105° (47%) [412].

-The reaction of acetyl chloride with a pentane solution of [AlCH$_3$(dbmp)$_2$] leads to acylation of one of the (dbmp) ligands and affords [AlCH$_3$(dbmp)(bhmap)]. Hydrolysis of this aluminium complex with a saturated aqueous solution of ammonium chloride gives the ketone attempted (65%) [1440].

N.B.: Hdbmp = 2,6-di-tert-butyl-4-methylphenol and Hbhmap = 3-tert-butyl-2-hydroxy-5-methylacetophenone.

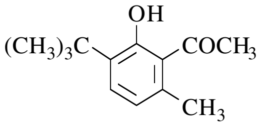
-Also obtained by reaction of p-tert-butyl alcohol with 2-hydroxy-5-methylacetophenone in concentrated sulfuric acid at r.t. for 24 h (49%) [1049].

-Also refer to: [1431].

m.p. 97-98° [412], 58° [1440]. One of the reported melting points is obviously wrong.
X-ray crystallography [1440]; GC/MS [1049];
^{1}H NMR [1049] [1440], ^{13}C NMR [1440], IR [1440], MS [1440].

1-[3-(1,1-Dimethylethyl)-2-hydroxy-6-methylphenyl]ethanone

$C_{13}H_{18}O_2$ mol.wt. 206.28



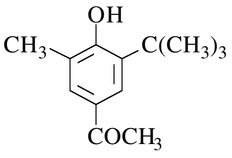
Synthesis

-Claimed to be prepared by Fries rearrangement of 2-tert-butyl-5-methylphenyl acetate with aluminium chloride, without solvent, at 110° (76%) [1800].

b.p.$_8$ 92° [1800].

1-[3-(1,1-Dimethylethyl)-4-hydroxy-5-methylphenyl]ethanone

[18606-50-3] $C_{13}H_{18}O_2$ mol.wt. 206.28



Syntheses

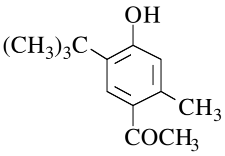
-Preparation by reaction of acetyl chloride or acetic anhydride with 2-tert-butyl-6-methylphenol in the presence of aluminium chloride, and saponification of keto ester obtained [1223].

-Also obtained (poor yield) by oxidation of 2-tert-butyl-4-ethyl-6-methylphenol. The oxidation was carried out by bubbling air at 80-100° into a solution of 2-tert-butyl-4-ethyl-6-methylphenol in cumene containing cobalt phthalate and cumene hydroperoxide as initiator (4%) [780].

m.p. 126° [780], 123-125° [1223].

1-[5-(1,1-Dimethylethyl)-4-hydroxy-2-methylphenyl]ethanone

$C_{13}H_{18}O_2$ mol.wt. 206.28



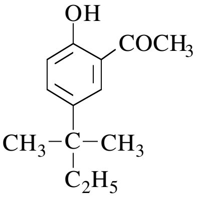
Synthesis

-Preparation by Fries rearrangement of 2-tert-butyl-5-methylphenyl acetate with aluminium chloride in nitrobenzene at 25° (22%) [1800].

m.p. 124° [1800].

1-[5-(1,1-Dimethylpropyl)-2-hydroxyphenyl]ethanone

$C_{13}H_{18}O_2$ mol.wt. 206.28



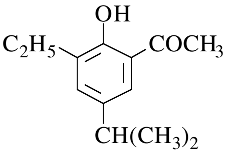
Synthesis

-Preparation by Fries rearrangement of 4-tert-pentylphenyl acetate with aluminium chloride at 120° (57%) [1583].

b.p.$_{12}$ 165° [1583].

1-[3-Ethyl-2-hydroxy-5-(1-methylethyl)phenyl]ethanone

$C_{13}H_{18}O_2$ mol.wt. 206.28



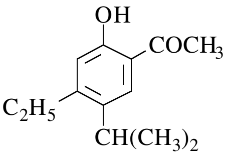
Synthesis

-Preparation by chromic acid degradation of 7-ethyl-2,3-dimethyl-5-isopropylbenzofuran (44%) [967].

b.p.$_{10}$ 139-140° [967].

1-[4-Ethyl-2-hydroxy-5-(1-methylethyl)phenyl]ethanone

$C_{13}H_{18}O_2$ mol.wt. 206.28



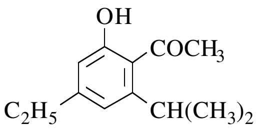
Synthesis

-Preparation by chromic acid degradation of 6-ethyl-2,3-dimethyl-5-isopropylbenzofuran (44%) [967].

b.p.$_{11}$ 152-153° [967].

1-[4-Ethyl-2-hydroxy-6-(1-methylethyl)phenyl]ethanone

$C_{13}H_{18}O_2$ mol.wt. 206.28



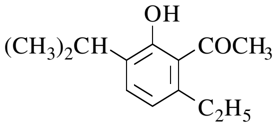
Synthesis

-Preparation by chromic acid degradation of 6-ethyl-2,3-dimethyl-4-isopropylbenzofuran (60%) [967].

m.p. 113° [967]; b.p.$_{14}$ 167-168° [967].

1-[6-Ethyl-2-hydroxy-3-(1-methylethyl)phenyl]ethanone

$C_{13}H_{18}O_2$ mol.wt. 206.28



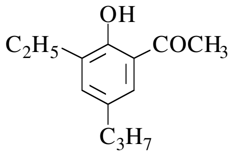
Synthesis

-Preparation by chromic acid degradation of 4-ethyl-2,3-dimethyl-7-isopropylbenzofuran (60%) [967].

b.p.$_{11}$ 145° [967].

1-(3-Ethyl-2-hydroxy-5-propylphenyl)ethanone

$C_{13}H_{18}O_2$ mol.wt. 206.28



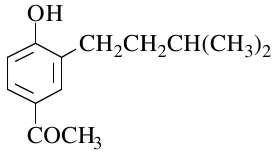
Synthesis

-Preparation by Fries rearrangement of 2-ethyl-4-propylphenyl acetate with aluminium chloride [100].

b.p.$_{18}$ 140-141° [100].

1-[4-Hydroxy-3-(3-methylbutyl)phenyl]ethanone

$C_{13}H_{18}O_2$ mol.wt. 206.28



Synthesis

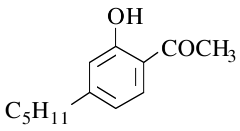
-Preparation by Fries rearrangement of 2-isopentylphenyl acetate [264] [500].

Isolation from natural sources

-Also obtained by catalytic hydrogenation of Tremetone in the presence of Pd/C. Tremetone has been isolated from the "*White Snakeroot* " plant (Eupatorium urticaefolium) [264] [500].

1-(2-Hydroxy-4-pentylphenyl)ethanone

[60441-58-9] $C_{13}H_{18}O_2$ mol.wt. 206.28



Syntheses

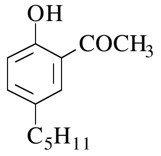
-Preparation by Fries rearrangement of 3-pentylphenyl acetate with aluminium chloride at 130° (50%) [81].

-Also obtained by demethylation of a mixture of 2-methoxy-4-pentylacetophenone and 4-methoxy-2-pentylacetophenone (**I**) with boron tribromide in methylene chloride at 0° and separation of isomers by chromatography (21%). The mixture of anisoles (**I**) was obtained by reaction of acetic anhydride with 3-pentylanisole in the presence of aluminium chloride in refluxing carbon disulfide [533].

oil [81] [533]; b.p.$_{0.5}$ 130° [533]; ^{1}H NMR [81] [533].

1-(2-Hydroxy-5-pentylphenyl)ethanone

$C_{13}H_{18}O_2$ mol.wt. 206.28



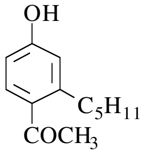
Synthesis

-Preparation by reaction of acetic acid on 4-pentylphenol with boron trifluoride at 140-150° (87%) [79].

b.p.$_7$ 145-148° [79]; n_D^{25} = 1.5249 [79].

1-(4-Hydroxy-2-pentylphenyl)ethanone

[60441-59-0] $C_{13}H_{18}O_2$ mol.wt. 206.28



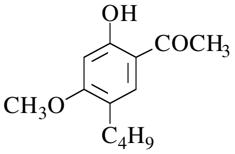
Synthesis

-Preparation by demethylation of a mixture of 2-methoxy-4-pentylacetophenone and 4-methoxy-2-pentylacetophenone (**I**) with boron tribromide in methylene chloride at 0° and separation of isomers by chromatography (46%). The mixture of anisoles (**I**) was obtained by reaction of acetic anhydride with 3-pentylanisole in the presence of aluminium chloride in refluxing carbon disulfide [533].

m.p. 58-59° [533]; ^{1}H NMR [533].

1-(5-Butyl-2-hydroxy-4-methoxyphenyl)ethanone

$C_{13}H_{18}O_3$ mol.wt. 222.28

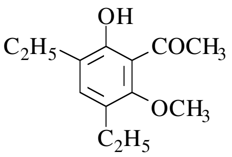


Synthesis

-Preparation by reaction of dimethyl sulfate on 5-butyl-2,4-dihydroxyacetophenone with potassium carbonate in boiling acetone [930].

1-(3,5-Diethyl-2-hydroxy-6-methoxyphenyl)ethanone

[37467-70-2] $C_{13}H_{18}O_3$ mol.wt. 222.28



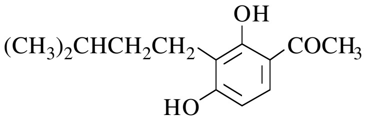
Synthesis

-Preparation by reaction of methyl iodide with 3,5-diethyl-2,6-dihydroxyacetophenone in the presence of potassium carbonate in boiling acetone (46%) [343].

oil [343]; MS [343].

1-[2,4-Dihydroxy-3-(3-methylbutyl)phenyl]ethanone

[50773-37-0] $C_{13}H_{18}O_3$ mol.wt. 222.28



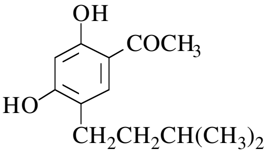
Synthesis

-Preparation by catalytic hydrogenation of 3-(dimethylallyl)-2,4-dihydroxacetophenone with platinic oxide as a catalyst in ethanol [1056].

m.p. 115° [1056]; ^{1}H NMR [1056], IR [1056].

1-[2,4-Dihydroxy-5-(3-methylbutyl)phenyl]ethanone

[56146-52-2] $C_{13}H_{18}O_3$ mol.wt. 222.28



Syntheses

-Obtained by Fries rearrangement of 4-isoamylresorcinol diacetate with aluminium chloride in nitrobenzene at 50-55° [264] [500], (11%) [500].

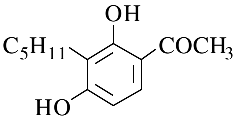
Isolation from natural sources

-Also obtained by hydrogenolysis of 6-hydroxytremetone in the presence of 10% Pd/C in ethanol at r.t. [264] [500], (62%) [500]. The 6-hydroxytremetone has been isolated from the *Eupatorium urticaefolium* Reichard (Compositae) (white snakeroot).

m.p. 93-95° [500], 92°5-94° [264]; IR [500].

1-(2,4-Dihydroxy-3-pentylphenyl)ethanone

[111224-14-7] $C_{13}H_{18}O_3$ mol.wt. 222.28

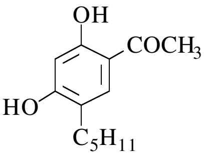


Synthesis

-Refer to: [1158].

1-(2,4-Dihydroxy-5-pentylphenyl)ethanone

[97304-17-1] $C_{13}H_{18}O_3$ mol.wt. 222.28



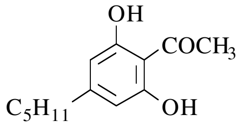
Syntheses

-Preparation by reaction of acetonitrile on 4-n-amylresorcinol (Hoesch reaction) (76%) [1277].
-Preparation from 2,4-dimethoxy-5-pentylacetophenone by demethylation with boron tribromide in methylene chloride at r.t. (53%) [256] [257].

m.p. 110-111° [1277].

1-(2,6-Dihydroxy-4-pentylphenyl)ethanone

[67895-11-8] $C_{13}H_{18}O_3$ mol.wt. 222.28

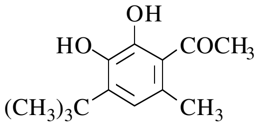


Synthesis

-Preparation by metallation of olivetol tetrahydropyranyl ether with n-butyllithium in tetrahydrofuran under nitrogen, followed by adding cuprous bromide in this solution. The condensation of 2,6-dihydroxy-4-pentylphenylcopper tetrahydropyranyl ether so obtained with acetyl chloride, connected with elimination of protective group under mild conditions gave the expected compound (80%) [1123].

1-[4-(1,1-Dimethylethyl)-2,3-dihydroxy-6-methylphenyl]ethanone

[84297-01-8] $C_{13}H_{18}O_3$ mol.wt. 222.28



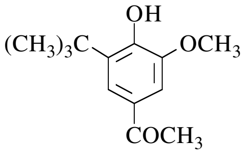
Synthesis

-Obtained by UV irradiation of a benzene solution of 3-tert-butyl-5-methyl-o-benzoquinone in the presence of a large excess of acetaldehyde (12%) [1758].

m.p. 72-73° [1758]; ^{1}H NMR [1758], IR [1758].

1-[3-(1,1-Dimethylethyl)-4-hydroxy-5-methoxyphenyl]ethanone

[153356-09-3] $C_{13}H_{18}O_3$ mol.wt. 222.28

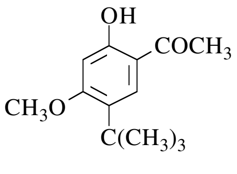


Syntheses

-Obtained by partial methylation of 3,4-dihydroxy-5-tert-butylacetophenone with diazomethane [1190].
-Also refer to: [1916].
N.B.: *(Catechol O-methyltransferase test).*
-Also obtained from 3,4-dihydroxy-5-tert-butylacetophenone in propylene glycol by incubation for 2 h at 37° with 0.5 M phosphate buffer (pH = 7.9), 0.5 M magnesium chloride, S-adenosylmethionine and catechol O-methyltransferase (enzyme). This enzyme solution was prepared from the blood of an adult male rat [1190].

1-[5-(1,1-Dimethylethyl)-2-hydroxy-4-methoxyphenyl]ethanone

[127371-46-4] $C_{13}H_{18}O_3$ mol.wt. 222.28

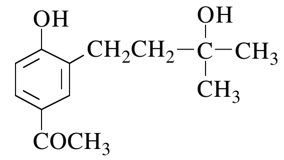


Synthesis

-Refer to: [1576] (patent).

1-[4-Hydroxy-3-(3-hydroxy-3-methylbutyl)phenyl]ethanone

[81944-40-3] $C_{13}H_{18}O_3$ mol.wt. 222.28



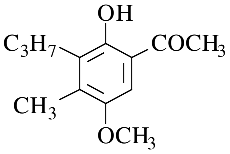
Isolation from natural sources

-From Senecio species of the North of Chile (*Senecio phylolleptus* Cuatr., *Senecio viridis* Phil., *Senecio nutans* Sch. Bip.) [1260].
-From the aerial parts of *Werneria poposa* [1429].
-Also refer to: [1704].

m.p. 100-101° [1260]; ^{1}H NMR [1260] [1429],
^{13}C NMR [1260] [1429], IR [1260], MS [1260] [1429].

1-(2-Hydroxy-5-methoxy-4-methyl-3-propylphenyl)ethanone

[43037-71-4] $C_{13}H_{18}O_3$ mol.wt. 222.28

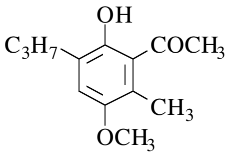


Synthesis

-Preparation by catalytic hydrogenation of 3-allyl-2-hydroxy-5-methoxy-4-methylacetophenone, previously obtained by thermal Claisen rearrangement of 2-(allyloxy)-5-methoxy-4-methylacetophenone in N,N-dimethylaniline at 170° (42%) [581].

1-(2-Hydroxy-5-methoxy-6-methyl-3-propylphenyl)ethanone

[43037-72-5] $C_{13}H_{18}O_3$ mol.wt. 222.28

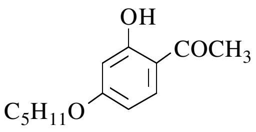


Synthesis

-Preparation by catalytic hydrogenation of 3-allyl-2-hydroxy-5-methoxy-6-methylacetophenone, previously obtained by thermal Claisen rearrangement of 2-(allyloxy)-5-methoxy-4-methylacetophenone — *via* a [1,5] sigmatropic rearrangement — in N,N-dimethylaniline at 170° (22%) [581].

1-[2-Hydroxy-4-(pentyloxy)phenyl]ethanone

[101002-29-3] $C_{13}H_{18}O_3$ mol.wt. 222.28



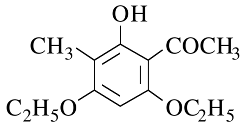
Syntheses

-Preparation by partial alkylation of resacetophenone with pentyl bromide in the presence of potassium carbonate in refluxing acetone for 20 h [183].
-Also refer to: [1771].

m.p. 36° [183].

1-(4,6-Diethoxy-2-hydroxy-3-methylphenyl)ethanone

$C_{13}H_{18}O_4$ mol.wt. 238.28



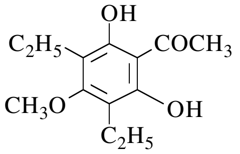
Synthesis

-Preparation by reaction of ethyl iodide or diethyl sulfate on 2,4,6-trihydroxy-3-methylacetophenone with potassium carbonate in boiling acetone (77%) [1883].

m.p. 147° [1883].

1-(3,5-Diethyl-2,6-dihydroxy-4-methoxyphenyl)ethanone

[175785-86-1] $C_{13}H_{18}O_4$ mol.wt. 238.28



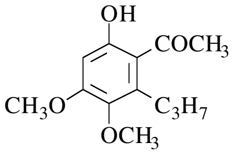
Synthesis

-Refer to: [1737] (Japanese patent).

N.B.: di-Na salt [175785-89-4] [1737].

1-(3,4-Dimethoxy-6-hydroxy-2-propylphenyl)ethanone

$C_{13}H_{18}O_4$ mol.wt. 238.28



Syntheses

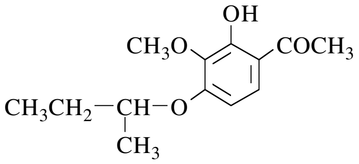
-Preparation by catalytic hydrogenation of 6-(benzyloxy)-3,4-dimethoxy-2-propenylacetophenone in the presence of Pd/C in methanol [498].

-Also obtained by addition of 6-(benzyloxy)-3,4-dimethoxy-2-propenylacetophenone in ethyl ether to calcium in liquid ammonia, and addition of ammonium chloride before evaporation of solvents [498].

yellow oil [498]; b.p.$_{0.2}$ 160° [498]; UV [498].

1-[2-Hydroxy-3-methoxy-4-(1-methylpropoxy)phenyl]ethanone

[94245-10-0] $C_{13}H_{18}O_4$ mol.wt. 238.28

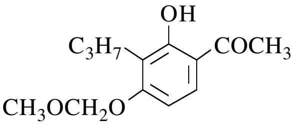


Synthesis

-Refer to: [1796] (Indian patent).

1-[2-Hydroxy-4-(methoxymethoxy)-3-propylphenyl]ethanone

[200355-19-7] $C_{13}H_{18}O_4$ mol.wt. 238.28



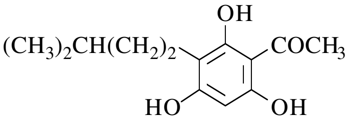
Synthesis

-Preparation by treatment of 2,4-dihydroxy-3-propylacetophenone according to the procedure [1395], (83%) [1394].

b.p.$_1$ 152-154° [1394]; ^{1}H NMR [1394], IR [1394].

1-[2,4,6-Trihydroxy-3-(3-methylbutyl)phenyl]ethanone

[39652-85-2] $C_{13}H_{18}O_4$ mol.wt. 238.28



Syntheses

-Preparation by reaction of acetonitrile on 2-isoamylphloroglucinol (Hoesch reaction) (93%) [1677].

-Preparation by reaction of 2-isoamylphloroglucinol with boron trifluoride-acetic acid complex at 28-30° (70%) [1146].

-Preparation by catalytic hydrogenolysis of 2-acetyl-4,4-bis-(3-methylbut-2-enyl)cyclohexane-1,3,5-trione at r.t. and pressure in the presence of 10% Pd/C in ethanol (93%) [426].

-Preparation by catalytic hydrogenation of 2',4',6'-trihydroxy-3'-(3-methylbut-2-enyl)acetophenone [426].

-Also obtained by catalytic hydrogenation of 7-acetyl-4,6-dihydroxy-2-isopropenylcoumaran in the presence of platinic oxide (Adams catalyst) in methanol (72%) [1322].

-Also obtained by catalytic hydrogenation of 9-acetyl-2,5-dihydro-3-methyl-1-benzoxepin-6,8-diol in ethyl acetate in the presence of Adams catalyst (25%) [1908].

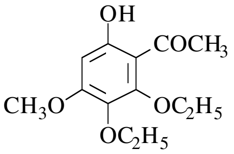
-Also obtained (by-product) by reaction of isoamyl iodide with phloroacetophenone in the presence of sodium methoxide in methanol (6%) [1491].

m.p. 190-192° [1908], 190° [1146], 188° [1491] [1677], 185° [1322], 184-185°5 [426], 183-184° [1611], 130-131° (compound **VIII**) [350]. One of the reported melting points is obviously wrong.

b.p.$_{0.01}$ 190° [1677]; ^{1}H NMR [350] [1908], IR [1908], UV [426].

1-(2,3-Diethoxy-6-hydroxy-4-methoxyphenyl)ethanone

$C_{13}H_{18}O_5$ mol.wt. 254.28



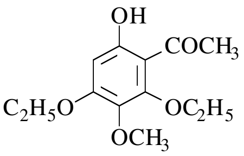
Synthesis

-Preparation by reaction of diethyl sulfate on 2-ethoxy-3,6-dihydroxy-4-methoxyacetophenone with potassium carbonate in boiling acetone [73].

oil [73].

1-(2,4-Diethoxy-6-hydroxy-3-methoxyphenyl)ethanone

[18086-01-6] $C_{13}H_{18}O_5$ mol.wt. 254.28



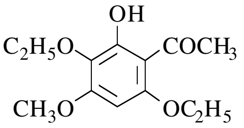
Syntheses

-Preparation by reaction of dimethyl sulfate on 2,4-diethoxy-3,6-dihydroxyacetophenone with potassium carbonate in refluxing acetone [73] [1516] [1550], (47%) [1516].
-The same ketone was also obtained by alkaline degradation of 4',5,7-triethoxy-3',6-dimethoxyflavone with potassium hydroxide in refluxing dilute ethanol [73].

oil [73] [1516].

1-(3,6-Diethoxy-2-hydroxy-4-methoxyphenyl)ethanone

[105342-72-1] $C_{13}H_{18}O_5$ mol.wt. 254.28



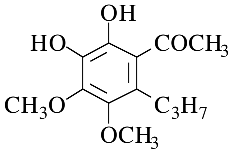
Syntheses

-Preparation from 1,4-diethoxy-2,6-dimethoxybenzene by reaction,
*with acetyl chloride in the presence of aluminium chloride in ethyl ether cooled in an ice bath (89%) [1467];
*with acetic acid in the presence of boron trifluoride for 5 h at 80° (50%) [198].

m.p. 104-105° [1467], 101-103° [198].

1-(2,3-Dihydroxy-4,5-dimethoxy-6-propylphenyl)ethanone

[76576-61-9] $C_{13}H_{18}O_5$ mol.wt. 254.28



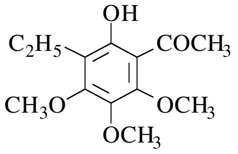
Synthesis

-Preparation by treatment of acetyldihydrodillapiole with boron trifluoride (almost quantitative yield) [1806].

m.p. 110° [1806];
^{1}H NMR [1806], IR [1806], MS [1806].

1-(3-Ethyl-2-hydroxy-4,5,6-trimethoxyphenyl)ethanone

$C_{13}H_{18}O_5$ mol.wt. 254.28



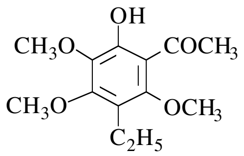
Synthesis

-Preparation by Fries rearrangement of 2-ethyl-3,4,5-trimethoxyphenyl acetate with aluminium chloride in nitrobenzene at r.t. (25%) [1452].

b.p.$_{0.15}$ 98-102° [1452]; n_D^{25} = 1.5293 [1452].

1-(3-Ethyl-6-hydroxy-2,4,5-trimethoxyphenyl)ethanone

$C_{13}H_{18}O_5$ mol.wt. 254.28



Syntheses

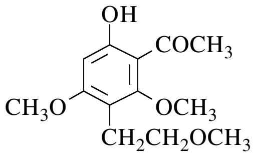
-Preparation by Fries rearrangement of 4-ethyl-2,3,5-trimethoxyphenyl acetate with aluminium chloride in nitrobenzene at r.t. (51%) [1452].

-Preparation by reaction of acetyl chloride on 1-ethyl-2,3,4,6-tetramethoxybenzene with aluminium chloride in ethyl ether between -20 to -15°, followed by standing overnight at r.t. (46%) [1452].

clear, orange coloured oil [1452]; b.p.$_{0.3}$ 117-118°5 [1452]; n_D^{25} = 1.5421 [1452].

1-[6-Hydroxy-2,4-dimethoxy-3-(2-methoxyethyl)phenyl]ethanone

[34288-74-9] $C_{13}H_{18}O_5$ mol.wt. 254.28



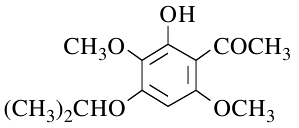
Synthesis

-Obtained by reaction of methyl iodide with 2-hydroxy-4,6-dimethoxy-5-(2-hydroxyethyl)acetophenone (m.p. 133-134°) in chloroform in the presence of silver oxide at r.t. overnight (25%) [1214].

m.p. 94-94°5 [1214];
^{1}H NMR [1214], UV [1214].

1-[2-Hydroxy-3,6-dimethoxy-4-(1-methylethoxy)phenyl]ethanone

[93344-52-6] $C_{13}H_{18}O_5$ mol.wt. 254.28

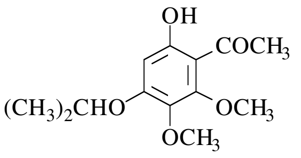


Syntheses

-Refer to: [846] (compound 11) and [1767] (Japanese paper).

1-[6-Hydroxy-2,3-dimethoxy-4-(1-methylethoxy)phenyl]ethanone

[119136-17-3] $C_{13}H_{18}O_5$ mol.wt. 254.28



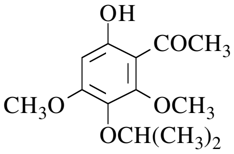
Synthesis

-Preparation by reaction of dimethyl sulfate with 2,5-dihydroxy-4-isopropoxy-6-methoxyacetophenone in the presence of potassium carbonate in refluxing acetone (82%) [841].

colourless oil [841]; ^{1}H NMR [841], IR [841], MS [841].

1-[6-Hydroxy-2,4-dimethoxy-3-(1-methylethoxy)phenyl]ethanone

[96501-84-7] $C_{13}H_{18}O_5$ mol.wt. 254.28



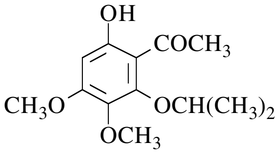
Synthesis

-Obtained by partial isopropylation of 2,5-dihydroxy-4,6-dimethoxyacetophenone with isopropyl bromide, according to [845], (compound 27) (44%) [842].

brown oil [842]; ^{1}H NMR [842].

1-[6-Hydroxy-3,4-dimethoxy-2-(1-methylethoxy)phenyl]ethanone

[188927-29-9] $C_{13}H_{18}O_5$ mol.wt. 254.28



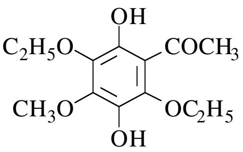
Synthesis

-Preparation by treatment of 3,4,6-trimethoxy-2-isopropoxyacetophenone (m.p. 69-71°) with aluminium bromide in acetonitrile at 0° for 10-15 min (80%) [804].
N.B.: The partial demethylation realized with aluminium bromide-sodium iodide system at 0° for 10 min gave a 94% yield.

m.p. 65-67° [804].

1-(3,6-Diethoxy-2,5-dihydroxy-4-methoxyphenyl)ethanone

$C_{13}H_{18}O_6$ mol.wt. 270.28



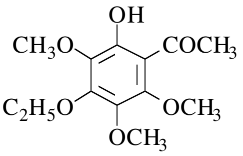
Synthesis

-Preparation from 3,6-diethoxy-2-hydroxy-4-methoxyacetophenone by persulfate oxidation (Elbs reaction) (33%) [1467].

m.p. 131-132° [1467].

1-(4-Ethoxy-2-hydroxy-3,5,6-trimethoxyphenyl)ethanone

$C_{13}H_{18}O_6$ mol.wt. 270.28



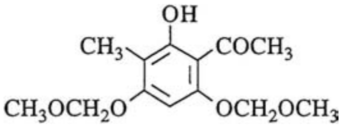
Synthesis

-Preparation by Friedel-Crafts acylation of 1-ethoxy-2,3,5,6-tetramethoxybenzene with acetyl chloride in the presence of aluminium chloride (46%) [801].

b.p.$_{0.1}$ 117-119° [801].

1-[2-Hydroxy-4,6-bis(methoxymethoxy)-3-methylphenyl]ethanone

[106929-57-1] $C_{13}H_{18}O_6$ mol.wt. 270.28



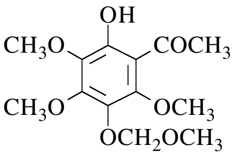
Synthesis

-Preparation by reaction of chloromethyl methyl ether with 2,4,6-trihydroxy-3-methylacetophenone in cooled acetone in the presence of potassium carbonate for 1 h (34%) [1228].

m.p. 77-78° [1228]; ^{1}H NMR [1228].

1-[2-Hydroxy-3,4,6-trimethoxy-5-(methoxymethoxy)phenyl]ethanone

[173217-34-0] $C_{13}H_{18}O_7$ mol.wt. 286.28

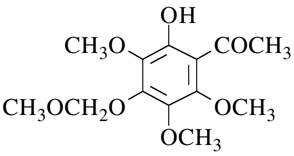


Synthesis

-Preparation by reaction of chloromethyl methyl ether with 2,5-dihydroxy-3,4,6-trimethoxyacetophenone in methylene chloride in the presence of N,N-diisopropylethylamine at r.t. for 3-4 h [795].

1-[2-Hydroxy-3,5,6-trimethoxy-4-(methoxymethoxy)phenyl]ethanone

[176662-07-0] $C_{13}H_{18}O_7$ mol.wt. 286.28

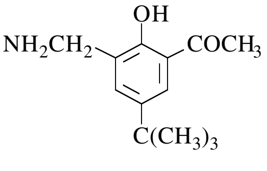


Synthesis

-Obtained by stirring a solution of 2,4-dihydroxy-3,5,6-trimethoxyacetophenone, N,N-diisopropylethylamine and chloromethyl methyl ether in methylene chloride at 5° for 40-50 min [797].

1-[3-(Aminomethyl)-5-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone

[75060-91-2] $C_{13}H_{19}NO_2$ mol.wt. 221.30

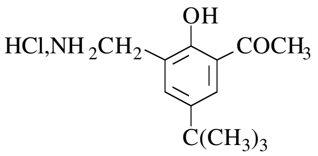


Synthesis

-Refer to: [1636].

1-[3-(Aminomethyl)-5-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone *(Hydrochloride)*

$C_{13}H_{19}NO_2$, HCl mol.wt. 268.77



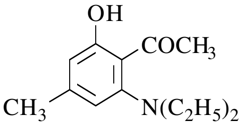
Synthesis

-Preparation by hydrolysis of 2-acetyl-4-tert-butyl-6-(N-chloroacetylaminomethyl)phenol with concentrated hydrochloric acid in refluxing ethanol (89%) [863].

m.p. 191-193° [863].

1-[2-(Diethylamino)-6-hydroxy-4-methylphenyl]ethanone

[97066-07-4] $C_{13}H_{19}NO_2$ mol.wt. 221.30



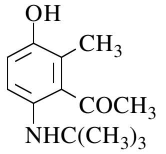
Synthesis

-Preparation by reaction of potassium hydroxide with 2-acetyl-3-diethylamino-5-hydroxy-5-methyl-2-cyclohexenone in ethanol at 40° (75%) [562].

yellow oil [562];
^1H NMR [562], IR [562], UV [562], MS [562].

1-[6-[(1,1-Dimethylethyl)amino]-3-hydroxy-2-methylphenyl]ethanone

[158013-69-5] $C_{13}H_{19}NO_2$ mol.wt. 221.30



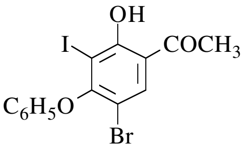
Synthesis

-Obtained from N-tert-butyl-2-acetyl-4-methyl quinol imine by refluxing overnight in trifluoroethanol (TFE) (quantitative yield) [1497].

red oil [1497]; ^1H NMR [1497],
^{13}C NMR [1497], IR [1497], MS [1497].

1-(5-Bromo-2-hydroxy-3-iodo-4-phenoxyphenyl)ethanone

[145489-48-1] $C_{14}H_{10}BrIO_3$ mol.wt. 433.04



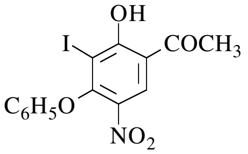
Synthesis

-Preparation by hypervalent iodine oxidation of 5-bromoresacetophenone with iodosobenzene diacetate in the presence of potassium hydroxide in methanol *via* the rearrangement of iodonium ylide previously formed (35%) [1441].

m.p. 160-161° [1441]; ^1H NMR [1441], MS [1441].

1-(2-Hydroxy-3-iodo-5-nitro-4-phenoxyphenyl)ethanone

[145489-93-6] $C_{14}H_{10}INO_5$ mol.wt. 399.14



Syntheses

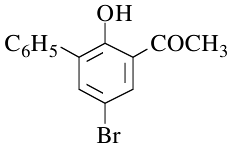
-Preparation by hypervalent iodine oxidation of 5-nitroresacetophenone with iodosobenzene diacetate in the presence of potassium hydroxide in methanol *via* the rearrangement of iodonium ylide previously formed (77%) [1441].

-Preparation by thermal rearrangement of 4-acetyl-3-hydroxy-6-nitro-2-phenyliodonio-phenolate (SM) in refluxing acetonitrile for 30 min (47%) [1681]. SM was obtained by reaction of iodosobenzene diacetate with 5-nitroresacetophenone in methanol in the presence of potassium hydroxide at 0° for 30 min (45%, m.p. 145-147°).

m.p. 190-191° [1441], 180-185° [1681];
^1H NMR [1441] [1681], IR [1441] [1681], MS [1681].

1-(5-Bromo-2-hydroxy[1,1'-biphenyl]-3-yl)ethanone

$C_{14}H_{11}BrO_2$ mol.wt. 291.14



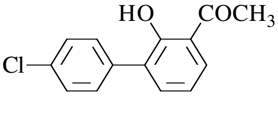
Synthesis

-Preparation by treatment of 1-(2-hydroxy[1,1'-biphenyl]-3-yl)ethanone in acetic acid with NBS at 85° for 2 h (quantitative yield) [1848].

^1H NMR [1848].

1-(4'-Chloro-2-hydroxy[1,1'-biphenyl]-3-yl)ethanone

[77893-89-1] $C_{14}H_{11}ClO_2$ mol.wt. 246.69



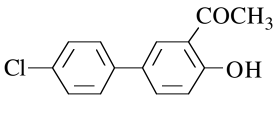
Synthesis

-Obtained by Fries rearrangement of 2-acetoxy-4'-chlorobiphenyl with aluminium chloride at 150° for 30 min (26%) [1762].

m.p. 76-78° [1762].

1-(4'-Chloro-4-hydroxy[1,1'-biphenyl]-3-yl)ethanone

[86608-89-1] $C_{14}H_{11}ClO_2$ mol.wt. 246.69

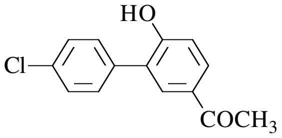


Synthesis

N.B.: It must be pointed out that in the referenced paper [835], the described product [(chloro-4 phenyl)-5 hydroxy-2 phenyl]-1 ethanone is not consistent with the mentioned starting material, (chloro-4 phenoxy)-4 phenol. In such a case, the obtained product should be the 1-[5-(4-chlorophenoxy)-2-hydroxyphenyl]-ethanone. One of the authors of this paper, Daniel Humbert, has confirmed this typing mistake [833].

1-(4'-Chloro-6-hydroxy[1,1'-biphenyl]-3-yl)ethanone

[77893-88-0] $C_{14}H_{11}ClO_2$ mol.wt. 246.69



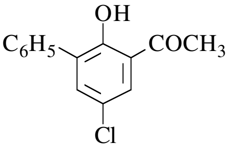
Synthesis

-Preparation by Fries rearrangement of 2-acetoxy-4'-chlorobiphenyl with aluminium chloride at 150° for 30 min (60%) [1762].

m.p. 165°5-167°5 [1762].

1-(5-Chloro-2-hydroxy[1,1'-biphenyl]-3-yl)ethanone

$C_{14}H_{11}ClO_2$ mol.wt. 246.69

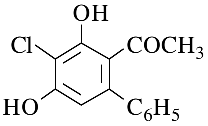


Synthesis

-Obtained by treatment of 1-(2-hydroxy[1,1'-biphenyl]-3-yl)ethanone in DMF solution with NCS at r.t. overnight (96%) (crude product) [1848].

1-(4-Chloro-3,5-dihydroxy[1,1'-biphenyl]-2-yl)ethanone

[76538-42-6] $C_{14}H_{11}ClO_3$ mol.wt. 262.69



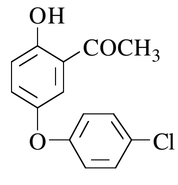
Synthesis

-Preparation by adding lithium chloride to a solution of 3-acetoxy-6-acetyl-2,6-dichloro-5-phenyl-2-cyclohexenone in DMF and heating for 2 h at 100° (83%) [1756].

m.p. 111-112° [1756]; ^{1}H NMR [1756], IR [1756], MS [1756].

1-[5-(4-Chlorophenoxy)-2-hydroxyphenyl]ethanone

[73051-30-6] $C_{14}H_{11}ClO_3$ mol.wt. 262.69



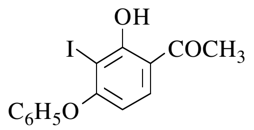
Syntheses

-Preparation by acetylation of 4-phenoxyphenol with,
*39.7% (w/w) boron trifluoride in acetic acid at 75° for 24 h (71%) [835];
*35-37% boron trifluoride in acetic acid at 90° for 3 days (quantitative yield) [833].
-Also refer to: [834].

m.p. 88° [834] [835].

1-(2-Hydroxy-3-iodo-4-phenoxyphenyl)ethanone

[144691-35-0] $C_{14}H_{11}IO_3$ mol.wt. 354.14



Syntheses

-Preparation by thermal rearrangement of 4-acetyl-3-hydroxy-2-phenyliodonio-phenolate (SM) in refluxing acetonitrile for 30 min (70%). SM was obtained by reaction of iodosobenzene diacetate with resacetophenone in methanol in the presence of potassium hydroxide at 0° for 30 min (40%, m.p. 81-85°) [1681].

-Preparation by reaction of resacetophenone with iodosobenzene diacetate in refluxing methanol (55%) [1139].

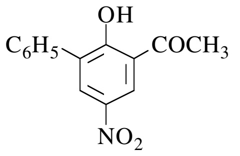
-Preparation by hypervalent iodine oxidation of resacetophenone with iodosobenzene diacetate in the presence of potassium hydroxide in methanol *via* the rearrangement of iodonium ylide previously formed (20%) [1441].

m.p. 116-118° [1441], 101-103° [1139], 72° [1681]. There is a discrepancy between the different melting points indicated in literature.

^1H NMR [1139] [1441] [1681], IR [1139], MS [1681].

1-(2-Hydroxy-5-nitro[1,1'-biphenyl]-3-yl)ethanone

[360791-69-1] $C_{14}H_{11}NO_4$ mol.wt. 257.25



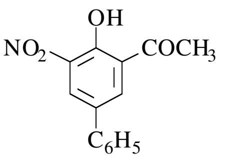
Synthesis

-Obtained by treatment of 3-bromo-2-hydroxy-5-nitroacetophenone and phenylboronic acid mixture in THF with tetrakis(triphenylphosphine)palladium (0) and 10% aqueous sodium carbonate. The mixture was heated at 80° for 3 h. Then, 10% Pd/C catalyst was added and heating continued for 1.5 h (70%) (compound 32) [1848].

^1H NMR [1848], ^{13}C NMR [1848].

1-(4-Hydroxy-5-nitro[1,1'-biphenyl]-3-yl)ethanone

[84942-37-0] $C_{14}H_{11}NO_4$ mol.wt. 257.25



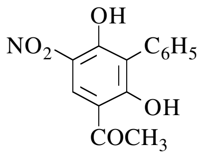
Synthesis

-Preparation by reaction of 100% nitric acid with 3-acetyl-4-hydroxybiphenyl in acetic acid at r.t. (90%) [318].

m.p. 113-114° [318].

1-(2,6-Dihydroxy-5-nitro[1,1'-biphenyl]-3-yl)ethanone

[160246-79-7] $C_{14}H_{11}NO_5$ mol.wt. 273.25



Syntheses

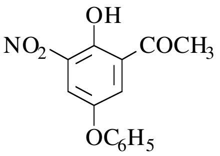
-Obtained by irradiation of 4-acetyl-3-hydroxy-6-nitro-2-phenyliodonio-phenolate (1 mmol),
*in benzene suspension (65%) [1681];
*in the presence of cyclohexene (3-5 mmol) in methylene chloride/acetonitrile solution (1:1) for 4 h (20-30%) [1681].

N.B.: The irradiations were performed with a 250 watt low pressure Hg lamp.

m.p. 160-161° [1681]; ^{1}H NMR [1681], IR [1681], MS [1681].

1-(2-Hydroxy-3-nitro-5-phenoxyphenyl)ethanone

[84942-38-1] $C_{14}H_{11}NO_5$ mol.wt. 273.25



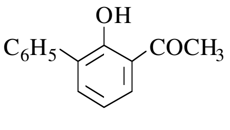
Synthesis

-Preparation by reaction of 100% nitric acid with 2-hydroxy-5-phenoxyacetophenone in acetic acid at r.t. (73%) [318].

m.p. 126-127° [318].

1-(2-Hydroxy[1,1'-biphenyl]-3-yl)ethanone

[21424-82-8] $C_{14}H_{12}O_2$ mol.wt. 212.25



Syntheses

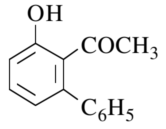
-Preparation by Fries rearrangement of 2-acetoxybiphenyl with aluminium chloride,
*without solvent between 130 to 160° [108] [746] [1181] [1182];
*in boiling o-dichlorobenzene for 30 min (15%) [859].

-Also obtained by UV light irradiation (254 nm) of 2-acetoxybiphenylyl in benzene (11%) [999].

m.p. 60-61° [108], 56°1-57°3 [859]; b.p.$_{14}$ 194-196° [108]; GC-MS [859]; ^{1}H NMR [859], IR [859].

1-(3-Hydroxy[1,1'-biphenyl]-2-yl)ethanone

[136819-93-7] $C_{14}H_{12}O_2$ mol.wt. 212.25



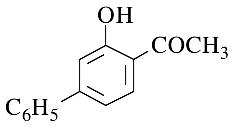
Synthesis

-Obtained by adding potassium fluoride to a solution of 1-phenyl-2-octene-1,5,7-trione in dry toluene and the whole refluxed overnight (32%) [1755].

colourless oil [1755];
^{1}H NMR [1755], IR [1755], MS [1755].

1-(3-Hydroxy[1,1'-biphenyl]-4-yl)ethanone

[32101-38-5] $C_{14}H_{12}O_2$ mol.wt. 212.25



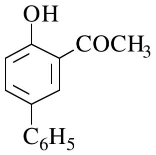
Syntheses

-Preparation by reaction of acetyl chloride with 3-methoxybiphenyl in the presence of aluminium chloride in refluxing methylene chloride for 11 h (50%) [281].
-Preparation by aromatization of 2-acetyl-3-chloro-5-phenyl-2-cyclohexenone in the presence of Pd/C in refluxing cyclohexene for 4 h (70%) [32].
-Preparation by dehydrogenation of 6-acetyl-3-phenyl-2-cyclohexen-1-one with refluxing 16% bromine solution in acetic acid [1059].
-Also refer to: [1166].

m.p. 91° [1059], 90°5-91°5 [281], 90-90°5 [32].

1-(4-Hydroxy[1,1'-biphenyl]-3-yl)ethanone

[14031-80-2] $C_{14}H_{12}O_2$ mol.wt. 212.25



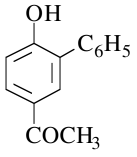
Syntheses

-Preparation by Fries rearrangement of 4-acetoxybiphenyl,
*with aluminium chloride without solvent at 120-140° [318] [595] [1280], (48%) [318] or in tetrachloroethane at 140° [381] [820] [1181] [1182], (46%) [820];
*with titanium tetrachloride in nitrobenzene at r.t. (6%) [1891].
-Also obtained by photo-Fries rearrangement of 4-acetoxybiphenylyl with 254 nm light in benzene (61%) [999].
-Also obtained — *via* an intermolecular photo-Fries rearrangement — by irradiation of a solution of pinacolone and p-phenylphenol in benzene for 5 h (42%) [898].
-Preparation by catalytic hydrogenation of 2-(benzyloxy)-5-phenylacetophenone in the presence of 10% Pd/C in 95% ethanol at r.t. under 35 psi for 2 h (84%) [1891].
-Preparation by adding an ethereal solution of methyl lithium to a solution of 5-phenylsalicylic acid in 1,2-dimethoxyethane under nitrogen and maintained at 10-12° (85%) [1891].
-Preparation by reaction of acetic acid with 4-hydroxybiphenyl in the presence of boron trifluoride-acetic acid complex (good yield) [1181] [1182].
-Also refer to: [392] [393] [394] [821].

m.p. 61°5-62° [381], 61-62° [318] [595], 60-61° [1891], 59-61° [820];
IR [1891].

1-(6-Hydroxy[1,1'-biphenyl]-3-yl)ethanone

[20281-51-0] $C_{14}H_{12}O_2$ mol.wt. 212.25



Syntheses

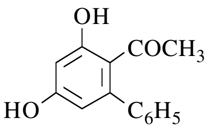
-Preparation by Fries rearrangement of 2-acetoxybiphenyl with aluminium chloride,
*without solvent between 130 to 160° [108] [746] [747], (60-62%) [108] [746];
*in nitrobenzene (58%) [1869] according to [1512];
*in boiling o-dichlorobenzene for 30 min (80%) [859].
-Also obtained by UV light irradiation (254 nm) of 2-acetoxybiphenyl in benzene (6%) [999].

-Preparation by direct condensation of 2-hydroxybiphenyl with acetic acid in the presence of boron trifluoride [331].
-Also refer to: [1870].

m.p. 184°1-184°4 [859], 177° [1869], 173° [331], 172-173° [108], 167-168°5 [746];
^{1}H NMR [859], IR [859]; GC-MS [859].

1-(3,5-Dihydroxy[1,1'-biphenyl]-2-yl)ethanone

[54439-83-7] $C_{14}H_{12}O_3$ mol.wt. 228.25



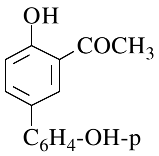
Synthesis

-Obtained (by-product) from 3-methyl-3'-phenyl-5,5'-di-isoxazolyl-methane by performing hydrogenolysis and subsequent hydrolysis with hydrochloric acid (12%) [97].

m.p. 139° [97]; ^{1}H NMR [97], MS [97].

1-(4,4'-Dihydroxy[1,1'-biphenyl]-3-yl)ethanone

[52189-90-9] $C_{14}H_{12}O_3$ mol.wt. 228.25



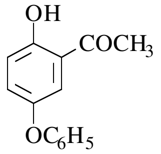
Syntheses

-Preparation by Fries rearrangement,
*of 4-acetoxy-4'-hydroxybiphenyl with aluminium chloride without solvent for 6 h at 168-170° (57%) [299];
*of 4,4'-diacetoxybiphenyl with aluminium chloride in tetrachloroethane for 6 h at 160° (34%) [299].
-Also obtained by irradiation of 4,4'-diphenoquinone [bi(cyclohexa-2,5-dienylidene)-4,4'-dione] in acetaldehyde for 2 days (28%) [299].

m.p. 193° [299]; ^{1}H NMR [299], IR [299], MS [299].

1-(2-Hydroxy-5-phenoxyphenyl)ethanone

[56926-34-2] $C_{14}H_{12}O_3$ mol.wt. 228.25



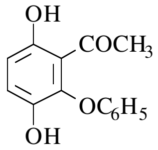
Syntheses

-Preparation by Fries rearrangement of 4-acetoxydiphenyl oxide in the presence of aluminium chloride at 120° (90%) [318].
-Preparation by catalytic hydrogenolysis of 2-(benzyloxy)-5-phenoxyacetophenone at r.t. at 35 psi in the presence of 10% Pd/C in ethanol (85%) [1891].
-Preparation by adding an etheral solution of methyllithium to a solution of 5-phenoxysalicylic acid in 1,2-dimethoxyethane (79%) [1891].

m.p. 160-161° [318], 71-73° [1891].
One of the reported melting points is obviously wrong.
^{1}H NMR [1891].

1-(3,6-Dihydroxy-2-phenoxyphenyl)ethanone

[52095-10-0] $C_{14}H_{12}O_4$ mol.wt. 244.25



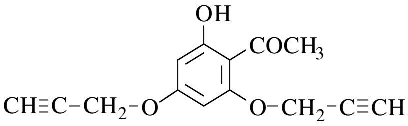
Synthesis

-Preparation by reaction of phenol on 2-acetylquinone with pyridine in benzene (40%) [586].

m.p. 68-70° [586]; ^{1}H NMR [586], IR [586].

1-[2-Hydroxy-4,6-bis(2-propynyloxy)phenyl]ethanone

[53771-23-6] $C_{14}H_{12}O_4$ mol.wt. 244.25



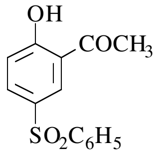
Synthesis

-Obtained by reaction of 2-propynyl bromide with phloroacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone in an atmosphere of nitrogen (12%) [427].

m.p. 111° [427]; IR [427], UV [427].

1-[2-Hydroxy-5-(phenylsulfonyl)phenyl]ethanone

[146575-61-3] $C_{14}H_{12}O_4S$ mol.wt. 276.31

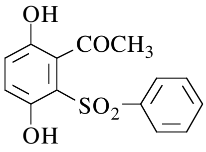


Synthesis

-Preparation by Fries rearrangement of 4-phenylsulfonylphenyl acetate with aluminium chloride at 190° (52%) [1919] [1920].

1-[3,6-Dihydroxy-2-(phenylsulfonyl)phenyl]ethanone

[145746-54-9] $C_{14}H_{12}O_5S$ mol.wt. 292.31



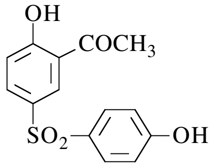
Synthesis

-Preparation by shaking an aqueous solution of sodium benzenesulfinate with a solution of 2-acetyl-1,4-benzoquinone and trifluoroacetic acid in methylene chloride for 4 h at r.t. (68%) [301].

m.p. 182-183° [301]; ^{1}H NMR [301], IR [301], MS [301].

1-[2-Hydroxy-5-[(4-hydroxyphenyl)sulfonyl]phenyl]ethanone

[147816-50-0] $C_{14}H_{12}O_5S$ mol.wt. 292.31

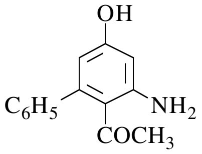


Syntheses

-Obtained by treatment of bisphenol-S diacetate (4,4'-diacetoxydiphenyl sulfone) with aluminium chloride (10 mol) at 160° (23%) [1684].
-Also obtained by UV light irradiation (254 nm) of bisphenol-S diacetate in acetonitrile for 5.5 h (18%) [1684].

1-(3-Amino-5-hydroxy[1,1'-biphenyl]-2-yl)ethanone

[54439-91-7] $C_{14}H_{13}NO_2$ mol.wt. 227.26



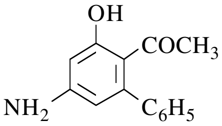
Synthesis

-Preparation from 5-methyl-3'-phenyl-3,5'-diisoxazolylmethane by performing hydrogenolysis and subsequent hydrolysis with hydrochloric acid (major product) [97].

m.p. 192° [97]; ^{1}H NMR [97], MS [97].

1-(5-Amino-3-hydroxy[1,1'-biphenyl]-2-yl)ethanone

[54439-90-6] $C_{14}H_{13}NO_2$ mol.wt. 227.26



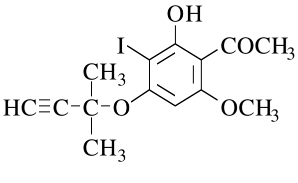
Synthesis

-Obtained (by-product) from 3'-methyl-5-phenyl-3,5'-diisoxazolyl-methane by performing hydrogenolysis and subsequent hydrolysis with hydrochloric acid (4%) [97].

m.p. 118° [97]; ^{1}H NMR [97], MS [97].

1-[4-[(1,1-Dimethyl-2-propynyl)oxy]-2-hydroxy-3-iodo-6-methoxyphenyl]ethanone

[82538-75-8] $C_{14}H_{15}IO_4$ mol.wt. 374.17



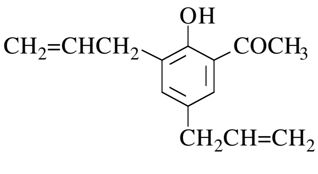
Synthesis

-Preparation by reaction of 3-chloro-3-methylbut-1-yne with 2,4-dihydroxy-3-iodo-6-methoxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (56%) [15].

m.p. 110-111° [15]; ^{1}H NMR [15].

1-[2-Hydroxy-3,5-bis(2-propenyl)phenyl]ethanone

[35158-35-1] $C_{14}H_{16}O_2$ mol.wt. 216.28



Syntheses

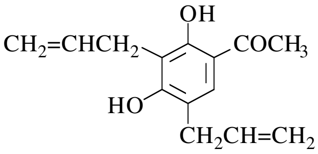
-Preparation by thermal Claisen rearrangement of 3-allyl-2-(allyloxy)acetophenone in N,N-diethylaniline for 4 h at 220° (93%) [343].

-Preparation by reaction of ethyl acetoacetate with 2-allyl-2,6-heptadienal in the presence of pyridine and piperidine as catalysts, in benzene at 60-70° (33%). The 2-allyl-2,6-heptadienal was obtained by self condensation of 4-pentenal in the presence of 15% potassium hydroxide solution [940] [941] [942].

oil [343] [940] [941] [942];
b.p.$_{1-2}$ 90-95° [940] [941] [942], b.p.$_{1.2}$ 100-120° [343];
IR [940] [941] [942], UV [940] [941] [942].

1-[2,4-Dihydroxy-3,5-bis(2-propenyl)phenyl]ethanone

[40815-80-3] $C_{14}H_{16}O_3$ mol.wt. 232.28



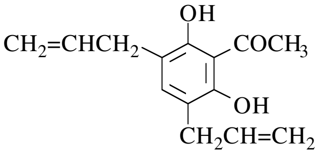
Syntheses

-Preparation by thermal Claisen rearrangement,
*of 3-allyl-4-(allyloxy)-2-hydroxyacetophenone without solvent at 210° (20%) [132];
*of 3'-acetyl-4',6'-bis(allyloxy)acetophenone in refluxing N,N-dimethylaniline (33%) [61] or in refluxing phenyl ether (11%) [61]:
*of 5'-acetyl-2',4'-bis(allyloxy)-3'-bromoacetophenone in refluxing N,N-dimethylaniline (16%) [61];
*of 3'-acetyl-2',4'-bis(allyloxy)acetophenone in refluxing N,N-dimethylaniline (18%) [61];
*of 2',4'-bis(allyloxy)acetophenone in refluxing N,N-dimethylaniline (40%) [61].

m.p. 90° [61], 89-90° [132]; ^{1}H NMR [61], IR [61], UV [61], MS [61].

1-[2,6-Dihydroxy-3,5-bis(2-propenyl)phenyl]ethanone

[37467-66-6] $C_{14}H_{16}O_3$ mol.wt. 232.28



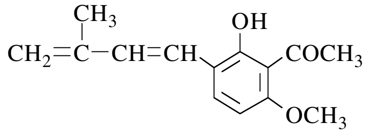
Syntheses

-Preparation by thermal Claisen rearrangement of,
*2',6'-bis(allyloxy)acetophenone in refluxing N,N-dimethylaniline (45%) [1251] or in N,N-diethylaniline for 4 h at 220° [343];
*3'-acetyl-4',6'-bis(allyloxy)acetophenone in refluxing N,N-dimethylaniline or in phenyl ether (6-7%) [61];
*3'-acetyl-2',4'-bis(allyloxy)acetophenone in refluxing N,N-dimethylaniline (6%) [61].

m.p. 57°5-58°5 [1251], 55-56° [343]; b.p.$_{0.03}$ 150° [1251];
^{1}H NMR [61], IR [61], UV [61], MS [61].

1-[2-Hydroxy-6-methoxy-3-(3-methyl-1,3-butadienyl)phenyl]ethanone *(Z)*

[141215-43-2] $C_{14}H_{16}O_3$ mol.wt. 232.28



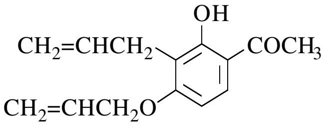
Synthesis

-Preparation by reaction of methylmagnesium iodide with 8-acetyl-7-methoxycoumarin in refluxing tetrahydrofuran during 1 h under nitrogen atmosphere (40%) [557].

m.p. 112° [557]; ^1H NMR [557], IR [557], UV [557], MS [557].

1-[2-Hydroxy-3-(2-propenyl)-4-(2-propenyloxy)phenyl]ethanone

[40903-02-4] $C_{14}H_{16}O_3$ mol.wt. 232.28



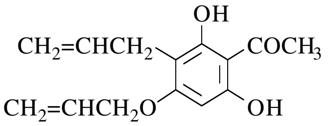
Synthesis

-Preparation by reaction of allyl bromide with 3-allyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone (62%) [132].

m.p. 34°5 [132].

1-[2,6-Dihydroxy-3-(2-propenyl)-4-(2-propenyloxy)phenyl]ethanone

[53771-28-1] $C_{14}H_{16}O_4$ mol.wt. 248.28



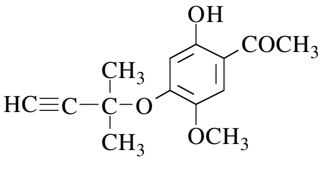
Synthesis

-Preparation by thermal Claisen rearrangement of 2,4-bis-(allyloxy)-6-hydroxyacetophenone in N-methylpiperazine at reflux in an atmosphere of nitrogen (53%) [427] or without solvent in a sealed vial at 130° (33%) [427].

m.p. 102-103°5 [427]; UV [427].

1-[4-[(1,1-Dimethyl-2-propynyl)oxy]-2-hydroxy-5-methoxyphenyl]ethanone

[70662-40-7] $C_{14}H_{16}O_4$ mol.wt. 248.28



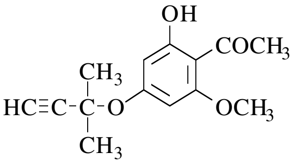
Synthesis

-Obtained by treatment of 2,4-dihydroxy-5-methoxy-acetophenone with 3-chloro-3-methyl-1-butyne in the presence of potassium carbonate and potassium iodide in DMF for 40 h at 80-85° (15%) [881].

yellow oil [881]; TLC [881]; ^1H NMR [881], UV [881].

1-[4-[(1,1-Dimethyl-2-propynyl)oxy]-2-hydroxy-6-methoxyphenyl]ethanone

[31273-60-6] $C_{14}H_{16}O_4$ mol.wt. 248.28



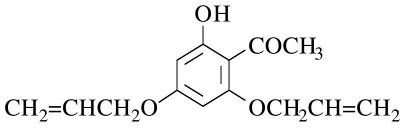
Synthesis

-Preparation by reaction of 2-methyl-2-chlorobut-3-yne on 2,4-dihydroxy-6-methoxyacetophenone with potassium carbonate and potassium iodide in refluxing acetone (80%) [127].

m.p. 107-108° [127].

1-[2-Hydroxy-4,6-bis(2-propenyloxy)phenyl]ethanone

[53771-27-0] $C_{14}H_{16}O_4$ mol.wt. 248.28



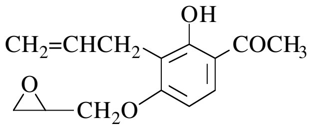
Synthesis

-Obtained by reaction of allyl bromide with phloroacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (10%) [427].

m.p. 62°5 [427]; UV [427].

1-[2-Hydroxy-4-(oxiranylmethoxy)-3-(2-propenyl)phenyl]ethanone

[40785-92-0] $C_{14}H_{16}O_4$ mol.wt. 248.28



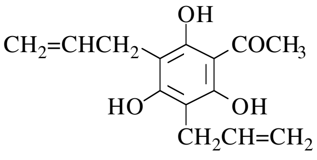
Synthesis

-Preparation by reaction of epichlorohydrin with 3-allyl-2,4-dihydroxyacetophenone in the presence of potassium hydroxide in refluxing ethanol [71].

m.p. 67°5-68°5 [71].

1-[2,4,6-Trihydroxy-3,5-bis(2-propenyl)phenyl]ethanone

[53771-29-2] $C_{14}H_{16}O_4$ mol.wt. 248.28



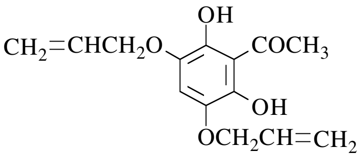
Synthesis

-Preparation by thermal Claisen rearrangement of 2,4-bis-(allyloxy)-6-hydroxyacetophenone in N,N-diethylaniline at reflux (215°) under nitrogen (87%) [427].

m.p. 67-68° [427]; UV [427].

1-[2,6-Dihydroxy-3,5-bis(2-propenyloxy)phenyl]ethanone

[73331-27-8] $C_{14}H_{16}O_5$ mol.wt. 264.28

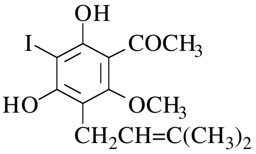


Synthesis

N.B.: In the paper [1251], the formula of the compound **59** displayed page 180, which is the formula of the titled compound $C_{14}H_{16}O_5$, does not fit at all with the one of the actually prepared compound. The Claisen rearrangement of 2,6-bis(allyloxy)acetophenone **58** leads to the formation of 3,5-diallyl-2,6-dihydroxyacetophenone $C_{14}H_{16}O_3$, page 183.

1-[2,4-Dihydroxy-3-iodo-6-methoxy-5-(3-methyl-2-butenyl)phenyl]ethanone

[82538-76-9] $C_{14}H_{17}IO_4$ mol.wt. 376.19



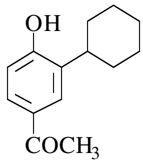
Synthesis

-Obtained by reaction of 2-methylbut-3-en-2-ol with 2,4-dihydroxy-3-iodo-6-methoxyacetophenone in the presence of boron trifluoride etherate in dioxane at 35-40° (11%) [15].

m.p. 136-137° [15]; ^{1}H NMR [15].

1-(3-Cyclohexyl-4-hydroxyphenyl)ethanone

[23299-00-5] $C_{14}H_{18}O_2$ mol.wt. 218.30



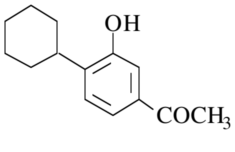
Synthesis

-Preparation by Fries rearrangement of 2-cyclohexylphenyl acetate with aluminium chloride in nitrobenzene at 85° [195] [1069], (55%) [1069].

m.p. 148-149° [195], 147-148° [1069].

1-(4-Cyclohexyl-3-hydroxyphenyl)ethanone

[73898-21-2] $C_{14}H_{18}O_2$ mol.wt. 218.30



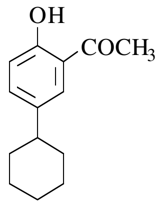
Synthesis

-Preparation by diazotization of 3-amino-4-cyclohexylacetophenone, followed by hydrolysis of diazonium salt obtained (48%) [1069].

m.p. 171° (Sadtler), 165-167° [1069];
^{1}H NMR, (Sadtler: standard n° 44602 M); IR, (Sadtler: standard n° 71630 K).

1-(5-Cyclohexyl-2-hydroxyphenyl)ethanone

[55168-33-7] $C_{14}H_{18}O_2$ mol.wt. 218.30



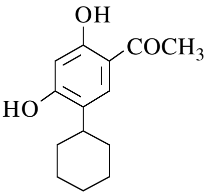
Syntheses

-Preparation by reaction of acetic acid with p-cyclohexylphenol in the presence of boron trifluoride at 75° for 24 h (91%) [835].
-Preparation by Fries rearrangement of p-cyclohexylphenyl acetate with aluminium chloride without solvent at 140° [1335] or at 170° [129], (47%) [1335].

colourless oil [129] [1335]; m.p. < 50° [835];
^{1}H NMR [1335].

1-(5-Cyclohexyl-2,4-dihydroxyphenyl)ethanone

[159977-36-3] $C_{14}H_{18}O_3$ mol.wt. 234.30



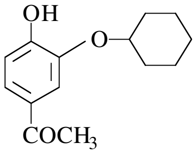
Synthesis

-Preparation by reaction of acetic acid with 4-cyclohexylresorcinol in the presence of boron trifluoride etherate at 105-108° for 15 min, followed by hydrolysis of the obtained boron difluoride chelate (m.p. 207-208°) with boiling aqueous ethanol for 15-20 min (89%) [1375].

m.p. 145-146° [1375]; IR [1375], UV [1375].

1-[3-(Cyclohexyloxy)-4-hydroxyphenyl]ethanone

$C_{14}H_{18}O_3$ mol.wt. 234.30



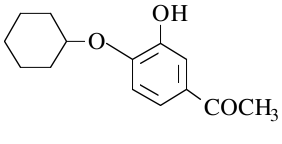
Syntheses

-Preparation by catalytic hydrogenolysis of 4-(benzyloxy)-3-cyclohexyloxyacetophenone in the presence of Pd/C in ethanol at r.t. (82%) [1210].
-Also obtained (poor yield) by reaction of cyclohexyl bromide with 3,4-dihydroxyacetophenone in the presence of sodium hydroxide in a refluxing mixture of ethanol and methanol (2%) [1210].

m.p. 88° [1210].

1-[4-(Cyclohexyloxy)-3-hydroxyphenyl]ethanone

$C_{14}H_{18}O_3$ mol.wt. 234.30



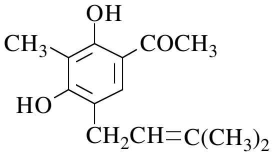
Synthesis

-Obtained (poor yield) by reaction of cyclohexyl bromide with 3,4-dihydroxyacetophenone in the presence of sodium hydroxide in a refluxing mixture of ethanol and methanol (8%) [1210].

m.p. 103° [1210].

1-[2,4-Dihydroxy-3-methyl-5-(3-methyl-2-butenyl)phenyl]ethanone

[74727-08-5] $C_{14}H_{18}O_3$ mol.wt. 234.30



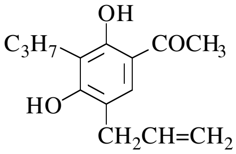
Synthesis

-Obtained by prenylation of 2,4-dihydroxy-3-methylacetophenone with 2-methyl-3-buten-2-ol in dioxane in the presence of boron trifluoride etherate for 1 h at r.t. (41%) [1607].

m.p. 117-118° [1607]; TLC [1607];
^{1}H NMR [1607], IR [1607].

1-[2,4-Dihydroxy-5-(2-propenyl)-3-propylphenyl]ethanone

[99370-48-6] $C_{14}H_{18}O_3$ mol.wt. 234.30

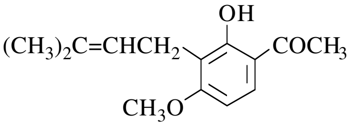


Synthesis

-Preparation by thermal Claisen rearrangement of 4-(allyloxy)-2-hydroxy-3-propylacetophenone without solvent at 210° (79%) [777].

1-[2-Hydroxy-4-methoxy-3-(3-methyl-2-butenyl)phenyl]ethanone

[52601-06-6] $C_{14}H_{18}O_3$ mol.wt. 234.30



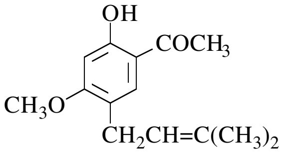
Synthesis

-Preparation by reaction of 2-methylbut-3-en-2-ol with 2-hydroxy-4-methoxyacetophenone in the presence of boron trifluoride etherate [43].

^{1}H NMR [43] [44], UV [43].

1-[2-Hydroxy-4-methoxy-5-(3-methyl-2-butenyl)phenyl]ethanone

[28448-83-1] $C_{14}H_{18}O_3$ mol.wt. 234.30



Syntheses

-Preparation by reaction of dimethyl sulfate with 2,4-dihydroxy-5-prenylacetophenone in the presence of potassium carbonate in refluxing acetone (89%) [884].
-Preparation by reaction of 2-methylbut-3-en-2-ol with 2-hydroxy-4-methoxyacetophenone in the presence of boron trifluoride etherate [43].

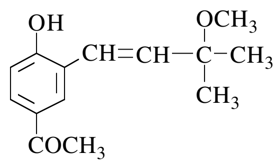
Isolation from natural sources

-By treatment of bavachinin with 50% potassium hydroxide aqueous solution at 180-200° (80%). The bavachinin is a flavonoid compound obtained from *Psoralea Corylifolia* Linn. [206].

oil [206] [884]; ^{1}H NMR [43] [44] [206], IR [206], UV [43] [206].

1-[4-Hydroxy-3-(3-methoxy-3-methyl-1-butenyl)phenyl]ethanone *(E)*

[26931-60-2] $C_{14}H_{18}O_3$ mol.wt. 234.30



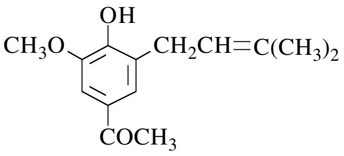
Isolation from natural sources

-From the roots of *Helianthella uniflor*a (tribe Heliantheae) [242].

m.p. 124° [242];
^{1}H NMR [242], IR [242], UV [242], MS [242].

1-[4-Hydroxy-3-methoxy-5-(3-methyl-2-butenyl)phenyl]ethanone

[73869-90-6] $C_{14}H_{18}O_3$ mol.wt. 234.30



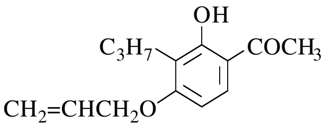
Synthesis

-Obtained by Claisen rearrangement of 3-methoxy-4-(3-methyl-2-butenyloxy)acetophenone (m.p. 41°5) in diethylaniline for 5 h at 170° (85%) [245].

m.p. 65° [245]; ^{1}H NMR [245], IR [245].

1-[2-Hydroxy-4-(2-propenyloxy)-3-propylphenyl]ethanone

[99370-47-5] $C_{14}H_{18}O_3$ mol.wt. 234.30



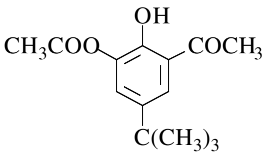
Synthesis

-Preparation by reaction of allyl bromide with 2,4-dihydroxy-3-propylacetophenone in the presence of potassium carbonate and potassium iodide in refluxing methyl ethyl ketone (78%) [777].

crystalline compound [777].

1-[3-(Acetyloxy)-5-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone

[84297-04-1] $C_{14}H_{18}O_4$ mol.wt. 250.29



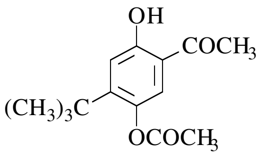
Syntheses

-Obtained by treatment of a benzene solution of 5-tert-butyl-2,3-dihydroxyacetophenone and acetaldehyde in the presence of di-tert-butyl diperoxyoxalate at 38° (25%) [1758].
-Also obtained by treatment of a benzene solution of 4-tert-butyl-o-benzoquinone and acetaldehyde in the presence of di-tert-butyl diperoxyoxalate at 38° (6%) [1758].

pale yellow oil [1758]; ^{1}H NMR [1758], IR [1758].

1-[5-(Acetyloxy)-4-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone

[107188-26-1] $C_{14}H_{18}O_4$ mol.wt. 250.29



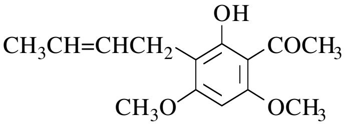
Synthesis

-Preparation by reaction of acetic anhydride with 2-tert-butylhydroquinone in the presence of boron trifluoride-acetic acid complex between 60 to 90° [1928].

m.p. 86°5-87°5 [1928].

1-[3-(2-Butenyl)-2-hydroxy-4,6-dimethoxyphenyl]ethanone

$C_{14}H_{18}O_4$ mol.wt. 250.29



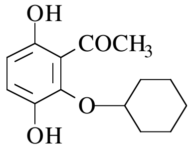
Synthesis

-Preparation by condensation of 2-hydroxy-4,6-dimethoxyacetophenone with 1,3-butadiene in the presence of 85% orthophosphoric acid in xylene at 30-35° (80%) [19].

m.p. 101-103° [19]; ^{1}H NMR [19].

1-[2-(Cyclohexyloxy)-3,6-dihydroxyphenyl]ethanone

[33537-80-3] $C_{14}H_{18}O_4$ mol.wt. 250.29



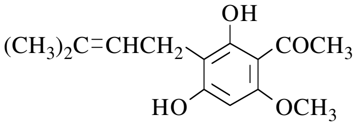
Syntheses

-Easy preparation by reduction of 2-acetyl-3-cyclohexyloxy-1,4-benzoquinone using conventional methods [587].
-Also obtained (low yield) by reaction of 2-acetyl-1,4-benzoquinone with an excess of cyclohexanol at r.t., with exclusion of light [587].

m.p. 75-76°5 [587]; ^{1}H NMR [587], IR [587].

1-[2,4-Dihydroxy-6-methoxy-3-(3-methyl-2-butenyl)phenyl]ethanone

[30403-01-1] $C_{14}H_{18}O_4$ mol.wt. 250.29



Synthesis

-Preparation by reaction of prenyl bromide with 2,4-dihydroxy-6-methoxyacetophenone in the presence of methanolic potassium hydroxide (major product) [876], (27%) [877].

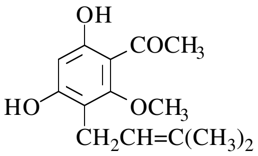
Isolation from natural sources

-From the rhizomes of *Remirea maritima* Aubl. (Cyperaceae) [38] [876].

m.p. 173°5-174° [38], 173-174° [876], 170-171° [877]; TLC [877];
^{1}H NMR [876] [877], UV [876] [877].

1-[4,6-Dihydroxy-2-methoxy-3-(3-methyl-2-butenyl)phenyl]ethanone *(Acronylin)*

[27364-64-3] $C_{14}H_{18}O_4$ mol.wt. 250.29



Syntheses

-Preparation by prenylation of 2,4-dihydroxy-6-methoxyacetophenone with 2-methyl-3-buten-2-ol in the presence of boron trifluoride etherate [876].
-Preparation by dehalogenation of 2,4-dihydroxy-3-iodo-6-methoxy-5-prenylacetophenone in the presence of zinc dust and concentrated hydrochloric acid in refluxing ethanol (75%) [15].

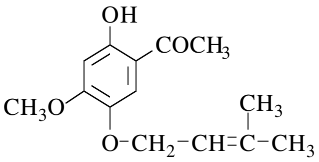
Isolation from natural sources

-From the bark of *Acronychia laurifolia* BL (Rutaceae) [230].

m.p. 128-129° [38] [230], 127-128° [876];
^{1}H NMR [230] [876], IR [230], UV [230] [876], MS [230].

1-[2-Hydroxy-4-methoxy-5-[(3-methyl-2-butenyl)oxy]phenyl]ethanone

[142608-87-5] $C_{14}H_{18}O_4$ mol.wt. 250.29

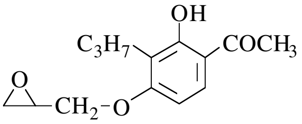


Synthesis

-Preparation by prenylation of 2,5-dihydroxy-4-methoxyacetophenone [1764].

1-[2-Hydroxy-4-(oxiranylmethoxy)-3-propylphenyl]ethanone

[57161-85-0] $C_{14}H_{18}O_4$ mol.wt. 250.29



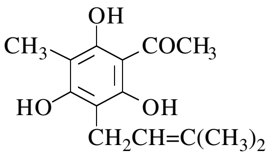
Syntheses

-Preparation by reaction of epichlorohydrin with 2,4-dihydroxy-3-propylacetophenone in the presence of,
*potassium hydroxide in refluxing ethanol (64%) [71];
*potassium carbonate in boiling 2-butanol for 10 h (62%) [1035].

m.p. 54-55° [71], 52-56°5 [1035]; b.p.$_{0.5}$ 170-175° [71]; GLC [1035];
^{1}H NMR [1035].

1-[2,4,6-Trihydroxy-3-methyl-5-(3-methyl-2-butenyl)phenyl]ethanone

[55380-58-0] $C_{14}H_{18}O_4$ mol.wt. 250.29



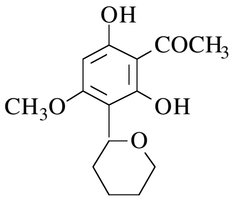
Synthesis

-Obtained by reaction of 2-methylbut-3-en-2-ol with methylphloroacetophenone in the presence of boron trifluoride etherate in dioxane (16%) [428].

m.p. 115-117° [350] [428], 114-116° [1611]; ^{1}H NMR [350] [428], UV [428], MS [428].

1-[2,6-Dihydroxy-4-methoxy-3-(tetrahydro-2*H*-pyran-2-yl)phenyl]ethanone

[136258-10-1] $C_{14}H_{18}O_5$ mol.wt. 266.29



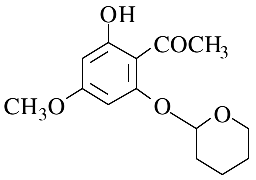
Synthesis

-Preparation by reaction of 3,4-dihydro-2*H*-pyran on 2,6-dihydroxy-4-methoxyacetophenone with p-toluenesulfonic acid in dioxane, first at 0°, then at r.t. (29%) [5].

m.p. 71-76° [5]; ^{1}H NMR [5], ^{13}C NMR [5].

1-[2-Hydroxy-4-methoxy-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]phenyl]ethanone

[136258-09-8] $C_{14}H_{18}O_5$ mol.wt. 266.29



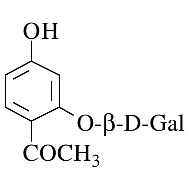
Synthesis

-Preparation by reaction of 3,4-dihydro-2*H*-pyran on 2,6-dihydroxy-4-methoxyacetophenone with p-toluenesulfonic acid in dioxane, first at 0°, then at r.t. (29%) [5].

m.p. 88-92° [5]; ^{1}H NMR [5], ^{13}C NMR [5].

1-[2-(β-D-Galactopyranosyloxy)-4-hydroxyphenyl]ethanone

$C_{14}H_{18}O_8$ mol.wt. 314.29



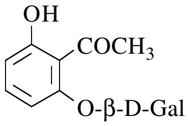
Synthesis

-Preparation from 2-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)-4-hydroxyacetophenone by boiling in 0.2 N methanolic sodium methoxide solution for 3 min (45%) [1861].

m.p. 114-115° [1861]; monohydrate [1861]; $(\alpha)_D^{20} = -73°$ (c = 1 in water) [1861].

1-[2-(β-D-Galactopyranosyloxy)-6-hydroxyphenyl]ethanone

[88087-04-1] $C_{14}H_{18}O_8$ mol.wt. 314.29



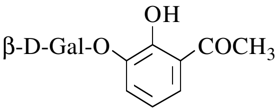
Synthesis

-Obtained by deprotection of 2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyloxy)-6-hydroxyacetophenone with 0.5 N methanolic sodium methoxide at r.t. overnight (20%) [1008].

m.p. 226-229° [1008]; $(\alpha)_D^{20}$ = -4°8 (c = 1.67 in pyridine) [1008]; ^{1}H NMR [1008].

1-[3-(β-D-Galactopyranosyloxy)-2-hydroxyphenyl]ethanone

[88086-97-9] $C_{14}H_{18}O_8$ mol.wt. 314.29



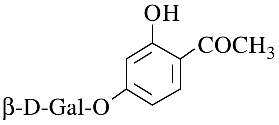
Synthesis

-Obtained from 3-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)-2-hydroxyacetophenone by treatment with 0.1 N methanolic sodium methoxide for 3 h at r.t. [1008].

m.p. 179-181° [1008]; dihydrate [1008];
$(\alpha)_D^{20}$ = -7° (c = 1 in pyridine) [1008]; ^{1}H NMR [1008].

1-[4-(β-D-Galactopyranosyloxy)-2-hydroxyphenyl]ethanone

[54918-26-2] $C_{14}H_{18}O_8$ mol.wt. 314.29



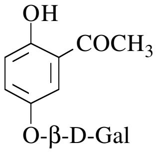
Syntheses

-Obtained from 4-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)-2-hydroxyacetophenone by treatment with methanolic sodium methoxide at r.t. [1008] [1480], (87%) (monohydrate) [1480] or in boiling methanol for 3 min [1861].

m.p. 207° [1008], 205-207° [1861], 198° [1480];
$(\alpha)_D^{18}$ = -62° (c = 2.3 in pyridine) [1480]; $(\alpha)_D^{22}$ = -68°3 (c = 1 in water) (monohydrate) [1861]; $(\alpha)_D^{22}$ = -73° (c = 1 in water) (anhydrous) [1861].

1-[5-(β-D-Galactopyranosyloxy)-2-hydroxyphenyl]ethanone

[88086-99-1] $C_{14}H_{18}O_8$ mol.wt. 314.29



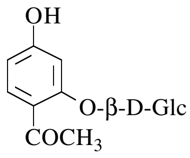
Synthesis

-Obtained from 5-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)-2-hydroxyacetophenone by treatment with 0.1 N methanolic sodium hydroxide solution for 2 h (22%) [1008].

m.p. 209-211° [1008]; ^{1}H NMR [1008].

1-[2-(β-D-Glucopyranosyloxy)-4-hydroxyphenyl]ethanone *(Cynanoneside B; Bungeiside B)*

[149561-88-6] $C_{14}H_{18}O_8$ mol.wt. 314.29



Synthesis

-Preparation from 2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyloxy)-4-hydroxyacetophenone by boiling in 0.2 N methanolic sodium methoxide solution for 3 min (65%) [1860].

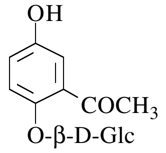
Isolation from natural sources

-From the roots of *Cynanchum bungei* DECNE (Asclepiadaceae) [1088].
-From the roots of *Cynanchum taiwanianum* (Asclepiadaceae) [1102].

Amorphous white powder [1088], Amorphous solid [1102];
m.p. 178-180° [1860];
$(\alpha)_D^{20}$ = -88°5 (c = 1 in water) [1860], $(\alpha)_D^{20}$ = -11°0 (c = 1 in ethanol) [1102],
$(\alpha)_D$ = -17°3 (c = 0.7 in methanol) [1088]; TLC [1860];
^1H NMR [1088] [1102], ^{13}C NMR [1088] [1102], IR [1102], UV [1102],
MS [1088] [1102].

1-[2-(β-D-Glucopyranosyloxy)-5-hydroxyphenyl]ethanone *(Bungeiside A)*

[149475-52-5] $C_{14}H_{18}O_8$ mol.wt. 314.29



Isolation from natural sources

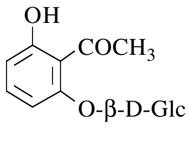
-From the roots of *Cynanchum bungei* DECNE (Asclepiadaceae) [1088].

white amorphous powder [1088];

$(\alpha)_D$ = -40°6 (c = 5 in methanol) [1088];
^1H NMR [1088], ^{13}C NMR [1088], IR [1088], MS [1088].

1-[2-(β-D-Glucopyranosyloxy)-6-hydroxyphenyl]ethanone

$C_{14}H_{18}O_8$ mol.wt. 314.29

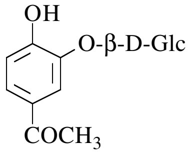


Synthesis

-Refer to: [1817].

1-[3-(β-D-Glucopyranosyloxy)-4-hydroxyphenyl]ethanone

[55483-00-6] $C_{14}H_{18}O_8$ mol.wt. 314.29



Synthesis

-Preparation by bubbling dry ammonia into an ice cooled solution of 3-(tetra-O-acetyl-β-D-glucopyranosyloxy)-4-hydroxyacetophenone in methanol for 40 min. Then, the solution was set aside at r.t. for 15 h (72%) [1700].

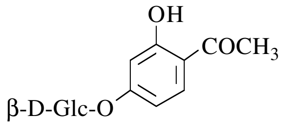
Isolation from natural sources

-From the leaves of *Picea pungens* Engelm. (Colorado spruce) [1315] [1316].
-From the leaves of *Picea pungens* Engelm. var. glauca Beiss. [1742].
-From shoots of *Picea abies* [1021].
-From white spruce of *Picea glauca* (Moench) Voss [1742].
-From galls and shoots of *Picea glauca* (Pinaceae) [1022].

m.p 198-199° [1315], 190-195° [1700], 190-191° [1742];
$(\alpha)_D^{25}$ = -96°8 (c = 0.53 in water) [1315], $(\alpha)_D$ = -88°9 (c = 0.53 in water) [1700],
$(\alpha)_D^{30}$ = -85.47 (c = 1.17 in water) [1742]; GC [1021], GC/MS [1021] [1022];
^{1}H NMR [948] [1700], IR [1700], MS [1700].

1-[4-(β-D-Glucopyranosyloxy)-2-hydroxyphenyl]ethanone

[54918-24-0] $C_{14}H_{18}O_8$ mol.wt. 314.29



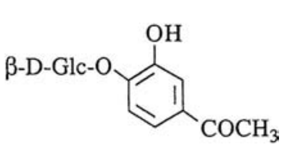
Syntheses

-Preparation by deacetylation of 4-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyloxy)-2-hydroxyacetophenone,
*with sodium methoxide in methanol (92%) [1478], (70-80%) [549], (60-70%) [1860];
*with barium hydroxide in aqueous solution for 16 h (84%) [1201].
-Also refer to: [1241] [1480].

m.p. 201-202° [1201] [1860], 198-200° [1478];
$(\alpha)_D^{20}$ = -86°9 (c = 50 in acetone) [1478]; TLC [1860].

1-[4-(β-D-Glucopyranosyloxy)-3-hydroxyphenyl]ethanone *(Cynanoneside A)*

[17063-43-3] $C_{14}H_{18}O_8$ mol.wt. 314.29



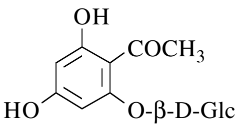
Isolation from natural sources

-From the shoots of *Picea abies* [1021].
-From the roots of *Cynanchum taiwanianum* (Asclepiadaceae) [1102].
-From galls and shoots of *Picea glauca* (Pinaceae) [1022].

Amorphous solid [1102]; $(\alpha)_D^{20}$ = -5°0 (c = 1 in ethanol) [1102];
GC [1021]; GC/MS [1021] [1022];
^{1}H NMR [1102], ^{13}C NMR [1102], IR [1102], UV [1102], MS [1102].

1-[2-(β-D-Glucopyranosyloxy)-4,6-dihydroxyphenyl]ethanone

[26089-54-3] $C_{14}H_{18}O_9$ mol.wt. 330.29



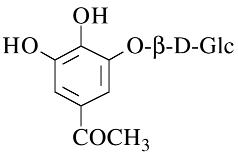
Isolation from natural sources

-From the aerial parts of *Artemisia stolonifera* (Compositae) [1075].

m.p. 201-203° [1075];
^{1}H NMR [1075], ^{13}C NMR [1075], IR [1075], UV [1075].

1-[3-(β-D-Glucopyranosyloxy)-4,5-dihydroxyphenyl]ethanone

[448949-59-5] $C_{14}H_{18}O_9$ mol.wt. 330.29

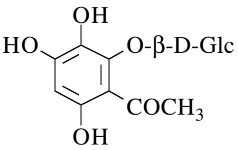


Isolation from natural sources

-From dried root of *Polygonum cuspidatum* SIEB. et ZUCC. (Polygonaceae) [1901].
-Also refer to: [1075].

1-[2-(β-D-Glucopyranosyloxy)-3,4,6-trihydroxyphenyl]ethanone *(Lalioside)*

[116964-03-5] $C_{14}H_{18}O_{10}$ mol.wt. 346.29



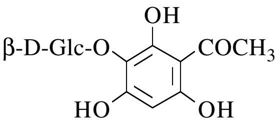
Isolation from natural sources

-From *Lawsonia inermis* [1752].

spectroscopic data [1752].

1-[3-(β-D-Glucopyranosyloxy)-2,4,6-trihydroxyphenyl]ethanone *(Polygoacetophenoside)*

[110906-84-8] $C_{14}H_{18}O_{10}$ mol.wt. 346.29



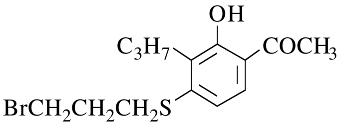
Isolation from natural sources

-From the leaves and stems of *Polygonum multiflorum* (Polygonaceae) [1929].

m.p. 214-216° [1929];
^{1}H NMR [1929], ^{13}C NMR [1929], IR [1929], UV [1929], MS [1929], HRMS [1929].

1-[4-[(3-Bromopropyl)thio]-2-hydroxy-3-propylphenyl]ethanone

[125617-43-8] $C_{14}H_{19}BrO_2S$ mol.wt. 331.27



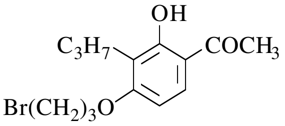
Synthesis

-Preparation by reaction of 1,3-dibromopropane with 2-hydroxy-4-mercapto-3-propylacetophenone in the presence of potassium carbonate and potassium iodide in refluxing methyl ethyl ketone [1680].

yellow oil [1680].

1-[4-(3-Bromopropoxy)-2-hydroxy-3-propylphenyl]ethanone

[40786-20-7] $C_{14}H_{19}BrO_3$ mol.wt. 315.21



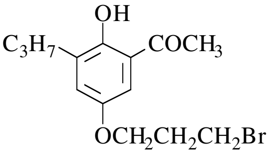
Synthesis

-Preparation by reaction of 1,3-dibromopropane with 2,4-dihydroxy-3-propylacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone [71].

b.p.$_{0.02}$ 172-180° [71].

1-[5-(3-Bromopropoxy)-2-hydroxy-3-propylphenyl]ethanone

[125617-25-6] $C_{14}H_{19}BrO_3$ mol.wt. 315.21



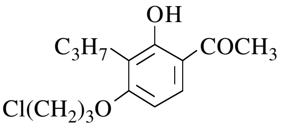
Synthesis

-Preparation by reaction of 1,3-dibromopropane with 2,5-dihydroxy-3-propylacetophenone in the presence of potassium carbonate and potassium iodide in refluxing methyl ethyl ketone [1680].

m.p. 69-70° [1680].

1-[4-(3-Chloropropoxy)-2-hydroxy-3-propylphenyl]ethanone

[79558-02-4] $C_{14}H_{19}ClO_3$ mol.wt. 270.76



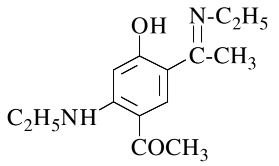
Syntheses

-Preparation by reaction of 1-bromo-3-chloropropane with 2,4-dihydroxy-3-propylacetophenone in the presence of potassium carbonate in refluxing acetone for 5 h (80%) [314], (67%) [1035].
-Also refer to: [1371].

m.p. 39-41° [1035], 37-38° [314]; GLC [1035]; ^1H NMR [1035].

1-[2-(Ethylamino)-5-[1-(ethylimino)ethyl]-4-hydroxyphenyl]ethanone

[115349-97-8] $C_{14}H_{20}N_2O_2$ mol.wt. 248.33



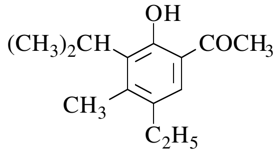
Synthesis

-Obtained by heating a mixture of 4,6-diacetylresorcinol, aqueous ethylamine and concentrated hydrochloric acid as catalyst, in an autoclave from 8 to 72 h [65].

m.p. 153-154° [65]; ^{1}H NMR [65], MS [65].

1-[5-Ethyl-2-hydroxy-4-methyl-3-(1-methylethyl)phenyl]ethanone

$C_{14}H_{20}O_2$ mol.wt. 220.31



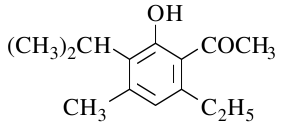
Synthesis

-Preparation by chromic degradation of 5-ethyl-2,3,6-trimethyl-7-isopropylbenzofuran (52%) [967].

b.p.$_{16}$ 164-167° [967].

1-[6-Ethyl-2-hydroxy-4-methyl-3-(1-methylethyl)phenyl]ethanone

$C_{14}H_{20}O_2$ mol.wt. 220.31



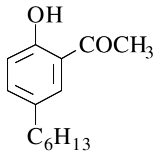
Synthesis

-Preparation by chromic degradation of 4-ethyl-2,3,6-trimethyl-7-isopropylbenzofuran (46%) [967].

b.p.$_{18}$ 165-166° [967].

1-(5-Hexyl-2-hydroxyphenyl)ethanone

[55168-32-6] $C_{14}H_{20}O_2$ mol.wt. 220.31



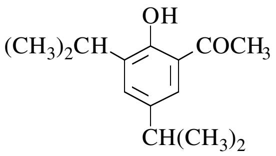
Synthesis

-Preparation by Fries rearrangement of p-n-hexylphenyl acetate with aluminium chloride without solvent (15%) [1335].

yellow oil [1335]; b.p.$_{0.7}$ 110° [1335]; MS [1335].

1-[2-Hydroxy-3,5-bis(1-methylethyl)phenyl]ethanone

[35158-23-7] $C_{14}H_{20}O_2$ mol.wt. 220.31



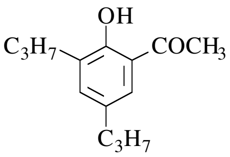
Synthesis

-Preparation by reaction of ethyl acetoacetate with 5-methyl-2-isopropyl-2-hexenal in the presence of pyridine and piperidine as catalysts in refluxing benzene (40%). The 5-methyl-2-isopropyl-2-hexenal was obtained by self-condensation of isovaleraldehyde in the presence of 15% potassium hydroxide solution [940] [941] [942].

m.p. 37° [940] [941] [942]; b.p.$_{0.05\text{-}0.10}$ 70-80° [940] [941] [942];
^{1}H NMR [940] [941] [942], IR [940] [941] [942], UV [940] [941] [942].

1-(2-Hydroxy-3,5-dipropylphenyl)ethanone

[35198-96-0] $C_{14}H_{20}O_2$ mol.wt. 220.31



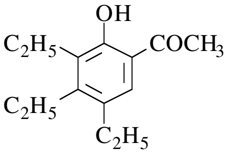
Synthesis

-Preparation by reaction of ethyl acetoacetate with 2-n-propyl-2-heptenal in the presence of pyridine and piperidine as catalysts in refluxing benzene (42%). The 2-n-propyl-2-heptenal was obtained by self-condensation of n-valeraldehyde in the presence of 15% potassium hydroxide solution [940] [941] [942].

liquid [940] [941] [942]; b.p.$_{0.075}$ 80-90° [940] [941] [942];
^{1}H NMR [940] [941] [942], IR [940] [941] [942], UV [940] [941] [942].

1-(3,4,5-Triethyl-2-hydroxyphenyl)ethanone

$C_{14}H_{20}O_2$ mol.wt. 220.31



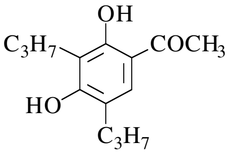
Synthesis

-Preparation by Fries rearrangement of 2,4,6-triethylphenyl acetate with aluminium chloride *via* a migration of two ethyl groups (65%) [102].

b.p.$_{12}$ 153-155° [102].

1-(2,4-Dihydroxy-3,5-dipropylphenyl)ethanone

[72018-36-1] $C_{14}H_{20}O_3$ mol.wt. 236.31



Syntheses

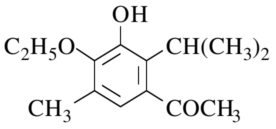
-Preparation by hydrogenation of 2,4-dihydroxy-3,5-dipropenylacetophenone in ethanol using 10% PdO/C as catalyst (98%) [1372].
-Also refer to: [43] [44].

N.B.: Pr indicates the *propyl* group -C_3H_7 in Chem. Abstr., **92**, 6368x (1980) and **98**, 54239b (1983), as usual abbreviation. However, in the two references [43] [44], Pr represented the *prenyl* group -$CH_2CH=C(CH_3)_2$. Therefore they concern the 2,4-dihydroxy-3,5-diprenylacetophenone and not the above mentioned 2,4-dihydroxy-3,5-dipropylacetophenone.

m.p. 98-99° [1372].

1-[4-Ethoxy-3-hydroxy-5-methyl-2-(1-methylethyl)phenyl]ethanone

$C_{14}H_{20}O_3$ mol.wt. 236.31



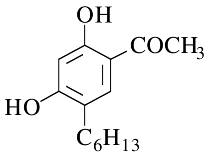
Synthesis

-Preparation by diazotization of 3-amino-4-ethoxy-5-methyl-2-isopropylacetophenone, followed by hydrolysis of the diazonium salt obtained (44%) [902].

m.p. 88° [902].

1-(5-Hexyl-2,4-dihydroxyphenyl)ethanone

[63411-88-1] $C_{14}H_{20}O_3$ mol.wt. 236.31



Syntheses

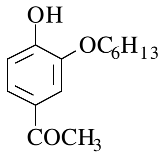
-Preparation by reaction of acetonitrile on 4-n-hexylresorcinol (Hoesch reaction) (84%) [1277].

-Preparation from 5-hexyl-2,4-dimethoxyacetophenone by demethylation with boron tribromide in methylene chloride at r.t. (70%) [256] [257].

m.p. 86-87° [1277].

1-[3-(Hexyloxy)-4-hydroxyphenyl]ethanone

$C_{14}H_{20}O_3$ mol.wt. 236.31



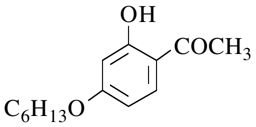
Synthesis

-Preparation from 4-(benzyloxy)-3-hexyloxyacetophenone by catalytic debenzylation on Pd/C (89%) [1211].

m.p. 48° [1211].

1-[4-(Hexyloxy)-2-hydroxyphenyl]ethanone

[143286-85-5] $C_{14}H_{20}O_3$ mol.wt. 236.31



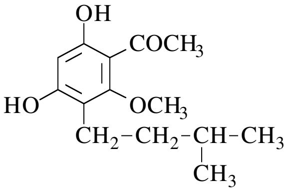
Synthesis

-Preparation by partial alkylation of resacetophenone with hexyl bromide in the presence of potassium carbonate in refluxing acetone for 20 h [183].

m.p. 22° [183].

1-[4,6-Dihydroxy-2-methoxy-3-(3-methylbutyl)phenyl]ethanone

[14764-76-2] $C_{14}H_{20}O_4$ mol.wt. 252.31



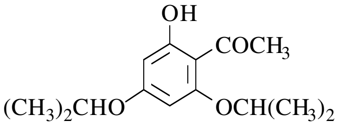
Synthesis

-Preparation from acronylin (4,6-dihydroxy-2-methoxy-3-isopentenylacetophenone) by catalytic reduction with Pd/C as catalyst in ethyl acetate [230].

m.p. 143° [230]; ^{1}H NMR [230].

1-[2-Hydroxy-4,6-bis(1-methylethoxy)phenyl]ethanone

[93344-48-0] $C_{14}H_{20}O_4$ mol.wt. 252.31



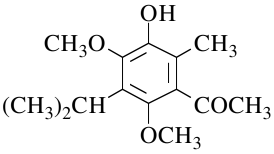
Synthesis

-Preparation by reaction of 2-bromopropane with phloroacetophenone in the presence of potassium carbonate in DMF at reflux (67%) [841].

dark red oil [841]; ^{1}H NMR [841], IR [841], MS [841].

1-[3-Hydroxy-4,6-dimethoxy-2-methyl-5-(1-methylethyl)phenyl]ethanone

[159848-01-8] $C_{14}H_{20}O_4$ mol.wt. 252.31



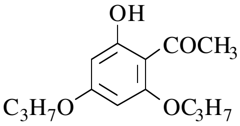
Synthesis

-Obtained by reaction of 3-chloroperbenzoic acid with 2,4-dimethoxy-6-methyl-3-isopropylacetophenone in refluxing ethylene dichloride for 48 h (34%) [1859].

m.p. 98-100° [1859]; ^{1}H NMR [1859].

1-[2-Hydroxy-4,6-bis(propyloxy)phenyl]ethanone

$C_{14}H_{20}O_4$ mol.wt. 252.31

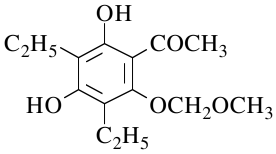


Synthesis

-Preparation by catalytic hydrogenation of 2-hydroxy-4,6-bis(2-propynyloxy)acetophenone in the presence of 10% Pd/C in methanol [427].

1-[3,5-Diethyl-2,4-dihydroxy-6-(methoxymethoxy)phenyl]ethanone

[175785-90-7] $C_{14}H_{20}O_5$ mol.wt. 268.31

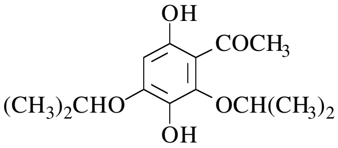


Synthesis

-Refer to: [1737] (Japanese patent).

1-[3,6-Dihydroxy-2,4-bis(1-methylethoxy)phenyl]ethanone

[93344-49-1] $C_{14}H_{20}O_5$ mol.wt. 268.31



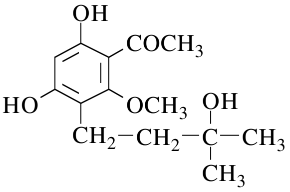
Synthesis

-Preparation from 2-hydroxy-4,6-diisopropoxy-acetophenone by persulfate oxidation (Elbs reaction) (12%) [841].

oil [841]; ^{1}H NMR [841], IR [841], MS [841].

1-[4,6-Dihydroxy-3-(3-hydroxy-3-methylbutyl)-2-methoxyphenyl]ethanone

[153399-41-8] $C_{14}H_{20}O_5$ mol.wt. 268.31



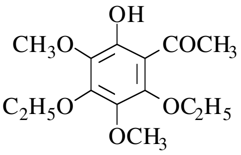
Synthesis

-Obtained by catalytic hydrogenation of 4,6-bis(benzyloxy)-3-(3-hydroxy-3-methylbutynyl)-2-methylacetophenone in methanol in the presence of Pd/C at 20° [1824].

m.p. 156-158° [1824];
^{1}H NMR [1824].

1-(2,4-Diethoxy-6-hydroxy-3,5-dimethoxyphenyl)ethanone

$C_{14}H_{20}O_6$ mol.wt. 284.31



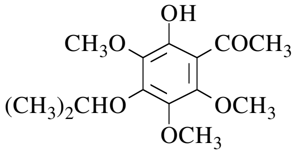
Synthesis

-Preparation by Friedel-Crafts acylation of 1,3-diethoxy-2,4,5-trimethoxybenzene with acetyl chloride in the presence of aluminium chloride (60%) [801].

b.p.$_{0.2}$ 119-121° [801].

1-[2-Hydroxy-3,5,6-trimethoxy-4-(1-methylethoxy)phenyl]ethanone

[56002-87-0] $C_{14}H_{20}O_6$ mol.wt. 284.31



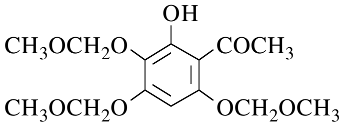
Synthesis

-Obtained (poor yield) by Friedel-Crafts acylation of 3-isopropyloxy-2,4,5-trimethoxyphenol with acetyl chloride in ethyl ether in the presence of aluminium chloride (9%) [802].

^1H NMR [802].

1-[2-Hydroxy-3,4,6-tris(methoxymethoxy)phenyl]ethanone

[53000-17-2] $C_{14}H_{20}O_8$ mol.wt. 316.31



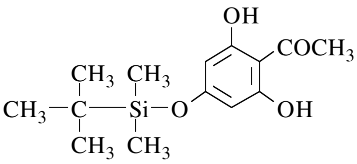
Synthesis

-Obtained by reaction of chloromethyl methyl ether with 2,3,4,6-tetrahydroxyacetophenone in ethanol in the presence of sodium ethoxide under nitrogen, first at 0°, then at 40° (13%) [1341].

yellow oil [1341]; ^1H NMR [1341], IR [1341].

1-[4-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-2,6-dihydroxyphenyl]ethanone

[139140-13-9] $C_{14}H_{22}O_4Si$ mol.wt. 282.41



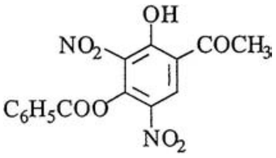
Synthesis

-Obtained by sonication of 2',4',6'-(tri-tert-butyldimethylsilyloxy)acetophenone in solution of methanol and carbon tetrachloride (1:1) at 50-55° for 12 h (85%) [487].

Colourless oil [487]; ^1H NMR [487], ^{13}C NMR [487], IR [487], MS [487].

1-[4-(Benzoyloxy)-2-hydroxy-3,5-dinitrophenyl]ethanone

$C_{15}H_{10}N_2O_8$ mol.wt. 346.25



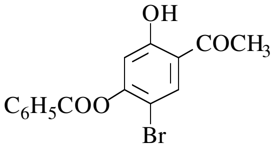
Synthesis

-Preparation (by-product) by reaction of concentrated nitric acid on 4-(benzoyloxy)-2-hydroxyacetophenone in acetic acid at r.t. [870].

m.p. 171-172° [870].

1-[4-(Benzoyloxy)-5-bromo-2-hydroxyphenyl]ethanone

$C_{15}H_{11}BrO_4$ mol.wt. 335.15



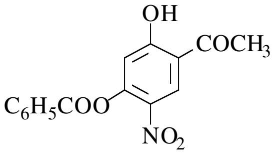
Synthesis

-Preparation by bromination of 4-(benzoyloxy)-2-hydroxyacetophenone [515] [870].

m.p. 176° [515], 175-177° [870].

1-[4-(Benzoyloxy)-2-hydroxy-5-nitrophenyl]ethanone

$C_{15}H_{11}NO_6$ mol.wt. 301.26



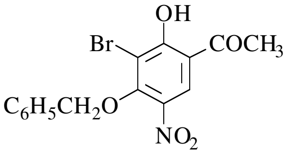
Synthesis

-Preparation by reaction of concentrated nitric acid on 4-(benzoyloxy)-2-hydroxyacetophenone in acetic acid at r.t. [870].

m.p. 125-126° [870].

1-[3-Bromo-2-hydroxy-5-nitro-4-(phenylmethoxy)phenyl]ethanone

$C_{15}H_{12}BrNO_5$ mol.wt. 366.17



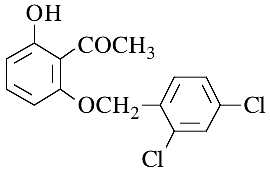
Synthesis

-Preparation by bromination of 4-(benzyloxy)-2-hydroxy-5-nitroacetophenone in chloroform solution in the presence of iron wire [870].

m.p. 150-151° [870].

1-[2-[(2,4-Dichlorophenyl)methoxy]-6-hydroxyphenyl]ethanone

[63411-86-9] $C_{15}H_{12}Cl_2O_3$ mol.wt. 311.16



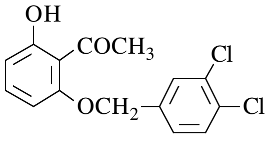
Synthesis

-Obtained by reaction of 2,4-dichlorobenzyl chloride with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone (62%) [237].

m.p. 126-127° [237].

1-[2-[(3,4-Dichlorophenyl)methoxy]-6-hydroxyphenyl]ethanone

[63411-85-8] $C_{15}H_{12}Cl_2O_3$ mol.wt. 311.16



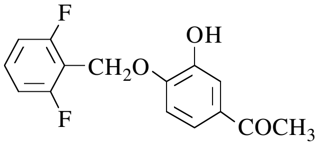
Synthesis

-Obtained by reaction of 3,4-dichlorobenzyl bromide or chloride with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone (52%) [237].

m.p. 175-176° [237].

1-[4-(2,6-Difluorophenyl)methoxy-3-hydroxyphenyl]ethanone

$C_{15}H_{12}F_2O_3$ mol.wt. 278.26



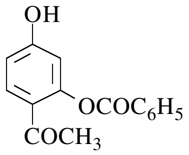
Synthesis

-Obtained by stirring a mixture of 3,4-dihydroxyacetophenone, lithium carbonate and α-bromo-2,6-difluorotoluene in DMF for 2 days at r.t. (38%) [701].

solid [701]; ^{1}H NMR [701].

1-[2-(Benzoyloxy)-4-hydroxyphenyl]ethanone

[144406-93-9] $C_{15}H_{12}O_4$ mol.wt. 256.26

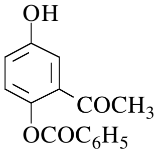


Synthesis

-Obtained by conventional acylation of resacetophenone with benzoyl chloride [1330].

1-[2-(Benzoyloxy)-5-hydroxyphenyl]ethanone

[88087-03-0] $C_{15}H_{12}O_4$ mol.wt. 256.26



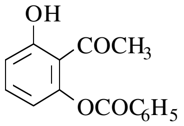
Synthesis

-Preparation by hydrogenolysis of 5-(benzyloxy)-2-(benzoyloxy)acetophenone in ethyl acetate using 10% Pd/C as catalyst, at r.t. for 5 h (78%) [1008].

m.p. 168-169° [1008]; ^{1}H NMR [1008].

1-[2-(Benzoyloxy)-6-hydroxyphenyl]ethanone

[50634-01-0] $C_{15}H_{12}O_4$ mol.wt. 256.26



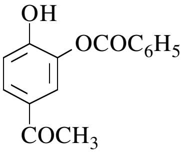
Synthesis

-Preparation by reaction of benzoyl chloride on 2,6-dihydroxyacetophenone in aqueous sodium hydroxide solution (60%) [763].

m.p. 99-100° [763].

1-[3-(Benzoyloxy)-4-hydroxyphenyl]ethanone

[101140-07-2] $C_{15}H_{12}O_4$ mol.wt. 256.26



Synthesis

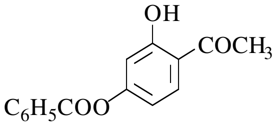
-Preparation by reaction of benzoyl chloride with 3,4-dihydroxyacetophenone in the presence of pyridine, first at 0° for 5 min, then at r.t. for 24 h under nitrogen atmosphere (77%) [1700].

m.p. 143-156° [1700]. This gap of 13° appears in the publication.

^{1}H NMR [1700], IR [1700], MS [1700].

1-[4-(Benzoyloxy)-2-hydroxyphenyl]ethanone

[109311-05-9] $C_{15}H_{12}O_4$ mol.wt. 256.26



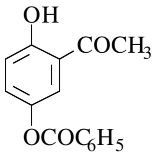
Syntheses

-Preparation by reaction of benzoyl chloride on resacetophenone [137] [515] [874] [982],
*with aqueous sodium hydroxide (68%) [137];
*with aqueous potassium hydroxide [982];
*with potassium carbonate in toluene by heating on a steam bath (52%) [137];
*with aluminium chloride in nitrobenzene by heating in a water bath (21%) [515].
-Also refer to: [816].

m.p. 110° [515], 107-108° [874], 106-107° [137], 105-106° [982].

1-[5-(Benzoyloxy)-2-hydroxyphenyl]ethanone

$C_{15}H_{12}O_4$ mol.wt. 256.26



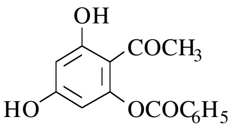
Synthesis

-Obtained by reaction of aluminium chloride on 4-(benzoyloxy)phenyl acetate without solvent between 125° and 155° (13%) [46].

m.p. 77-78° [46].

1-[2-(Benzoyloxy)-4,6-dihydroxyphenyl]ethanone

[83332-29-0] $C_{15}H_{12}O_5$ mol.wt. 272.26



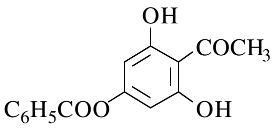
Synthesis

-Obtained by reaction of benzoyl chloride on phloroacetophenone with 2% aqueous potassium hydroxide solution at 0° (6%) [352] or with dilute aqueous sodium hydroxide solution [1673].

m.p. 186° [352], 177-178° [1673].

1-[4-(Benzoyloxy)-2,6-dihydroxyphenyl]ethanone

[130471-75-9] $C_{15}H_{12}O_5$ mol.wt. 272.26



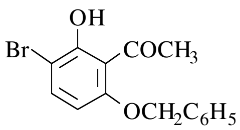
Synthesis

-Obtained by reaction of benzoyl chloride on phloroacetophenone with 2% aqueous potassium hydroxide solution at 0° (19%) [352].

m.p. 210-211° [352].

1-[3-Bromo-2-hydroxy-6-(phenylmethoxy)phenyl]ethanone

$C_{15}H_{13}BrO_3$ mol.wt. 321.17



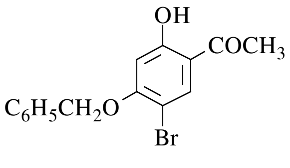
Synthesis

-Preparation by reaction of bromine on 2-(benzyloxy)-6-hydroxyacetophenone in methylene chloride (84%) [1873] or in acetic acid at r.t. (58%) [1213].

m.p. 125-126° [1213], 124° [1873]; IR [1873].

1-[5-Bromo-2-hydroxy-4-(phenylmethoxy)phenyl]ethanone

$C_{15}H_{13}BrO_3$ mol.wt. 321.17



Syntheses

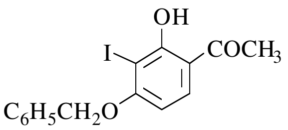
-Obtained from 3,3'-diacetyl-4,4'-dihydroxy-6,6'-dibenzyloxydiphenyl thioether by treatment with bromine in the presence of a crystal of iodine in boiling acetic acid for 8 h then at r.t. overnight [871].

-Also obtained by bromination of 4-(benzyloxy)-2-hydroxyacetophenone with bromine in carbon disulfide in the presence of a trace of iodine [534].

m.p. 154-155° [534] [871].

1-[2-Hydroxy-3-iodo-4-(phenylmethoxy)phenyl]ethanone

$C_{15}H_{13}IO_3$ mol.wt. 368.17



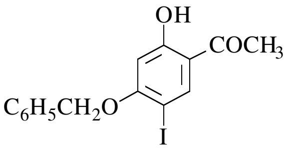
Synthesis

-Preparation by iodination of 4-(benzyloxy)-2-hydroxyacetophenone [928].

m.p. 165° [928].

1-[2-Hydroxy-5-iodo-4-(phenylmethoxy)phenyl]ethanone

$C_{15}H_{13}IO_3$ mol.wt. 368.17

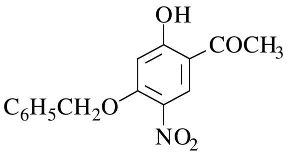


Synthesis

-Obtained (by-product) during the rearrangement of 2-(benzoyloxy)-4-(benzyloxy)-3-iodoacetophenone to give 7-(benzyloxy)-8-iodoflavone [928].

1-[2-Hydroxy-5-nitro-4-(phenylmethoxy)phenyl]ethanone

$C_{15}H_{13}NO_5$ mol.wt. 287.27



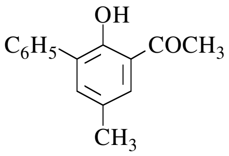
Synthesis

-Preparation by nitration of 4-(benzyloxy)-2-hydroxyacetophenone in acetic acid at r.t. [870].

m.p. 140-141° [870].

1-(2-Hydroxy-5-methyl[1,1'-biphenyl]-3-yl)ethanone

[360791-68-0] $C_{15}H_{14}O_2$ mol.wt. 226.27



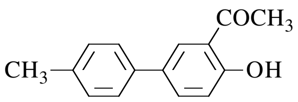
Synthesis

-Obtained by successively adding an aqueous solution of sodium bicarbonate (6 mmol), then tetrakis(triphenylphosphine)palladium (0) (0.1 mmol) to a solution of 3-bromo-2-hydroxy-5-methylacetophenone (2 mmol) and phenylboronic acid (2 mmol) in ethylene glycol dimethyl ether (DME). After, the reaction mixture was refluxed for 10 min and then heated at 75° overnight (71%) (compound 26) [1848].

yellow solid [1848]; ^{1}H NMR [1848], MS [1848].

1-(4-Hydroxy-4'-methyl[1,1'-biphenyl]-3-yl)ethanone

[229007-00-5] $C_{15}H_{14}O_2$ mol.wt. 226.27



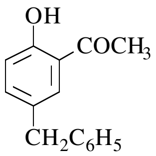
Synthesis

-Obtained by Fries rearrangement of 4'-methyl-4-biphenylyl acetate (1 mol) with aluminium chloride (1.1 mol) in refluxing o-dichlorobenzene for 3 h (67%) [1910].

m.p. 82°5-83°3 [1910]; ^{1}H NMR [1910], IR [1910], GC-MS [1910].

1-[2-Hydroxy-5-(phenylmethyl)phenyl]ethanone

[61300-15-0] $C_{15}H_{14}O_2$ mol.wt. 226.27



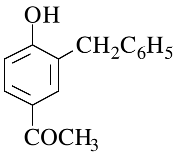
Synthesis

-Preparation by Fries rearrangement of 4-hydroxydiphenylmethane acetate with aluminium chloride in chlorobenzene at 130° [71] [1896], (85%) [1896].

m.p. 56° [1896], 55-56° [71].

1-[4-Hydroxy-3-(phenylmethyl)phenyl]ethanone

[95102-24-2] $C_{15}H_{14}O_2$ mol.wt. 226.27



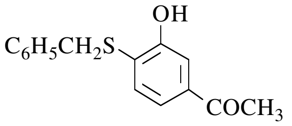
Syntheses

-Preparation by Fries rearrangement of 2-hydroxydiphenylmethane acetate in the presence of aluminium chloride in nitrobenzene at 50-60° (70%) [1896].
-Also refer to: [949] [1545].

m.p. 137-138° [1896].

1-[3-Hydroxy-4-(phenylmethyl)thiophenyl]ethanone

$C_{15}H_{14}O_2S$ mol.wt. 258.34



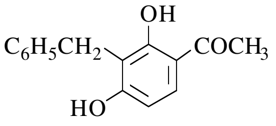
Synthesis

-Obtained by reaction of benzyl bromide with 3-hydroxy-4-mercaptoacetophenone (SM) in the presence of potassium carbonate in refluxing acetone for 2 h (20%). SM was prepared by demethylation of 3-methoxy-4-mercaptoacetophenone with boron tribromide in methylene chloride for 2 h at -78° [701].

^{1}H NMR [701].

1-[2,4-Dihydroxy-3-(phenylmethyl)phenyl]ethanone

[67088-16-8] $C_{15}H_{14}O_3$ mol.wt. 242.27



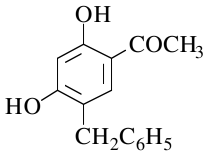
Syntheses

-Preparation by reaction of boron tribromide with 3-benzyl-2,4-dimethoxyacetophenone in methylene chloride, first at -50°, then at r.t. (90%) [297].
-Preparation by reaction of concentrated hydrochloric acid with 3-benzyl-4-(benzyloxy)-2-hydroxyacetophenone in refluxing acetic acid (69%) [1274].
-Also obtained by reacting 4-(benzyloxy)-2-hydroxyacetophenone with trifluoroacetic acid at r.t. for 70 h (17%) [878].
-Also obtained by reaction of benzyl alcohol with resacetophenone in the presence of boron trifluoride etherate and dioxane at 60-70° (16%) [878].
-Also obtained by reaction of acetonitrile on 2-benzylresorcinol (Hoesch reaction) (11%) [1274].
-Also obtained by reaction of benzyl bromide with resacetophenone in the presence of methanolic potassium hydroxide at r.t. (18%) [885].
-Also obtained by catalytic reduction of 2',4'-dihydroxy-3'-[phenyl-(1-piperidyl)methyl]-acetophenone in the presence of Pd/C [937] [939], (68%) [939]. An alternative route of reduction consisted in heating the starting material and Pd/C in tetralin between 140 and 150° for 8 h (57%) [939]. The starting material was obtained by treatment of resacetophenone in ethanol or benzene with benzylidene-bis-piperidine.
-Also refer to: [938].

m.p. 207-208° [937] [939], 196-198° [885], 195-197° [1274], 195-196° [878];
^{1}H NMR [297] [878] [939], IR [878] [939], UV [878].

1-[2,4-Dihydroxy-5-(phenylmethyl)phenyl]ethanone

[93898-99-8] $C_{15}H_{14}O_3$ mol.wt. 242.27



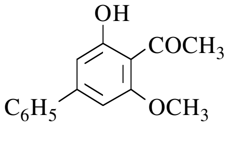
Syntheses

-Preparation by Fries rearrangement of 4-benzylresorcinol diacetate with aluminium chloride in the presence of 4-benzylresorcinol in nitrobenzene at 50° (85%) [1896].
-Also obtained by reacting 2-hydroxy-4-(benzyloxy)acetophenone with trifluoroacetic acid at r.t. for 70 h (29%) [878].
-Also obtained by reaction of benzyl alcohol with resacetophenone in the presence of boron trifluoride etherate and dioxane at 60-70° (24%) [878].
-Also obtained (poor yield) by reaction of benzyl bromide with resacetophenone in the presence of methanolic potassium hydroxide at r.t. (< 2%) [885].

m.p. 149° [1896], 140-142° [885], 140-141° [878]; ^{1}H NMR [878], IR [878], UV [878].

1-(3-Hydroxy-5-methoxy[1,1'-biphenyl]-4-yl)ethanone

[32101-40-9] $C_{15}H_{14}O_3$ mol.wt. 242.27



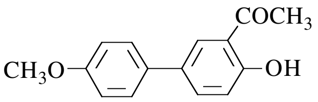
Synthesis

-Preparation by dehydrogenation of 2-acetyl-3-methoxy-5-phenyl-2-cyclohexenone in the presence of Pd black powder in refluxing cyclohexene for 6 h (70%) [32].

m.p. 96-97° [32]; IR [32], UV [32].

1-(4-Hydroxy-4'-methoxy[1,1'-biphenyl]-3-yl)ethanone

[114412-47-4] $C_{15}H_{14}O_3$ mol.wt. 242.27

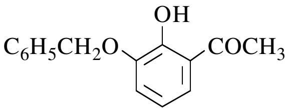


Synthesis

-Obtained by Fries rearrangement of 4-acetoxy-4'-methoxydiphenyl with aluminium chloride in tetrachloroethane at 140° for 30 min [771].

1-[2-Hydroxy-3-(phenylmethoxy)phenyl]ethanone

[30992-64-4] $C_{15}H_{14}O_3$ mol.wt. 242.27



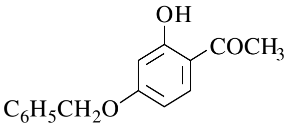
Synthesis

-Preparation by reaction of benzyl chloride with 2,3-dihydroxyacetophenone in the presence of potassium iodide and potassium carbonate in refluxing acetone for 4 h (43%) [776] or for 18 h (40%) [1427].

m.p. 55-56° [1427]; b.p.$_{0.05}$ 122-130° [776]; ^{1}H NMR [1427], IR [1427].

1-[2-Hydroxy-4-(phenylmethoxy)phenyl]ethanone

[29682-12-0] $C_{15}H_{14}O_3$ mol.wt. 242.27



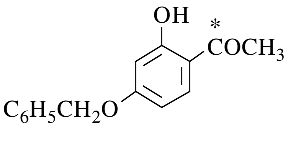
Syntheses

-Preparation by reaction of resacetophenone,
-with benzyl chloride,
*in the presence of potassium carbonate in refluxing acetone [183] [1068], (85%) [314], (50-52%) [8] [712] [943].
N.B.: The butanone can also be used instead of acetone [314]. The addition of potassium iodide improved yields [1068],
*in the presence of potassium carbonate in DMF at 150-153° (62%) [1821];
*in the presence of potassium carbonate and potassium iodide in refluxing acetone for 4 h [776] or for 18 h (67%) [1427];
*in the presence of potassium hydroxide in refluxing methanol [1274].
-with benzyl bromide,
*in the presence of potassium carbonate in a methyl ethyl ketone and DMSO mixture (53%) [1664];
*in the presence of methanolic potassium hydroxide at r.t. (10%) [885].
-Also obtained by hydrolysis of 2-(acetyloxy)-4-(benzyloxy)acetophenone (m.p. 111-112°) with 10% aqueous sodium hydroxide in boiling methanol for 5 min (76%) [927].
-Also obtained (trace) by heating 4-acetyloxy-2-hydroxyacetophenone with benzyl chloride (< 1%) [25].
-Also refer to: [417] [607] [1133] [1135] [1311] [1557] [1615] [1663] [1840].

m.p. 111° [712], 110° [878], 109-110° [885], 106-107° [1274], 105-106° [776], 104-104°5 [927], 104-105° [314], 103-105° [183], 103-104° [8], 102-103° [25], 101-102° [1427], 94-95° [1821];
^{1}H NMR [25] [1427] [1821], ^{13}C NMR [1396], UV [25] [927].

1-[2-Hydroxy-4-(phenylmethoxy)phenyl]ethanone-*1*-^{14}C

[71815-42-4] $C_{15}H_{14}O_3$ mol.wt. 244.27



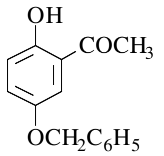
Syntheses

-Preparation by reaction of benzyl chloride with [carbonyl-^{14}C]resacetophenone in the presence of potassium carbonate and potassium iodide in DMF at 80° for 2 h [518], (69%) [519] or at 50-55° for 1 h (63%) [116].

m.p. 105°5-106°5 [116], 103-105° [519];
sp. act. 6.09×10^7 dpm/mM [519]; 0.316 mCi/mM [518].
sp. act. 6.09×10^7 dpm/mM [519]; 0.316 mCi/mM [518].

1-[2-Hydroxy-5-(phenylmethoxy)phenyl]ethanone

[30992-63-3] $C_{15}H_{14}O_3$ mol.wt. 242.27



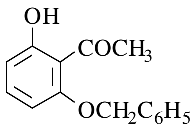
Syntheses

-Preparation by reaction of benzyl chloride with quinacetophenone [130] [302] [943] in refluxing acetone in the presence of potassium carbonate,
*with potassium iodide (85%) [302], (71%) [776], (55%) [1427];
*without potassium iodide (31%) [130].

m.p. 100-102° [302], 69-70° [130] [776], 67-68° [1427]. One of the reported melting points is obviously wrong.
^1H NMR [302] [1427], IR [302], MS [302].

1-[2-Hydroxy-6-(phenylmethoxy)phenyl]ethanone

[4047-24-9] $C_{15}H_{14}O_3$ mol.wt. 242.27



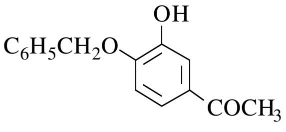
Syntheses

-Preparation by reaction of benzyl chloride with 2,6-dihydroxyacetophenone,
*in the presence of potassium carbonate in refluxing acetone [140] [1077], (58%) [140];
*in the presence of potassium carbonate and potassium iodide in refluxing acetone for 18 h (40%) [1427];
*in the presence of 15% aqueous sodium hydroxide, by heating in a water bath (67%) [1610].
-Preparation by reaction of benzyl bromide with 2,6-dihydroxyacetophenone monosodium salt (SM) in DMSO at r.t. for 1 h (76%). SM was prepared by reaction of sodium hydride (1 mol) with 2,6-dihydroxyacetophenone (1 mol) in DMSO at r.t. for 10 min [1815].
-Preparation by reaction of benzyl bromide with 2,6-dihydroxyacetophenone,
*in the presence of potassium carbonate in refluxing acetone (60%) [1873];
*in the presence of potassium carbonate and potassium iodide in refluxing acetone (about 80°) for 12 h (72%) [1423].

monohydrate [1423];
m.p. 110-111° [1423], 109-110° [140] [916] [1815], 109° [1873], 108-109° [1427] 106-109° [1077], 106-107° [1610];
^1H NMR [1423] [1427] [1815], ^{13}C NMR [1423], MS [1423].

1-[3-Hydroxy-4-(phenylmethoxy)phenyl]ethanone

[21092-94-4] $C_{15}H_{14}O_3$ mol.wt. 242.27



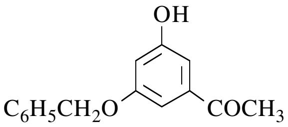
Syntheses

-Preparation by reaction of benzyl chloride with 3,4-dihydroxyacetophenone in the presence of potassium hydroxide in a refluxing mixture of ethanol, methanol and water (53%) [1210].
-Also refer to: [1702].

m.p. 118° [1210].

1-[3-Hydroxy-5-(phenylmethoxy)phenyl]ethanone

[81732-54-9] $C_{15}H_{14}O_3$ mol.wt. 242.27



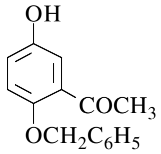
Synthesis

-Preparation by partial catalytic hydrogenolysis of 3,5-bis (benzyloxy)acetophenone in acetone in the presence of Pd/C (48%) [222].

m.p. 126-128° [222]; ^1H NMR [222].

1-[5-Hydroxy-2-(phenylmethoxy)phenyl]ethanone

[83069-04-9] $C_{15}H_{14}O_3$ mol.wt. 242.27



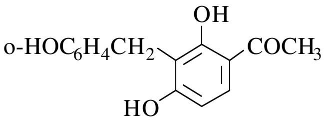
Synthesis

-Preparation by hydrolysis of 5-acetoxy-2-(benzyloxy)-acetophenone (m.p. 111-112°) with 5% sodium hydroxide in boiling aqueous methanol (69%) [927].

m.p. 117° [927]; UV [927].

1-[2,4-Dihydroxy-3-[(2-hydroxyphenyl)methyl]phenyl]ethanone

[103633-38-1] $C_{15}H_{14}O_4$ mol.wt. 258.27



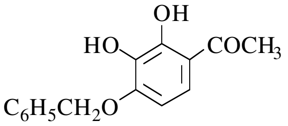
Synthesis

-Preparation by catalytic hydrogenolysis of 3-(o-benzyloxybenzyl)-2,4-dihydroxyacetophenone at r.t. in the presence of 10% Pd/C in ethyl acetate (67%) [873].

m.p. 204-205° [873]; ^1H NMR [873], IR [873], UV [873].

1-[2,3-Dihydroxy-4-(phenylmethoxy)phenyl]ethanone

[69114-99-4] $C_{15}H_{14}O_4$ mol.wt. 258.27



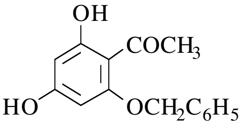
Synthesis

-Preparation by reaction of benzyl chloride on gallacetophenone with sodium bicarbonate and sodium iodide in refluxing acetone-ethanol mixture (33-37%) [972] [1571].

m.p. 137-138° [972], 133-133°5 [1571]; ^{1}H NMR [1571].

1-[2,4-Dihydroxy-6-(phenylmethoxy)phenyl]ethanone

[39548-86-2] $C_{15}H_{14}O_4$ mol.wt. 258.27



Syntheses

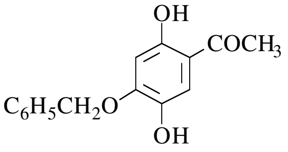
-Preparation from 2-(benzyloxy)-4,6-dihydroxyacetophenone ditosilate (SM) by hydrolysis with 5% sodium hydroxide in ethanol (72%). The starting ketone (SM) was prepared by a two-step procedure from phloroacetophenone [10].

-Also obtained (poor yield) by reaction of benzyl chloride on phloroacetophenone with potassium carbonate in refluxing acetone (4%) [880].

m.p. 239-240° [880], 233°5 [10]; ^{1}H NMR [880], UV [880].

1-[2,5-Dihydroxy-4-(phenylmethoxy)phenyl]ethanone

[34176-17-5] $C_{15}H_{14}O_4$ mol.wt. 258.27



Syntheses

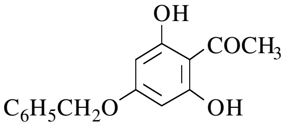
-Preparation by reaction of benzyl halide with 2,4,5-trihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone (62%) [1900].

-Preparation from 4-(benzyloxy)-2-hydroxyacetophenone by persulfate oxidation (Elbs reaction) (25%) [8] [703] [1068].

m.p. 160-162° [1068], 159-160° [8], 157-159° [1900].

1-[2,6-Dihydroxy-4-(phenylmethoxy)phenyl]ethanone

[35028-02-5] $C_{15}H_{14}O_4$ mol.wt. 258.27



Syntheses

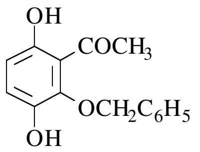
-Preparation from 2,4-diacetyl-5-(benzyloxy)resorcinol by selective deacetylation by refluxing in 1 N sodium hydroxide for 1 h [342].

-Also obtained by reaction of benzyl chloride on phloroacetophenone with potassium carbonate in refluxing acetone (13%) [1281].

m.p. 188-189° (compound VIII) [1281],
139-140° (compound II, R=H; R'=$PhCH_2$-) [342]; ^{1}H NMR [342].

1-[3,6-Dihydroxy-2-(phenylmethoxy)phenyl]ethanone

[33537-81-4] $C_{15}H_{14}O_4$ mol.wt. 258.27



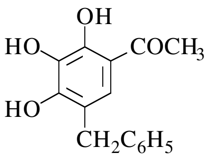
Syntheses

-Preparation from 2-(benzyloxy)-6-hydroxyacetophenone by persulfate oxidation (Elbs reaction) (49%) [140].
-Easy preparation by reduction of 2-acetyl-3-(benzyloxy)-1,4-benzoquinone using conventional methods [587].
-Also obtained in low yield by reaction of 2-acetyl-1,4-benzoquinone with an excess of benzyl alcohol at r.t., with exclusion of light [587].

m.p. 94° [140], 87°5-89° [587]; ^1H NMR [587], IR [587].

1-[2,3,4-Trihydroxy-5-(phenylmethyl)phenyl]ethanone

[105485-44-7] $C_{15}H_{14}O_4$ mol.wt. 258.27



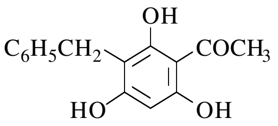
Syntheses

-Preparation by reaction of benzyl alcohol with gallacetophenone in the presence of boron trifluoride etherate in dioxane at 60-70° (49%) [885].
-Preparation by Claisen rearrangement of 3,4-bis-(benzyloxy)-2-hydroxyacetophenone in the presence of trifluoroacetic acid at r.t. (54%) [885].

m.p. 127-128° [885]; ^1H NMR [885], IR [885], UV [885].

1-[2,4,6-Trihydroxy-3-(phenylmethyl)phenyl]ethanone

$C_{15}H_{14}O_4$ mol.wt. 258.27



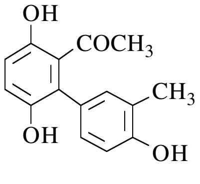
Syntheses

-Obtained (poor yield) by reaction of a benzyl halogenide with phloroacetophenone in the presence of sodium methoxide in methanol at r.t. (8%) [1491].
-Also obtained from 3-benzyl-4,6-bis(benzyloxy)-2-hydroxyacetophenone by hydrogenolysis in the presence of 5% Pd/C in ethanol [406].

m.p. 208° [1491], 207-208° [406]; IR [406], UV [406].

1-(3,4',6-Trihydroxy-3'-methyl[1,1'-biphenyl]-2-yl)ethanone

[32541-10-9] $C_{15}H_{14}O_4$ mol.wt. 258.27



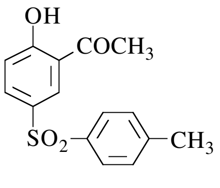
Synthesis

-Obtained by catalytic reduction of 2-acetyl-3-(4-hydroxy-3-methylphenyl)-1,4-benzoquinone (SM). SM was obtained by condensation of o-cresol with 2-acetyl-1,4-benzoquinone in ethyl ether in the presence of trifluoroacetic acid at 0° (12%) [1054].

m.p. 194° [1054].

1-[2-Hydroxy-5-[(4-methylphenyl)sulfonyl]phenyl]ethanone

[147816-51-1] $C_{15}H_{14}O_4S$ mol.wt. 290.34



Syntheses

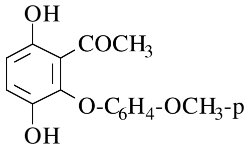
-Preparation by Fries rearrangement of 4-(p-tolylsulfonyl)-phenyl acetate with aluminium chloride (5 mol) at 160° for 1 h (58%) [1684].

-Also obtained by photo-Fries rearrangement of the same ester in acetonitrile (26%) or (40%) based on consumed starting material [1684].

m.p. 206-208° [1684]; ^{1}H NMR [1684], UV [1684].

1-[3,6-Dihydroxy-2-(4-methoxyphenoxy)phenyl]ethanone

[52095-11-1] $C_{15}H_{14}O_5$ mol.wt. 274.27



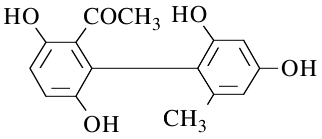
Synthesis

-Preparation by reaction of hydroquinone monomethyl ether on 2-acetylquinone with pyridine in benzene (43%) [586].

m.p. 74-77° [586]; ^{1}H NMR [586], IR [586].

1-(2',3,4',6-Tetrahydroxy-6'-methyl[1,1'-biphenyl]-2-yl)ethanone

[32546-66-0] $C_{15}H_{14}O_5$ mol.wt. 274.27



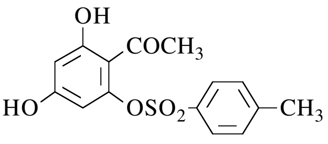
Synthesis

-Obtained by condensation of 2-acetyl-1,4-benzoquinone with orcinol in a acetic acid/ethyl ether solution at r.t. for 1 h (50%) [1054].

m.p. 185° [1054]; IR [1054].

1-[2,4-Dihydroxy-6-[[(4-methylphenyl)sulfonyl]oxy]phenyl]ethanone

[225088-72-2] $C_{15}H_{14}O_6S$ mol.wt. 322.05



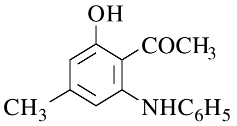
Synthesis

-Preparation by hydrogenolysis of 2-toluenesulfonyloxy-4,6-bis(benzyloxy)acetophenone (m.p. 122-123°) in methanol with hydrogen in the presence of 10% Pd/C at r.t. for 20 h (94%) [825].

m.p. 150-152° [825]; ^{1}H NMR [825], IR [825], MS [825].

1-[2-Hydroxy-4-methyl-6-(phenylamino)phenyl]ethanone

[97066-04-1] $C_{15}H_{15}NO_2$ mol.wt. 241.29



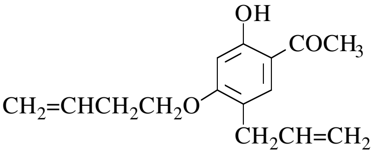
Synthesis

-Obtained by reaction of aniline with 2-acetyl-3-dimethylamino-5-hydroxy-5-methyl-2-cyclohexenone in refluxing ethanol (17%) [562].

m.p. 115-117° [562]; ^{1}H NMR [562], IR [562], UV [562], MS [562].

1-[4-(3-Butenyloxy)-2-hydroxy-5-(2-propenyl)phenyl]ethanone

[117690-53-6] $C_{15}H_{18}O_3$ mol.wt. 246.31



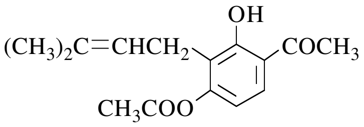
Synthesis

-Preparation by reaction of 3-butenyl bromide with 5-allyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide at reflux (26%) [256] [257].

m.p. < 25° [256] [257].

1-[4-(Acetyloxy)-2-hydroxy-3-(3-methyl-2-butenyl)phenyl]ethanone

[95604-05-0] $C_{15}H_{18}O_4$ mol.wt. 262.31



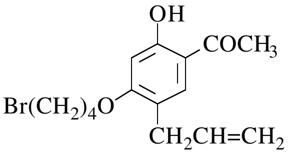
Synthesis

-Preparation by acetylation of 3-prenylresacetophenone with acetic anhydride in the presence of boric acid, first under reflux for 5 min, then at r.t. for 24 h (60%) [1847].

m.p. 66° [1847]; ^{1}H NMR [1847].

1-[4-(4-Bromobutoxy)-2-hydroxy-5-(2-propenyl)phenyl]ethanone

[117706-42-0] $C_{15}H_{19}BrO_3$ mol.wt. 327.22



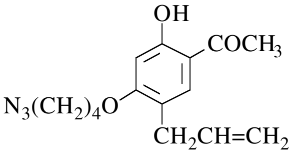
Synthesis

-Preparation by reaction of 4-bromobutyl bromide with 5-allyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide at reflux (56%) [256] [257].

m.p. < 25° [256] [257].

1-[4-(4-Azidobutoxy)-2-hydroxy-5-(2-propenyl)phenyl]ethanone

[140660-37-3] $C_{15}H_{19}N_3O_3$ mol.wt. 289.33

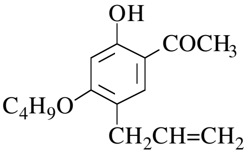


Synthesis

-Preparation by reaction of sodium azide on 5-allyl-4-(4-bromobutoxy)-2-hydroxyacetophenone in DMF at r.t. [257] [777].

1-[4-Butoxy-2-hydroxy-5-(2-propenyl)phenyl]ethanone

[117690-48-9] $C_{15}H_{20}O_3$ mol.wt. 248.32



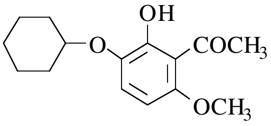
Synthesis

-Preparation by reaction of n-butyl bromide with 5-allyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing methyl ethyl ketone (60%) [256] [257] [777].

oil [256] [257] [777].

1-[3-(Cyclohexyloxy)-2-hydroxy-6-methoxyphenyl]ethanone

[126405-80-9] $C_{15}H_{20}O_4$ mol.wt. 264.32



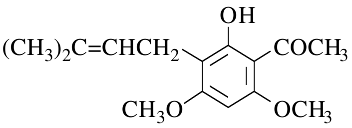
Synthesis

-Preparation by adding 2-hydroxy-3-iodo-6-methoxyacetophenone and cuprous iodide to a solution of sodium cyclohexanolate, previously prepared from cyclohexanol and sodium hydride in DMF [1873].

oil [1873]; ^{1}H NMR [1873], IR [1873].

1-[2-Hydroxy-4,6-dimethoxy-3-(3-methyl-2-butenyl)phenyl]ethanone

[33523-62-5] $C_{15}H_{20}O_4$ mol.wt. 264.32



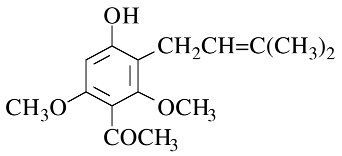
Synthesis

-Obtained by partial methylation of 2,4-dihydroxy-6-methoxy-3-prenylacetophenone [876].

m.p. 113-114° [876].

1-[4-Hydroxy-2,6-dimethoxy-3-(3-methyl-2-butenyl)phenyl]ethanone

[18780-96-6] $C_{15}H_{20}O_4$ mol.wt. 264.32



Syntheses

-Preparation: γ,γ-dimethylallyl bromide was added to the lithium salt of 4-acetyl-3,5-dimethoxyphenol, which is easily prepared in benzene by reaction with butyl lithium (6%) [353].

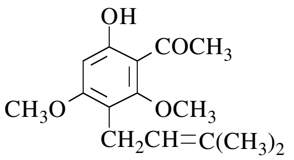
-Preparation by thermal Claisen rearrangement of 4-(γ,γ-dimethylallyloxy)-2,6-dimethoxyacetophenone in refluxing diethylaniline [786] [787], (> 90%) [786].

m.p. 66-68° [353]; ^{1}H NMR [353], UV [353], MS [353].

1-[6-Hydroxy-2,4-dimethoxy-3-(3-methyl-2-butenyl)phenyl]ethanone

(Acronylin methyl ether).

[4683-33-4] $C_{15}H_{20}O_4$ mol.wt. 264.32



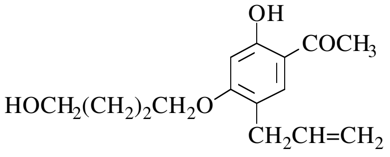
Synthesis

-Obtained by reaction of dimethyl sulfate with 4,6-dihydroxy-2-methoxy-3-prenylacetophenone (m.p. 127-128°) in the presence of potassium carbonate in refluxing acetone for 3 h (38%) [877].

m.p. 78-79° [877]; TLC [877].

1-[2-Hydroxy-4-(4-hydroxybutoxy)-5-(2-propenyl)phenyl]ethanone

[117690-52-5] $C_{15}H_{20}O_4$ mol.wt. 264.32



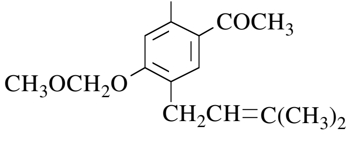
Synthesis

-Obtained by reaction of 4-hydroxybutyl bromide on 5-allyl-2,4-dihydroxyacetophenone with potassium carbonate and potassium iodide in refluxing methyl ethyl ketone (5-12%) [256] [257] [777].

m.p. 117-119° [256] [257] [777].

1-[2-Hydroxy-4-(methoxymethoxy)-5-(3-methyl-2-butenyl)phenyl]ethanone

[99217-72-8] $C_{15}H_{20}O_4$ mol.wt. 264.32



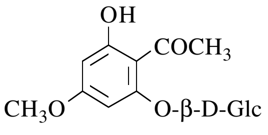
Synthesis

-Preparation by treatment of 2,4-dihydroxy-5-prenylacetophenone with methoxymethyl chloride in the presence of potassium carbonate in acetone [1179], (good yield) [1713].

^{1}H NMR [1179], IR [1179], UV [1179].

1-[2-(β-D-Glucopyranosyloxy)-6-hydroxy-4-methoxyphenyl]ethanone

[24587-97-1] $C_{15}H_{20}O_9$ mol.wt. 344.32



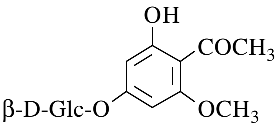
Isolation from natural sources

-From the leaves of *Ribes alpinum* L. (alpine currant) (Grossulariaceae) [685].

spectral data [853]; TLC [685].

1-[4-(β-D-Glucopyranosyloxy)-2-hydroxy-6-methoxyphenyl]ethanone *(Annphenone)*

[61775-18-6] $C_{15}H_{20}O_9$ mol.wt. 344.32



Synthesis

-Preparation by reaction, first, of a saturated aqueous barium hydroxide solution on 2-hydroxy-6-methoxy-4-(tetraacetyl-β-D-glucoside)acetophenone, and then carbon dioxide (38%) [1945].

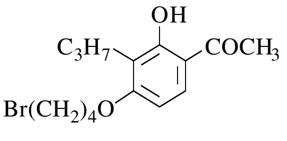
Isolation from natural sources

-From the aerial parts of *Artemisia iwayomogi* (Compositae) [977].
-From the aerial parts of *Artemisia sacrorum* [1947] and from *Artemisia sacrorum* Ledeb. (Compositae) [1007].
-From the aerial parts of *Artemisia stolonifera* (Max.) Kom (Compositae) [1075].
-From the rhizomes of *Rhodiola linearifolia* Boriss. [1556].
-From the aerial parts of *Artemisia annua* [1645].
-From the leaves of *Monochaetum multiflorum* (Melastomataceae) [854].

m.p. 215° [1945], 185-188° [1007], 160-162° [1645], 156-158° [977] [1075];
$(\alpha)_D^{20}$ = -56°4 (pyridine) [1945];
^{1}H NMR [977] [1007] [1075] [1645], ^{13}C NMR [977] [1007] [1075] [1645],
IR [977] [1007] [1075] [1645], UV [977] [1075] [1645],
MS [977] [1007], EIMS [1645].

1-[4-(4-Bromobutoxy)-2-hydroxy-3-propylphenyl]ethanone

[92518-06-4] $C_{15}H_{21}BrO_3$ mol.wt. 329.23



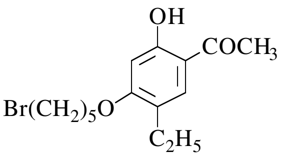
Synthesis

-Preparation by reaction of 1,4-dibromobutane with 2,4-dihydroxy-3-propylacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (78%) [1156].

b.p.$_{0.25}$ 180° [1156].

1-[4-[(5-Bromopentyl)oxy]-5-ethyl-2-hydroxyphenyl]ethanone

[117690-80-9] $C_{15}H_{21}BrO_3$ mol.wt. 329.23



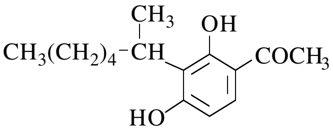
Synthesis

-Preparation by reaction of 5-bromopentyl bromide with 2,4-dihydroxy-5-ethylacetophenone in the presence of potassium carbonate and potassium iodide at reflux (60%) [256] [257].

m.p. 60-62° [256] [257]; ^{1}H NMR [256] [257].

1-[2,4-Dihydroxy-3-(1-methylhexyl)phenyl]ethanone

[79557-94-1] $C_{15}H_{22}O_3$ mol.wt. 250.34



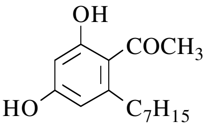
Synthesis

-Preparation by hydrogenation of 2,4-dihydroxy-3-(1-methyl-2-hexenyl)acetophenone in ethanol using 10% PdO/C as catalyst (54%) [1372].

m.p. 78-81° [1372].

1-(2-Heptyl-4,6-dihydroxyphenyl)ethanone

[83375-18-2] $C_{15}H_{22}O_3$ mol.wt. 250.34



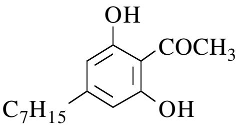
Syntheses

-Preparation by reaction of acetonitrile with 5-heptylresorcinol according to Hoesch reaction (57%) [986].
-Also refer to: [987].

m.p. 61-62° [986]; ^{1}H NMR [986].

1-(4-Heptyl-2,6-dihydroxyphenyl)ethanone

[83375-19-3] $C_{15}H_{22}O_3$ mol.wt. 250.34



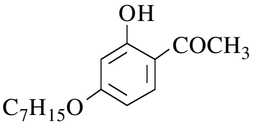
Synthesis

-Obtained (poor yield) by reaction of acetonitrile with 5-heptylresorcinol according to Hoesch reaction (5%) [986].

m.p. 46-47° [986]; ^{1}H NMR [986].

1-[4-(Heptyloxy)-2-hydroxyphenyl]ethanone

[219696-56-7] $C_{15}H_{22}O_3$ mol.wt. 250.34



Synthesis

-Preparation by reaction of 1-heptanol with resacetophenone using polymer-bound triphenylphosphine* and diethyl azodicarboxylate (DEAD) in methylene chloride at 25° for 5 h (72%) [1827].

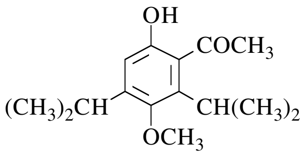
*Polystyryl-diphenylphosphine-2% divinylbenzene.

N.B.: The polymer-bound triphenylphosphines — commercially available — are easily removed by filtration from the reaction products.

oil [1827].

1-[6-Hydroxy-3-methoxy-2,4-bis(1-methylethyl)phenyl]ethanone

[188903-79-9] $C_{15}H_{22}O_3$ mol.wt. 250.34



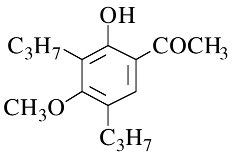
Synthesis

-Refer to: [889].

N.B.: this compound, that has never been prepared, is however mistakenly mentioned in Chem. Abstr., **126**, 277303r (1997). However, it is not mentioned in the original paper [889]. In this paper, the compound is the 2-hydroxy-4,6-diisopropyloxy-5-methoxyacetophenone, a ketone already obtained by [842].

1-(2-Hydroxy-4-methoxy-3,5-dipropylphenyl)ethanone

[72018-37-2] $C_{15}H_{22}O_3$ mol.wt. 250.34



Synthesis not yet described

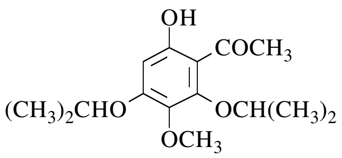
-Refer to: [43] [44].

N.B.: Pr indicates the *propyl* group -C_3H_7 in Chem. Abstr., **92**, 6368x (1980) and **98**, 54239b (1983), an usual abbreviation. However, in the two references [43] [44], Pr represented the *prenyl* group -$CH_2CH{=}C(CH_3)_2$.

Therefore they concern the 2-hydroxy-4-methoxy-3,5-diprenylacetophenone and not the above mentioned 2-hydroxy-4-methoxy-3,5-dipropylacetophenone.

1-[6-Hydroxy-3-methoxy-2,4-bis(1-methylethoxy)phenyl]ethanone

[93344-50-4] $C_{15}H_{22}O_5$ mol.wt. 282.34



Syntheses

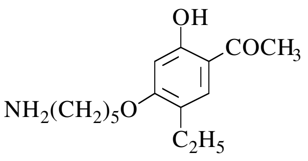
-Obtained by partial methylation of 2,5-dihydroxy-4,6-diisopropyloxyacetophenone (m.p. 37°) according to [845], (67%) (compound 14) [842].

-Also refer to: [846] [847].

pale yellow oil [842]; ^{1}H NMR [842].

1-[4-[(5-Aminopentyl)oxy]-5-ethyl-2-hydroxyphenyl]ethanone

[117705-90-5] $C_{15}H_{23}NO_3$ mol.wt. 265.35



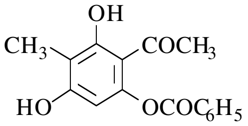
Synthesis

-Preparation by hydrogenation of 5-(4-acetyl-2-ethyl-5-hydroxyphenoxy)pentane nitrile in the presence of 10% Pd/C in acetic acid (> 98%) [256] [257].

m.p. 75-76° [256] [257]; ^{1}H NMR [256] [257].

1-[6-(Benzoyloxy)-2,4-dihydroxy-3-methylphenyl]ethanone

$C_{16}H_{14}O_5$ mol.wt. 286.28



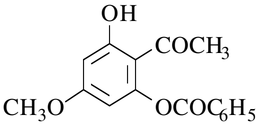
Synthesis

-Obtained by reaction of benzoyl chloride on 2,4,6-trihydroxy-3-methylacetophenone with 2% sodium hydroxide solution at 0° (13%) [1883].

m.p. 189° [1883].

1-[2-(Benzoyloxy)-6-hydroxy-4-methoxyphenyl]ethanone

[49602-08-6] $C_{16}H_{14}O_5$ mol.wt. 286.28



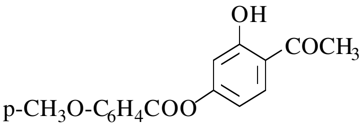
Synthesis

-Preparation by reaction of benzoyl chloride with 2,6-dihydroxy-4-methoxyacetophenone in the presence of 1.5 N sodium hydroxide at r.t. [762].

oil [762].

1-[2-Hydroxy-4-(4-methoxybenzoyloxy)phenyl]ethanone

$C_{16}H_{14}O_5$ mol.wt. 286.28



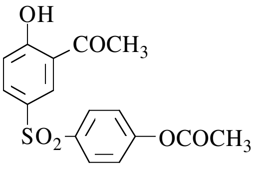
Synthesis

-Preparation by reaction of p-anisoyl chloride on resacetophenone with potassium carbonate in toluene (70%) [137] or in aqueous sodium hydroxide solution (the best way) [137].

m.p. 151° [137].

1-[5-[[4-(Acetyloxy)phenyl]sulfonyl]-2-hydroxyphenyl]ethanone

[147816-49-7] $C_{16}H_{14}O_6S$ mol.wt. 334.35



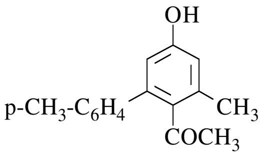
Syntheses

-Obtained by UV light irradiation (254 nm) of 0.02 M bisacetate of bisphenol-S in acetonitrile for 3.5 h (20%) [1684].
-Also obtained by Fries rearrangement of bisacetate of bisphenol-S with aluminium chloride (3 equiv.) at 160° (17%) [1684].

m.p. 166°6 [1684]; ^1H NMR [1684], UV [1684].

1-(5-Hydroxy-3,4'-dimethyl[1,1'-biphenyl]-2-yl)ethanone

[108909-47-3] $C_{16}H_{16}O_2$ mol.wt. 240.30



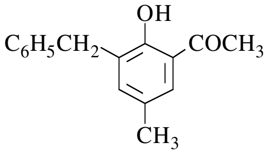
Syntheses

-Obtained by aromatization of 4-acetyl-3-methyl-5-(4-methylphenyl)-2-cyclohexen-1-one (m.p. 130°) with bromine in chloroform (60%) or by heating at 170° for 3 h [731].
-Also obtained by deacylation of 1,1'-(3-hydroxy-4',5-dimethyl[1,1'-biphenyl]-2,6-diyl)bis-ethanone (m.p. 165°) with sodium hydroxide in refluxing dilute ethanol for 3 h (60%) [731].
-Also refer to: [730].

m.p. 180° [731]; IR [731].

1-[2-Hydroxy-5-methyl-3-(phenylmethyl)phenyl]ethanone

[350981-92-9] $C_{16}H_{16}O_2$ mol.wt. 240.30



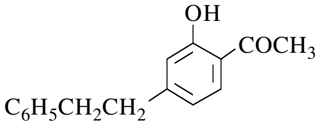
Synthesis

-Obtained from 3-acetyl-2-hydroxy-5-methylbenzyl O,O-dimethylphosphorothionothiolate (m.p. 99°5) on treatment with aluminium chloride in refluxing benzene for 5-10 min (93%) [695].

m.p. 84° [695]; ^{1}H NMR [695], IR [695], MS [695].

1-[2-Hydroxy-4-(2-phenylethyl)phenyl]ethanone

[122379-44-6] $C_{16}H_{16}O_2$ mol.wt. 240.30

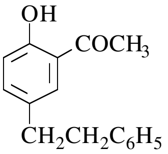


Synthesis

-Refer to: [636].

1-[2-Hydroxy-5-(2-phenylethyl)phenyl]ethanone

[136608-20-3] $C_{16}H_{16}O_2$ mol.wt. 240.30



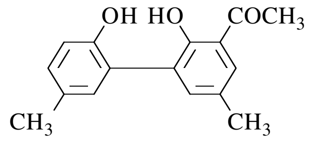
Syntheses

-Preparation by Fries rearrangement of 4-acetoxydiphenylmethane with aluminium chloride in boiling chlorobenzene (70%) [1896].
-Also refer to: [857].

m.p. 52° [1896]; b.p.$_{18}$ 250° [1896].

1-(2,2'-Dihydroxy-5,5'-dimethyl[1,1'-biphenyl]-3-yl)ethanone

[24046-00-2] $C_{16}H_{16}O_3$ mol.wt. 256.30



Syntheses

-Obtained by Fries rearrangement of 2,2'-diacetoxy-5,5'-dimethylbiphenyl with aluminium chloride in nitrobenzene at 120° for 2 h (53%) [1816].

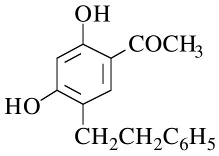
-Also refer to: [1750].

m.p. 129-130° [1816]; TLC [1816];

^{1}H NMR [1750] [1816], IR [1750] [1816].

1-[2,4-Dihydroxy-5-(2-phenylethyl)phenyl]ethanone

[60640-95-1] $C_{16}H_{16}O_3$ mol.wt. 256.30



Syntheses

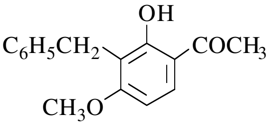
-Preparation by Fries rearrangement of 2,4-dihydroxydiphenylethane diacetate with aluminium chloride in the presence of 2,4-dihydroxydiphenylethane in nitrobenzene at 50° [1893].

-Also refer to: [754].

m.p. 136° [1893].

1-[2-Hydroxy-4-methoxy-3-(phenylmethyl)phenyl]ethanone

[95832-45-4] $C_{16}H_{16}O_3$ mol.wt. 256.30



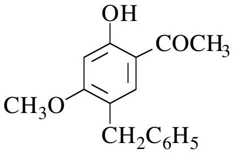
Synthesis

-Preparation by partial methylation of 3-benzyl-2,4-dihydroxyacetophenone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone (87%) [878].

m.p. 119-120° [878]; ^{1}H NMR [878].

1-[2-Hydroxy-4-methoxy-5-(phenylmethyl)phenyl]ethanone

[93434-27-6] $C_{16}H_{16}O_3$ mol.wt. 256.30



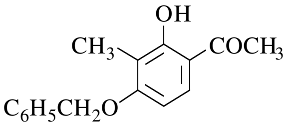
Synthesis

-Preparation by partial methylation of 5-benzyl-2,4-dihydroxyacetophenone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone (82%) [878].

m.p. 95-96° [878]; ^{1}H NMR [878].

1-[2-Hydroxy-3-methyl-4-(phenylmethoxy)phenyl]ethanone

[73640-74-1] $C_{16}H_{16}O_3$ mol.wt. 256.30



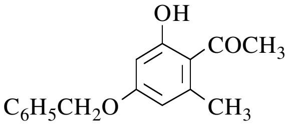
Syntheses

-Preparation by reaction of benzyl chloride on 2,4-dihydroxy-3-methylacetophenone with potassium carbonate and potassium iodide in refluxing acetone (81%) [1470].
-Also refer to: [1264] [1927].

m.p. 87-88° [1470]; ^{1}H NMR [1470], IR [1470], MS [1470].

1-[2-Hydroxy-6-methyl-4-(phenylmethoxy)phenyl]ethanone

[72545-51-8] $C_{16}H_{16}O_3$ mol.wt. 256.30



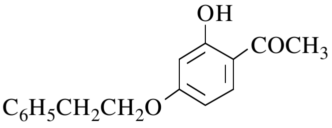
Synthesis

-Preparation by partial benzylation of 2,4-dihydroxy-6-methylacetophenone [12].

m.p. 83-84° [12].

1-[2-Hydroxy-4-(2-phenylethoxy)phenyl]ethanone

[63359-84-2] $C_{16}H_{16}O_3$ mol.wt. 256.30



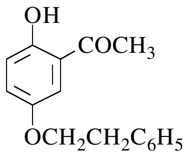
Synthesis

-Obtained by reaction of 1-bromo-2-phenylethane with resacetophenone in the presence of potassium carbonate in refluxing acetone for 24 h (45%) [314].
N.B.: the 1-chloro derivative and butanone can also be used instead of the mentioned starting materials.

m.p. 69° [314].

1-[2-Hydroxy-5-(2-phenylethoxy)phenyl]ethanone

[63359-85-3] $C_{16}H_{16}O_3$ mol.wt. 256.30



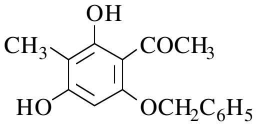
Synthesis

-Obtained by reaction of 1-bromo-2-phenylethane with quinacetophenone in the presence of potassium carbonate in refluxing acetone for 24 h (21%) [314].
N.B.: the 1-chloro derivative and the butanone can also be used instead of the mentioned starting materials.

m.p. 36° [314].

1-[2,4-Dihydroxy-3-methyl-6-(phenylmethoxy)phenyl]ethanone

[39548-93-1] $C_{16}H_{16}O_4$ mol.wt. 272.30



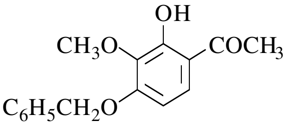
Synthesis

-Obtained by reaction of benzyl chloride on the 2,4,6-trihydroxy-3-methylacetophenone with potassium carbonate in boiling acetone (20%) [880], (< 2%) [1186].

m.p. 212° [1186], 187-188° [880]. One of the reported melting points is obviously wrong. ^{1}H NMR [880], UV [880].

1-[2-Hydroxy-3-methoxy-4-(phenylmethoxy)phenyl]ethanone

[52249-85-1] $C_{16}H_{16}O_4$ mol.wt. 272.30



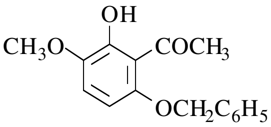
Synthesis

-Preparation by reaction of dimethyl sulfate on 4-(benzyloxy)-2,3-dihydroxyacetophenone with potassium carbonate in refluxing acetone [589] [972] [1571], (82%) [972].

m.p. 146° [972], 143-145° [1571]; ^{1}H NMR [1571].

1-[2-Hydroxy-3-methoxy-6-(phenylmethoxy)phenyl]ethanone

[126405-75-2] $C_{16}H_{16}O_4$ mol.wt. 272.30



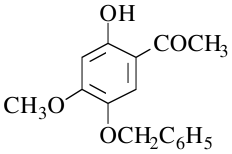
Synthesis

-Preparation by adding 6-(benzyloxy)-2-hydroxy-3-iodoacetophenone and cuprous iodide to a solution of sodium methoxide, previously prepared from methyl alcohol and sodium hydride in DMF [1873].

m.p. 103° [1873]; IR [1873].

1-[2-Hydroxy-4-methoxy-5-(phenylmethoxy)phenyl]ethanone

[52249-88-4] $C_{16}H_{16}O_4$ mol.wt. 272.30



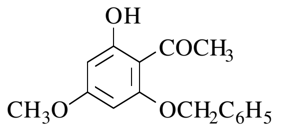
Synthesis

-Preparation by reaction of benzyl bromide on 2,5-dihydroxy-4-methoxyacetophenone with potassium carbonate in boiling acetone (67%) [498].

m.p. 151° [498].

1-[2-Hydroxy-4-methoxy-6-(phenylmethoxy)phenyl]ethanone

[10299-59-9] $C_{16}H_{16}O_4$ mol.wt. 272.30



Syntheses

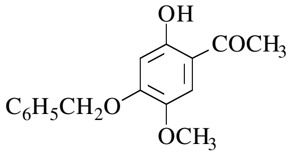
-Preparation by reaction of dimethyl sulfate on 2-(benzyloxy)-4,6-dihydroxyacetophenone with potassium carbonate in refluxing acetone (95%) [880], (85%) [10].

-Preparation by reaction of benzyl bromide with phloroacetophenone 4-methyl ether in the presence of potassium carbonate in acetone at r.t. under nitrogen (82%) [311].

m.p. 120-121° [880], 110-113° [10], 110-111°5 [311]; ^{1}H NMR [311].

1-[2-Hydroxy-5-methoxy-4-(phenylmethoxy)phenyl]ethanone

[34176-18-6] $C_{16}H_{16}O_4$ mol.wt. 272.30



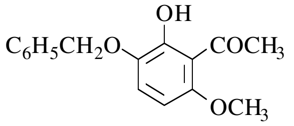
Synthesis

-Preparation by reaction of dimethyl sulfate on 4-(benzyloxy)-2,5-dihydroxyacetophenone with potassium carbonate in refluxing acetone [8] [60] [1068], (85-86%) [8] [60].

m.p. 130° [60], 128-129° [8], 126° [1068].

1-[2-Hydroxy-6-methoxy-3-(phenylmethoxy)phenyl]ethanone

[126405-79-6] $C_{16}H_{16}O_4$ mol.wt. 272.30



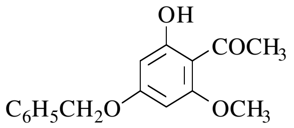
Synthesis

-Preparation by adding 2-hydroxy-3-iodo-6-methoxyacetophenone and cuprous iodide to a solution of sodium benzylate, previously prepared from benzyl alcohol and sodium hydride in DMF [1873].

oil [1873]; ^{1}H NMR [1873], IR [1873].

1-[2-Hydroxy-6-methoxy-4-(phenylmethoxy)phenyl]ethanone

[39548-89-5] $C_{16}H_{16}O_4$ mol.wt. 272.30



Syntheses

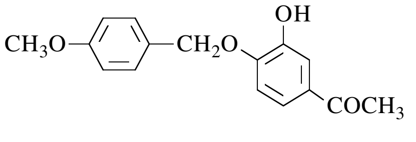
-Preparation by reaction of benzyl chloride on 2,4-dihydroxy-6-methoxyacetophenone with potassium carbonate in boiling acetone [710] [880] [1281], (55%) [880].

-Preparation by reaction of dimethyl sulfate on 4-(benzyloxy)-2,6-dihydroxyacetophenone with potassium carbonate in refluxing acetone (73%) [1281].

m.p. 90-91° [880], 73-74° [1281], 72° [710]. A melting points is obviously wrong.
^{1}H NMR [880], UV [880]; TLC [379].

1-[3-Hydroxy-4-(4-methoxybenzyloxy)phenyl]ethanone

[187966-38-7] $C_{16}H_{16}O_4$ mol.wt. 272.30



Syntheses

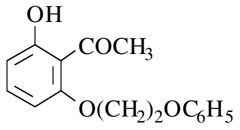
-Preparation by reaction of p-methoxybenzyl bromide with the sodium salt of 3,4-dihydroxyacetophenone (SM) in DMF at r.t. for 24 h (75%). SM was obtained by adding a solution of 3,4-dihydroxyacetophenone in DMF to a suspension of sodium hydride (2 mol) in the same solvent [566].

-Also refer to: [567].

crystals [566] (m.p. not mentioned); ^{1}H NMR [566].

1-[2-Hydroxy-6-(2-phenoxyethoxy)phenyl]ethanone

[61270-14-2] $C_{16}H_{16}O_4$ mol.wt. 272.30



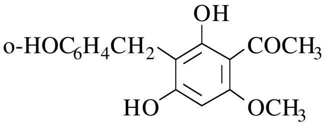
Synthesis

-Preparation by reaction of 2-bromoethoxybenzene with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone (34%) [71].

m.p. 79-80° [71].

1-[2,4-Dihydroxy-3-[(2-hydroxyphenyl)methyl]-6-methoxyphenyl]ethanone

[102056-82-6] $C_{16}H_{16}O_5$ mol.wt. 288.30



Syntheses

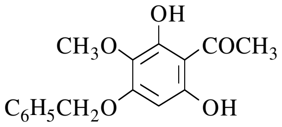
-Preparation by catalytic hydrogenolysis of 3-(o-benzyloxybenzyl)-2,4-dihydroxy-6-methoxyacetophenone at r.t. and atmospheric pressure in the presence of 10% Pd/C in ethyl acetate (66%) [873].

-Preparation from the 2',4'-dihydroxy-3'-[(2-hydroxyphenyl)-(1-piperidino)methyl]-6'-methoxyacetophenone, the piperidine moiety was removed by catalytic hydrogenation using 10% Pd/C as catalyst (50-60%) [1140].

m.p. 184-185° [873]; ^{1}H NMR [873], IR [873], UV [873].

1-[2,6-Dihydroxy-3-methoxy-4-(phenylmethoxy)phenyl]ethanone

[204590-48-7] $C_{16}H_{16}O_5$ mol.wt. 288.30



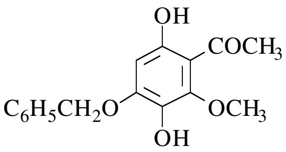
Synthesis

-Preparation by hydrolysis of 4-benzyloxy-6-hydroxy-3-methoxy-2-tosyloxyacetophenone with potassium carbonate in refluxing methanol for 2 h (94%) [803].

m.p. 149-150° [803].

1-[3,6-Dihydroxy-2-methoxy-4-(phenylmethoxy)phenyl]ethanone

[25892-94-8] $C_{16}H_{16}O_5$ mol.wt. 288.30



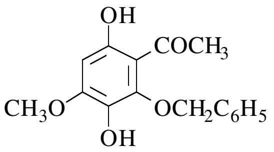
Syntheses

-Obtained from 4-(benzyloxy)-2-hydroxy-6-methoxyacetophenone by persulfate oxidation (Elbs reaction) [588], (23%) [1281].
-Also refer to: [716] [1453].

m.p. 161-162° [1281], 109-110° [588]. One of the reported melting points is obviously wrong. ^{1}H NMR [588].

1-[3,6-Dihydroxy-4-methoxy-2-(phenylmethoxy)phenyl]ethanone

[41997-38-0] $C_{16}H_{16}O_5$ mol.wt. 288.30



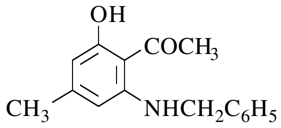
Synthesis

-Obtained from 6-(benzyloxy)-2-hydroxy-4-methoxyacetophenone by persulfate oxidation (Elbs reaction) (17%) [10].

m.p. 119-120° [10]; TLC [379].

1-[2-Hydroxy-4-methyl-6-[(phenylmethyl)amino]phenyl]ethanone

[97066-16-5] $C_{16}H_{17}NO_2$ mol.wt. 255.32



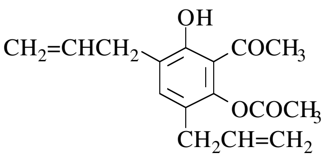
Synthesis

-Preparation by reaction of potassium hydroxide with 2-acetyl-3-benzylamino-5-hydroxy-5-methyl-2-cyclohexene-1-one in ethanol at 40° (73%) [562].

m.p. 160° [562]; ^{1}H NMR [562], IR [562], UV [562], MS [562].

1-[2-(Acetyloxy)-6-hydroxy-3,5-di-2-propenylphenyl]ethanone

[117156-76-0] $C_{16}H_{18}O_4$ mol.wt. 274.32



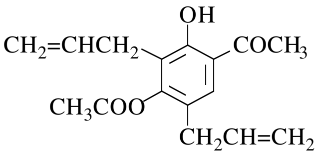
Synthesis

-Obtained (by-product) by thermal rearrangement of 3-acetyl-4,6-bis(allyloxy)acetophenone in refluxing diphenyl ether (3%) [61].

^{1}H NMR [61], IR [61].

1-[4-(Acetyloxy)-2-hydroxy-3,5-di-2-propenylphenyl]ethanone

[106987-29-5] $C_{16}H_{18}O_4$ mol.wt. 274.32



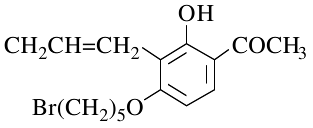
Synthesis

-Obtained (by-product) by thermal Claisen rearrangement of 3-acetyl-4,6-bis(allyloxy)acetophenone or of 3-acetyl-2,4-bis(allyloxy)acetophenone in refluxing N,N-dimethylaniline (5-6%) [61].

pale greenish yellow oil [61]; ^{1}H NMR [61], IR [61], UV [61], MS [61].

1-[4-[(5-Bromopentyl)oxy]-2-hydroxy-3-(2-propenyl)phenyl]ethanone

[61270-23-3] $C_{16}H_{21}BrO_3$ mol.wt. 341.24



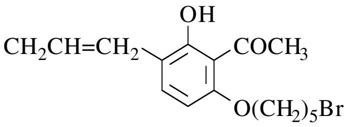
Synthesis

-Preparation by reaction of 1,5-dibromopentane with 3-allyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone [71].

oil [71].

1-[6-[(5-Bromopentyl)oxy]-2-hydroxy-3-(2-propenyl)phenyl]ethanone

[61270-18-6] $C_{16}H_{21}BrO_3$ mol.wt. 341.24



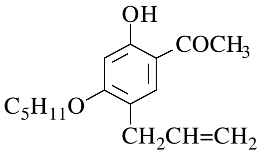
Synthesis

-Preparation by reaction of 1,5-dibromopentane with 3-allyl-2,6-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone [71].

b.p.$_{0.1}$ 180-200° [71].

1-[2-Hydroxy-4-(pentyloxy)-5-(2-propenyl)phenyl]ethanone

[117690-49-0] $C_{16}H_{22}O_3$ mol.wt. 262.35



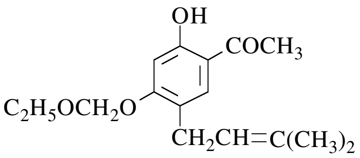
Synthesis

-Preparation by reaction of n-pentyl bromide with 5-allyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing methyl ethyl ketone (43-44%) [256] [257] [777].

oil [256] [257] [777].

1-[4-(Ethoxymethoxy)-2-hydroxy-5-(3-methyl-2-butenyl)phenyl]ethanone

[175546-56-2] $C_{16}H_{22}O_4$ mol.wt. 278.35



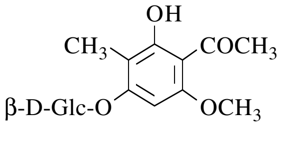
Synthesis

-Preparation by reaction of ethoxymethyl chloride with 2,4-dihydroxy-5-(3-methyl-2-butenyl)acetophenone in acetone for 10 min at 30° (66%) [1378].

^{1}H NMR [1378].

1-[4-(β-D-Glucopyranosyloxy)-2-hydroxy-6-methoxy-3-methylphenyl]ethanone

[145194-40-7] $C_{16}H_{22}O_9$ mol.wt. 358.35

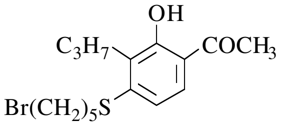


Isolation from natural sources

-From the roots of *Euphorbia ebracteolata* Hayata (Euphorbiaceae) [1950].

1-[4-[(5-Bromopentyl)thio]-2-hydroxy-3-propylphenyl]ethanone

[125617-44-9] $C_{16}H_{23}BrO_2S$ mol.wt. 359.33



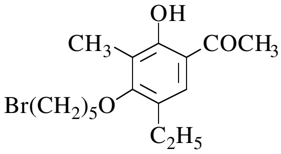
Synthesis

-Preparation by reaction of 1,5-dibromopentane with 2-hydroxy-4-mercapto-3-propylacetophenone in the presence of potassium carbonate and potassium iodide in refluxing methyl ethyl ketone [1680].

pale yellow oil [1680].

1-[4-[(5-Bromopentyl)oxy]-5-ethyl-2-hydroxy-3-methylphenyl]ethanone

[140660-35-1] $C_{16}H_{23}BrO_3$ mol.wt. 343.26



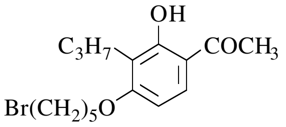
Synthesis

-Preparation by reaction of 1,5-dibromopentane with 5-ethyl-2,4-dihydroxy-3-methylacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (76%) [777].

oil [777].

1-[4-[(5-Bromopentyl)oxy]-2-hydroxy-3-propylphenyl]ethanone

[99453-85-7] $C_{16}H_{23}BrO_3$ mol.wt. 343.26



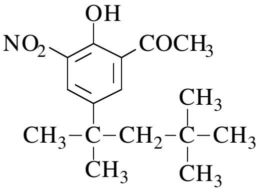
Synthesis

-Preparation by reaction of 1,5-dibromopentane with 2,4-dihydroxy-3-propylacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone [71] [1156], (22%) [1156].

b.p.$_{0.02}$ 172-180° [71]; MS [1156].

1-[2-Hydroxy-3-nitro-5-(1,1,3,3-tetramethylbutyl)phenyl]ethanone

[30299-56-0] $C_{16}H_{23}NO_4$ mol.wt. 293.36



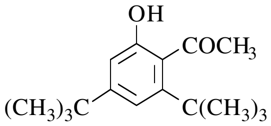
Synthesis

-Preparation by reaction of 65% nitric acid with 2-hydroxy-5-tert-octylacetophenone in acetic acid, first at 0°, then at 20° [1386].

m.p. 86°5 [1386]; IR [1386], UV [1386].

1-[2,4-Bis(1,1-dimethylethyl)-6-hydroxyphenyl]ethanone

$C_{16}H_{24}O_2$ mol.wt. 248.37



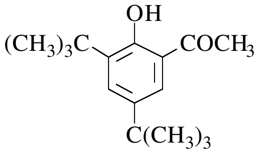
Synthesis

-Obtained by UV light irradiation of 3,5-di-tert-butylphenyl acetate in benzene at r.t. (photo-Fries rearrangement) [597].

m.p. 198°5 [597].

1-[3,5-Bis(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone

[37456-29-4] $C_{16}H_{24}O_2$ mol.wt. 248.37



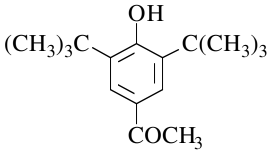
Syntheses

-Preparation by reaction of methylmagnesium iodide on 3,5-di-tert-butyl-2-hydroxybenzonitrile in ethyl ether, first at 0° and then at r.t. (58%) [1331].
-Also obtained by reaction of sec-butyllithium on 2-bromo-4,6-di-tert-butylphenyl acetate in ethyl ether at -95° and -78°, followed by hydrolysis of mixture with saturated ammonium chloride (metal-promoted Fries rearrangement) (43-52%) [1234].
-Preparation by reaction of acetic anhydride with 2,4-di-tert-butylphenol in the presence of boron trifluoride-acetic acid complex at 100° [343].

m.p. 45-46° [343], 43-44°5 [1331]; b.p.$_{0.45}$ 100° [343];
^1H NMR [1331], IR [1331].

1-[3,5-Bis(1,1-dimethylethyl)-4-hydroxyphenyl]ethanone

[14035-33-7] $C_{16}H_{24}O_2$ mol.wt. 248.37



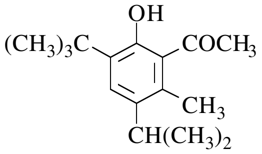
Syntheses

-Preparation by reaction of acetic acid on 2,6-di-tert-butylphenol with trifluoroacetic anhydride at r.t. [1027] [1190] [1332] [1333], (78-87%) [1190] [1333].
-Preparation by reaction of acetic anhydride on 2,6-di-tert-butylphenol with sulfodifluoroacetic acid in acetic acid at 20° (81%) [654] or with boron trifluoride etherate at 5° (30%) [705].
-Preparation by reaction of acetyl chloride on 2,6-di-tert-butylphenol with aluminium chloride at -10° (95%) [1436] and at 0° (70%) [430].
-Also obtained by reaction of potassium ferricyanide on 2,6-di-tert-butyl-4-(1-methoxyethyl)-phenol with aqueous sodium hydroxide in benzene (20%) [430].
-Also obtained (poor yield) by bubbling air into a cumene solution of 2,6-di-tert-butyl-4-ethylphenol in the presence of cumene hydroperoxide and cobalt phthalate between 80-100° (2%) [780].

m.p. 150-151°5 [705] [1190], 148° [780], 147-148° [430] [1332] [1333], 146-147° [1436], 141-143° [654];
^{1}H NMR [705] [1333], ^{13}C NMR [705], IR [705], MS [1030].

1-[3-(1,1-Dimethylethyl)-2-hydroxy-6-methyl-5-(1-methylethyl)phenyl]ethanone

[129375-13-9] $C_{16}H_{24}O_2$ mol.wt. 248.37



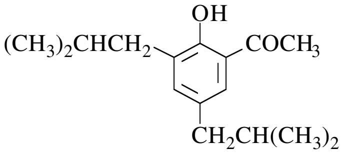
Synthesis

-Preparation by Fries rearrangement of 2-tert-butyl-5-methyl-4-isopropylphenyl acetate with titanium tetrachloride in chlorobenzene at 100° (23%) [1162].

m.p. 44° [1162];
^{1}H NMR [1162], (Sadtler: standard n° 52742 M);
IR [1162], (Sadtler: standard n° 79801 K); UV [1162], MS [1162].

1-[2-Hydroxy-3,5-bis(2-methylpropyl)phenyl]ethanone

[35158-27-1] $C_{16}H_{24}O_2$ mol.wt. 248.37



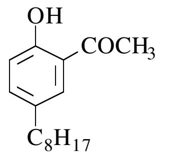
Synthesis

-Preparation by reaction of ethyl acetoacetate with 2-isobutyl-6-methyl-2-heptenal in the presence of pyridine and piperidine as catalysts in refluxing benzene (29%). The 2-isobutyl-6-methyl-2-heptenal was obtained by self-condensation of isocaproaldehyde in the presence of 15% potassium hydroxide solution (Aldol condensation) [940] [941] [942].

b.p.$_{1-2}$ 116-118° [940] [941] [942];
IR [940] [941] [942], UV [940] [941] [942], MS [940] [941] [942].

1-(2-Hydroxy-5-octylphenyl)ethanone

[74604-19-6] $C_{16}H_{24}O_2$ mol.wt. 248.37



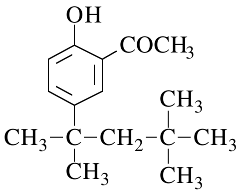
Synthesis

-Preparation by reaction of acetyl chloride on 4-octylphenol with aluminium chloride in ethylene dichloride at 110-120° (58%) [1033].

b.p.$_4$ 168-170° [1033].

1-[2-Hydroxy-5-(1,1,3,3-tetramethylbutyl)phenyl]ethanone

[57373-80-5] $C_{16}H_{24}O_2$ mol.wt. 248.37
and
[30299-53-7] (2'-Hydroxy-5'-(1,1,3,3-tetramethylbutyl)acetophenone)



Syntheses

-Obtained by Fries rearrangement of 4-(1,1,3,3-tetramethylbutyl)phenyl acetate also called 4-tert-octylphenyl acetate with aluminium chloride [1842] [1906], in 1,2,3-trichloropropane or in tetrachloroethane at 120° under nitrogen (71-77%) [1842]; (high yield) [1906].

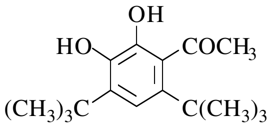
-Preparation by demethylation of 2-methoxy-5-tert-octylacetophenone with 4% hydrobromic acid in refluxing acetic acid (47-52%) [1906].

-Preparation by UV light irradiation of 4-tert-octylphenyl acetate in benzene or in ethanol solution (37%) (photo-Fries rearrangement) [1386].

^{1}H NMR [1386], IR [1386], UV [1386].

1-[4,6-Bis(1,1-dimethylethyl)-2,3-dihydroxyphenyl]ethanone

[84296-99-1] $C_{16}H_{24}O_3$ mol.wt. 264.37



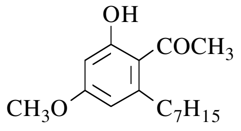
Synthesis

-Obtained by irradiation of a benzene solution of 3,5-di-tert-butyl-o-benzoquinone in the presence of a large excess of acetaldehyde (6%) [1758].

m.p. 169-170° [1758]; ^{1}H NMR [1758], IR [1758].

1-(2-Heptyl-6-hydroxy-4-methoxyphenyl)ethanone

[4670-13-7] $C_{16}H_{24}O_3$ mol.wt. 264.37



Synthesis

-Preparation by partial methylation of 2,4-dihydroxy-6-heptylacetophenone in acetone with dimethyl sulfate in the presence of 10% sodium hydroxide at 45° for 4 h (70%) [986].

Isolation from natural sources

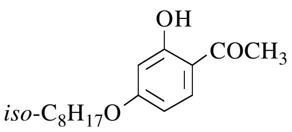
-Obtained by alkaline degradation of various *siphulin* derivatives* with potassium hydroxide in refluxing methanol [307]. The siphulin (an homoflavone) 7-hydroxy-5-heptyl-2-[3',5'-dihydroxy-2-carboxybenzyl]chroman-4-one (m.p. 180°) [308] is a constituent of the North Scandinavican lichen *siphula ceratites* (Wahlenberg) Fr.

*siphulin methyl ester trimethyl ether [308], decarboxysiphulin trimethyl ether or a lactol.

oil [307] [986], liquid compound [308];
b.p.$_{0.01}$ 110° [308], b.p.$_{0.01}$ 120° [307]; $n_D^{18} = 1.5372$ [307], $n_D^{19} = 1.5339$ [308];
^{1}H NMR [307] [986], IR [307] [308], UV [307] [308].

1-[2-Hydroxy-4-(isooctyloxy)phenyl]ethanone

[127313-67-1] $C_{16}H_{24}O_3$ mol.wt. 264.37

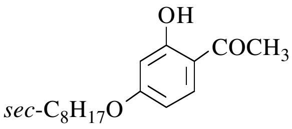


Synthesis

-Refer to: [1932] (Chinese paper).

1-[2-Hydroxy-4-(sec-octyloxy)phenyl]ethanone

[127313-63-7] $C_{16}H_{24}O_3$ mol.wt. 264.37

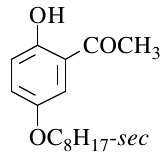


Synthesis

-Refer to: [1932] (Chinese paper).

1-[2-Hydroxy-5-(sec-octyloxy)phenyl]ethanone

[127313-62-6] $C_{16}H_{24}O_3$ mol.wt. 264.37

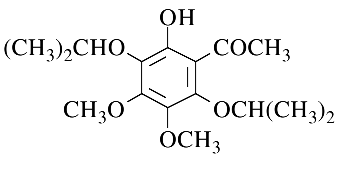


Synthesis

-Refer to: [1932] (Chinese paper).

1-[2-Hydroxy-4,5-dimethoxy-3,6-bis(1-methylethoxy)phenyl]ethanone

[169130-25-0] $C_{16}H_{24}O_6$ mol.wt. 312.36

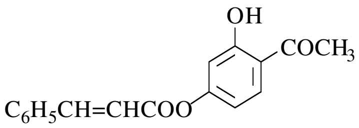


Synthesis

-Preparation by smooth demethylation of 2,5-diisopropyloxy-3,4,6-trimethoxyacetophenone with aluminium bromide in acetonitrile (high yield) [796].

1-[4-(Cinnamoyloxy)-2-hydroxyphenyl]ethanone

$C_{17}H_{14}O_4$ mol.wt. 282.30



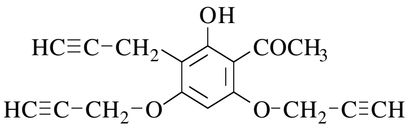
Synthesis

-Obtained by reaction of cinnamoyl chloride on resacetophenone with potassium carbonate in toluene (17%) [137].

m.p. 131° [137].

1-[2-Hydroxy-3-(2-propynyl)-4,6-bis(2-propynyloxy)phenyl]ethanone

[53771-25-8] $C_{17}H_{14}O_4$ mol.wt. 282.30



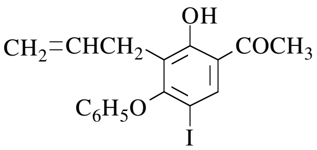
Synthesis

-Obtained (poor yield) by reaction of 2-propynyl bromide with phloroacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (4%) [427].

m.p. 150-151° [427]; IR [427], UV [427].

1-[2-Hydroxy-5-iodo-4-phenoxy-3-(2-propenyl)phenyl]ethanone

[144691-36-1] $C_{17}H_{15}IO_3$ mol.wt. 394.21



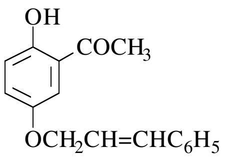
Synthesis

-Obtained by reaction of iodosobenzene diacetate (DAIB) with 3-allyl-2,4-dihydroxyacetophenone in refluxing methanol (38%) [1143].

m.p. 160° [1143]; ^{1}H NMR [1143], IR [1143].

1-[2-Hydroxy-5-[(3-phenyl-2-propenyl)oxy]phenyl]ethanone

[79950-56-4] $C_{17}H_{16}O_3$ mol.wt. 268.31



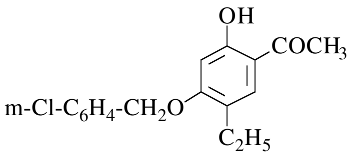
Synthesis

-Preparation by reaction of cinnamyl bromide with quinacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone under nitrogen (90%) [303].

m.p. 105-107° [303]; ^{1}H NMR [303], IR [303], MS [303].

1-[4-[(3-Chlorophenyl)methoxy]-5-ethyl-2-hydroxyphenyl]ethanone

[117706-49-7] $C_{17}H_{17}ClO_3$ mol.wt. 304.77

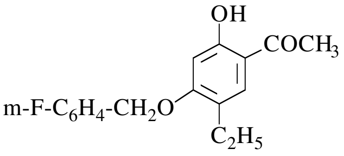


Synthesis

-Preparation by reaction of 3-chlorobenzyl bromide with 5-ethyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide (47%) [256] [257].

1-[5-Ethyl-4-[(3-fluorophenyl)methoxy]-2-hydroxyphenyl]ethanone

[117706-48-6] $C_{17}H_{17}FO_3$ mol.wt. 288.32



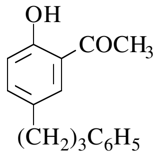
Synthesis

-Preparation by reaction of 3-fluorobenzyl bromide with 5-ethyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide (18%) [256] [257].

m.p. 104-105° [256] [257].

1-[2-Hydroxy-5-(3-phenylpropyl)phenyl]ethanone

[61270-17-5] $C_{17}H_{18}O_2$ mol.wt. 254.33



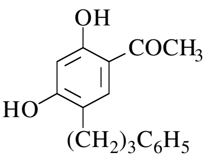
Syntheses

-Preparation by Fries rearrangement of 4'-acetoxy-1,3-diphenylpropane with aluminium chloride in boiling chlorobenzene [1896].
-Preparation by reaction of acetic anhydride with 4-(3-phenylpropyl)phenol in the presence of boron trifluoride-acetic acid complex at 100° [71].

oil [71]; b.p.$_{18.5}$ 232° [1896]; ^{1}H NMR [71], MS [71].

1-[2,4-Dihydroxy-5-(3-phenylpropyl)phenyl]ethanone

$C_{17}H_{18}O_3$ mol.wt. 270.33



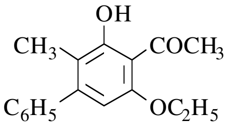
Synthesis

-Preparation by Fries rearrangement of 2',4'-diacetoxy-1,3-diphenylpropane with aluminium chloride in the presence of 2',4'-dihydroxy-1,3-diphenylpropane in nitrobenzene at 50° [1896].

m.p. 106° [1896].

1-(5-Ethoxy-3-hydroxy-2-methyl[1,1'-biphenyl]-4-yl)ethanone

[138151-67-4] $C_{17}H_{18}O_3$ mol.wt. 270.33



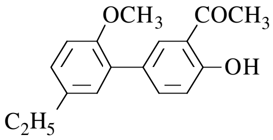
Synthesis

-Preparation by heating at 100° for 18 h a dioxane solution of 4-chloro-2-methyl-3-phenyl-2-cyclobutenone and 4-ethoxy-4-(tri-n-butylstannyl)-3-buten-2-one (**I**) with Pd(benzonitrile)$_2$Cl$_2$ and tris(2-furyl)phosphine (50%). The compound (**I**) was obtained by adding a tetrahydrofuran solution of tetrabutylammonium cyanide (Bu_4NCN) to a tetrahydrofuran solution of 3-ethoxy-2-cyclobutenone and n-$(C_4H_9)_3$ $SnSi(CH_3)_3$ cooled to -22° and then the mixture was warmed at r.t. [1032].

m.p. 78-80° [1032]; ^{1}H NMR [1032], ^{13}C NMR [1032], IR [1032].

1-(5'-Ethyl-4-hydroxy-2'-methoxy[1,1'-biphenyl]-3-yl)ethanone

[131845-25-5] $C_{17}H_{18}O_3$ mol.wt. 270.33

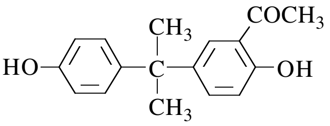


Synthesis

-Refer to: [1768].

1-[2-Hydroxy-5-[1-(4-hydroxyphenyl)-1-methylethyl]phenyl]ethanone

[104676-26-8] $C_{17}H_{18}O_3$ mol.wt. 270.33



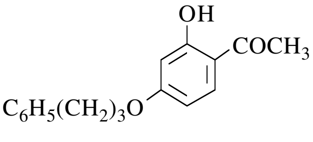
Synthesis

-Obtained by Fries rearrangement of 2,2-bis(acetoxyphenyl)propane (bisphenol-A diacetate) (1 mol) with titanium tetrachloride (4 mol) in nitrobenzene, first for 24 h at r.t., then for 6 h at 55° (23%) [1339].

m.p. 139-140° [1339]; ^{1}H NMR [1339], ^{13}C NMR [1339], IR [1339].

1-[2-Hydroxy-4-(3-phenylpropoxy)phenyl]ethanone

[63359-86-4] $C_{17}H_{18}O_3$ mol.wt. 270.33



Syntheses

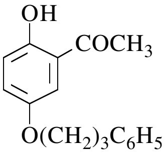
-Obtained by reaction of 1-bromo-3-phenylpropane with resacetophenone in the presence of potassium carbonate in refluxing acetone for 24 h. The 1-chloro derivative and butanone can also be used instead of the mentioned starting materials (83%) [314].

-Also refer to: [312].

m.p. 75-77° [314].

1-[2-Hydroxy-5-(3-phenylpropoxy)phenyl]ethanone

[63359-87-5] $C_{17}H_{18}O_3$ mol.wt. 270.33



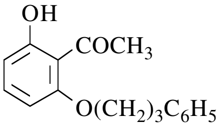
Syntheses

-Obtained by reaction of 1-bromo-3-phenylpropane with quinacetophenone in the presence of potassium carbonate in refluxing acetone for 24 h. The 1-chloro derivative and butanone can also be used instead of the mentioned starting material and solvent (54%) [314].
-Also refer to: [312].

m.p. 34-35° [314].

1-[2-Hydroxy-6-(3-phenylpropoxy)phenyl]ethanone

[69079-93-2] $C_{17}H_{18}O_3$ mol.wt. 270.33



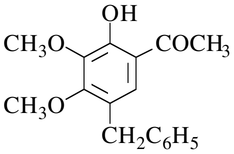
Synthesis

-Obtained by reaction of 1-bromo-3-phenylpropane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 24 h. The 1-chloro derivative and butanone can also be used instead of the mentioned starting material and solvent (75%) [314].

m.p. 95-96° [314].

1-[2-Hydroxy-3,4-dimethoxy-5-(phenylmethyl)phenyl]ethanone

[105485-57-2] $C_{17}H_{18}O_4$ mol.wt. 286.33



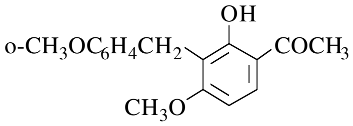
Synthesis

-Preparation by reaction of dimethyl sulfate with 5-benzyl-2,3,4-trihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone (68%) [885].

m.p. 42-43° [885]; ^{1}H NMR [885], IR [885], UV [885].

1-[2-Hydroxy-4-methoxy-3-[(2-methoxyphenyl)methyl]phenyl]ethanone

[103633-39-2] $C_{17}H_{18}O_4$ mol.wt. 286.33



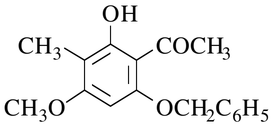
Synthesis

-Obtained by reaction of dimethyl sulfate with 2,4-dihydroxy-3-(o-hydroxybenzyl)acetophenone in the presence of potassium carbonate in refluxing acetone (9%) [873].

oil [873]; ^{1}H NMR [873].

1-[2-Hydroxy-4-methoxy-3-methyl-6-(phenylmethoxy)phenyl]ethanone

$C_{17}H_{18}O_4$ mol.wt. 286.33



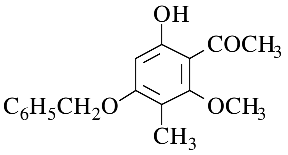
Synthesis

-Preparation by reaction of methyl iodide with 6-(benzyloxy)-2,4-dihydroxy-3-methylacetophenone in the presence of potassium carbonate in refluxing acetone (88%) [1186].

m.p. 127° [1186].

1-[6-Hydroxy-2-methoxy-3-methyl-4-(phenylmethoxy)phenyl]ethanone

$C_{17}H_{18}O_4$ mol.wt. 286.33



Syntheses

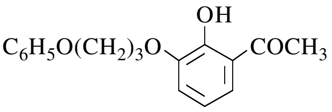
-Preparation by reaction of benzyl bromide on 4,6-dihydroxy-2-methoxy-3-methylacetophenone with potassium carbonate in boiling acetone (48%) [1883].

-Preparation by partial catalytic hydrogenolysis of 4,6-bis-(benzyloxy)-2-methoxy-3-methylacetophenone with $PdCl_2/C$ in methanol (86%) [1883] or by reaction of 10% ethanolic hydrochloric acid on the same starting material in refluxing dioxane (42%) [1186].

m.p. 105° [1883], 103° [1186].

1-[2-Hydroxy-3-(3-phenoxypropoxy)phenyl]ethanone

[69079-92-1] $C_{17}H_{18}O_4$ mol.wt. 286.33



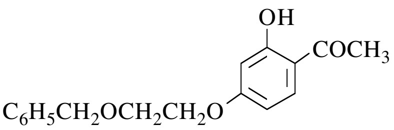
Synthesis

-Obtained by reaction of 1-bromo-3-phenoxypropane with 2,3-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 24 h. The 1-chloro derivative and butanone can also be used instead of the mentioned starting material and solvent (32%) [314].

m.p. 56-57° [314].

1-[2-Hydroxy-4-[2-(phenylmethoxy)ethoxy]phenyl]ethanone

[307520-94-1] $C_{17}H_{18}O_4$ mol.wt. 286.33

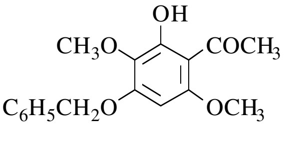


Synthesis

-Refer to: [1840] (compound 1d).

1-[2-Hydroxy-3,6-dimethoxy-4-(phenylmethoxy)phenyl]ethanone

[3162-52-5] $C_{17}H_{18}O_5$ mol.wt. 302.33



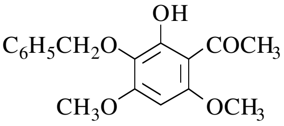
Syntheses

-Preparation by reaction of benzyl chloride with 2,4-dihydroxy-3,6-dimethoxyacetophenone in the presence of potassium carbonate [671] [1452] or potassium carbonate and potassium iodide [215] in refluxing acetone (72%) [671], (63%) [215], (53%) [1452].
The same reaction using benzyl bromide instead of benzyl chloride led to an inseparable mixture (68%) of 2-benzyl- and 4-benzyl ethers (m.p. 105-107°) [664].
-Preparation by reaction of acetyl chloride on 2,5-dimethoxyresorcinol dibenzyl ether with aluminium chloride in benzene at 0° (35%) [671].
-Obtained (by-product) by reaction of acetonitrile with 2,6-bis(benzyloxy)-1,4-dimethoxybenzene (Hoesch reaction) [1452].

m.p. 113-115° [215], 111-111°5 [1452], 109°5-110° [671].

1-[2-Hydroxy-4,6-dimethoxy-3-(phenylmethoxy)phenyl]ethanone

[54299-57-9] $C_{17}H_{18}O_5$ mol.wt. 302.33



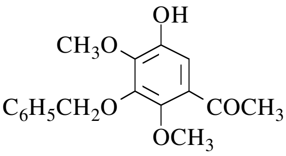
Syntheses

-Preparation by reaction of benzyl chloride with 2,3-dihydroxy-4,6-dimethoxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (56%) [215].
-Preparation from 2,3-bis(benzyloxy)-4,6-dimethoxyacetophenone. The 2-benzyloxy group was selectively split with concentrated hydrochloric acid in acetic acid at r.t. (80%) [799].

m.p. 95-97° [799], 90-92° [215].

1-[5-Hydroxy-2,4-dimethoxy-3-(phenylmethoxy)phenyl]ethanone

[65039-99-8] $C_{17}H_{18}O_5$ mol.wt. 302.33

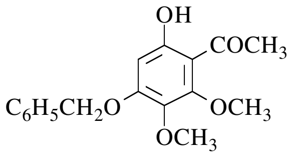


Synthesis

-Obtained [1864] according to the procedure [1696].

1-[6-Hydroxy-2,3-dimethoxy-4-(phenylmethoxy)phenyl]ethanone

[25892-95-9] $C_{17}H_{18}O_5$ mol.wt. 302.33



Syntheses

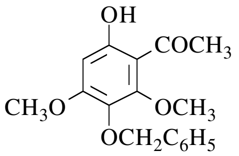
-Obtained by partial methylation of 4-(benzyloxy)-3,6-dihydroxy-2-methoxyacetophenone [23] [215] [588] [778] [804] [807] [1862] [1863], with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone [1453], for 5 h (57%) [716].

-Also refer to: [1865] [1918].

m.p. 86-87° [716], 84-85° [588]; IR [716].

1-[6-Hydroxy-2,4-dimethoxy-3-(phenylmethoxy)phenyl]ethanone

[52249-87-3] $C_{17}H_{18}O_5$ mol.wt. 302.33



Syntheses

-Preparation by reaction of benzyl chloride with 3,6-dihydroxy-2,4-dimethoxyacetophenone,

*in the presence of potassium carbonate and sodium iodide in refluxing acetone for 10 h, then at r.t. for 6 h [1536] [1863], (57%) [1696];

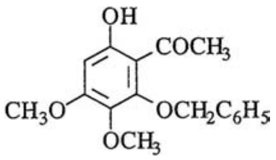
*in the presence of potassium carbonate in DMF [843].

-Also refer to: [208] [210] [590] [1005] [1136] [1864].

oil [1696] [843]; ^{1}H NMR [843].

1-[6-Hydroxy-3,4-dimethoxy-2-(phenylmethoxy)phenyl]ethanone

[41997-39-1] $C_{17}H_{18}O_5$ mol.wt. 302.33



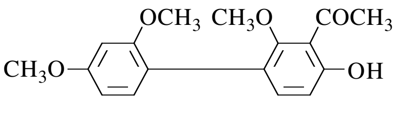
Synthesis

-Preparation by reaction of dimethyl sulfate on 6-(benzyloxy)-2,5-dihydroxy-4-methoxyacetophenone with potassium carbonate in refluxing acetone (57%) [10].

m.p. 87-89° [10].

1-(4-Hydroxy-2,2',4'-trimethoxy[1,1'-biphenyl]-3-yl)ethanone

$C_{17}H_{18}O_5$ mol.wt. 302.33



Syntheses

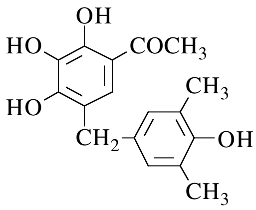
-Obtained by alkaline degradation of 2-(2,4-dimethoxyphenyl)-1,9-di-O-methylhemiergoflavinone ($C_{25}H_{24}O_9$) with 10% sodium hydroxide on a steam bath for 1.75 h [72].

-Also obtained by alkaline degradation of 6-(2,4-dimethoxyphenyl)-5-methoxy-2-methylchromone (m.p. 141-142°) with 25%(w/v) aqueous sodium hydroxide during 2 h on a steam bath (72%) [794].

m.p. 94° [72], 93° [794]; IR [794].

1-[2,3,4-Trihydroxy-5-[(4-hydroxy-3,5-dimethylphenyl)methyl]phenyl]ethanone

[142045-74-7] $C_{17}H_{18}O_5$ mol.wt. 302.33

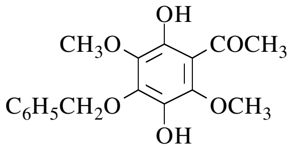


Synthesis

-Refer to: [1834] (Japanese patent).

1-[2,5-Dihydroxy-3,6-dimethoxy-4-(phenylmethoxy)phenyl]ethanone

[3162-50-3] $C_{17}H_{18}O_6$ mol.wt. 318.33



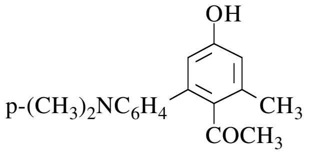
Syntheses

-Obtained by oxidation of 4-(benzyloxy)-2-hydroxy-3,6-dimethoxyacetophenone with potassium persulfate (Elbs reaction), (46%) [1072], (14%) [592].
-Also refer to: [591] [593] [1071] [1793].

m.p. 60-62° [592], 59-61° [1072];
IR [1072]; TLC [592].

1-[4'-(Dimethylamino)-5-hydroxy-3-methyl[1,1'-biphenyl]-2-yl]ethanone

[108909-48-4] $C_{17}H_{19}NO_2$ mol.wt. 269.34



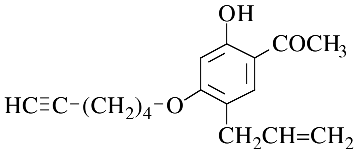
Syntheses

-Obtained by aromatization of 4-acetyl-5-[4-(dimethylamino)phenyl]-3-methyl-2-cyclohexen-1-one (m.p. 162°) with bromine in chloroform (70%) or by heating at 170° for 3 h [731].
-Also obtained by deacylation of 1,1'-[4'-(dimethylamino)-3-hydroxy-5-methyl[1,1'-biphenyl]-2,6-diyl]bis-ethanone (m.p. 153°) with sodium hydroxide in refluxing dilute ethanol for 3 h (70%) [731].
-Also refer to: [730].

m.p. 192° [731].

1-[4-(5-Hexynyloxy)-2-hydroxy-5-(2-propenyl)phenyl]ethanone

[117706-50-0] $C_{17}H_{20}O_3$ mol.wt. 272.34



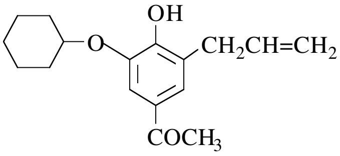
Synthesis

-Preparation by reaction of 6-bromo-1-hexyne with 5-allyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing methyl ethyl ketone (15-20%) [256] [257] [777].

oil [777]; m.p. < 25° [256] [257]; ^{1}H NMR [256] [257].

1-[3-(Cyclohexyloxy)-4-hydroxy-5-(2-propenyl)phenyl]ethanone

$C_{17}H_{22}O_3$ mol.wt. 274.36



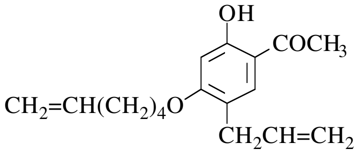
Synthesis

-Preparation by thermal Claisen rearrangement of 4-(allyloxy)-3-cyclohexyloxyacetophenone in boiling N,N-diethylaniline (69%) [1211].

m.p. 58° [1211]; b.p.$_{0.6}$ 170-180° [1211].

1-[4-(5-Hexenyloxy)-2-hydroxy-5-(2-propenyl)phenyl]ethanone

[117690-54-7] $C_{17}H_{22}O_3$ mol.wt. 274.36



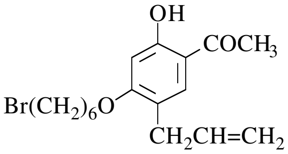
Synthesis

-Preparation by reaction of 6-bromo-1-hexene with 5-allyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing methyl ethyl ketone (30%) [256] [257] [777].

oil [777]; m.p. < 25° [256] [257].

1-[4-[(6-Bromohexyl)oxy]-2-hydroxy-5-(2-propenyl)phenyl]ethanone

[117706-41-9] $C_{17}H_{23}BrO_3$ mol.wt. 355.27

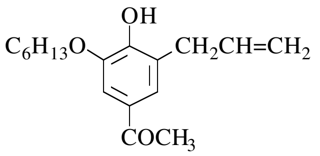


Synthesis

-Preparation by reaction of 1,6-dibromohexane with 5-allyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide at reflux (42%) [256] [257].

1-[3-(Hexyloxy)-4-hydroxy-5-(2-propenyl)phenyl]ethanone

$C_{17}H_{24}O_3$ mol.wt. 276.38



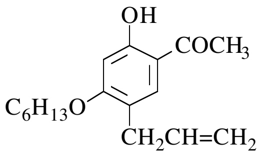
Synthesis

-Preparation by thermal Claisen rearrangement of 4-(allyloxy)-3-(hexyloxy)acetophenone without solvent at 200° (47%) [1211].

m.p. 83° [1211]; b.p.$_{0.9}$ 175-180° [1211].

1-[4-(Hexyloxy)-2-hydroxy-5-(2-propenyl)phenyl]ethanone

[117690-47-8] $C_{17}H_{24}O_3$ mol.wt. 276.38



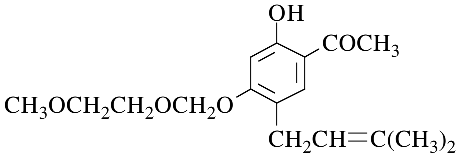
Synthesis

-Preparation by reaction of hexyl bromide with 5-allyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing methyl ethyl ketone (85%) [777], (36%) [256] [257].

m.p. 42-44° [256] [257] [777].

1-[2-Hydroxy-4-[(2-methoxyethoxy)methoxy]-5-(3-methyl-2-butenyl)phenyl]ethanone

[181047-51-8] $C_{17}H_{24}O_5$ mol.wt. 308.37



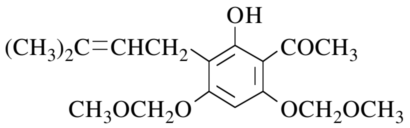
Synthesis

-Preparation by treatment of 4-(2-methoxyethoxymethoxy)-2-(3,3-dimethylallyloxy)-acetophenone in refluxing N,N-diethylaniline at 220° for 4 h under argon atmosphere (77%) (Claisen rearrangement) [1338].

^{1}H NMR [1338], ^{13}C NMR [1338], MS [1338].

1-[2-Hydroxy-4,6-bis(methoxymethoxy)-3-(3-methyl-2-butenyl)phenyl]ethanone

[84092-45-5] $C_{17}H_{24}O_6$ mol.wt. 324.37



Syntheses

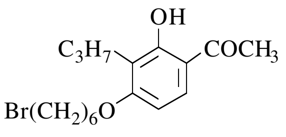
-Obtained by reaction of prenyl bromide with 2-hydroxy-4,6-di-(methoxymethoxy)acetophenone in methanolic potassium hydroxide solution, first at 0°, then at r.t. for 24 h (74%) [1620].

-Also refer to: [310].

liquid [1620]; ^{1}H NMR [1620], IR [1620], UV [1620].

1-[4-[(6-Bromohexyl)oxy]-2-hydroxy-3-propylphenyl]ethanone

[92518-46-2] $C_{17}H_{25}BrO_3$ mol.wt. 357.29

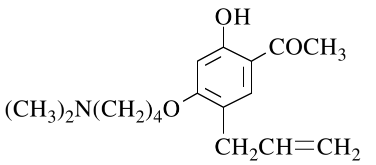


Synthesis

-Preparation by reaction of 1,6-dibromohexane with 2,4-dihydroxy-3-propylacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (37%) [1156].

1-[4-[4-(Dimethylamino)butoxy]-2-hydroxy-5-(2-propenyl)phenyl]ethanone

$C_{17}H_{25}NO_3$ mol.wt. 291.39

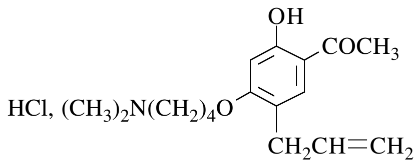


Synthesis

-Preparation by reaction of dimethylamine with 5-allyl-4-(4-bromobutoxy)-2-hydroxyacetophenone during 16 h [777].

1-[4-[4-(Dimethylamino)butoxy]-2-hydroxy-5-(2-propenyl)phenyl]ethanone
(Hydrochloride)

[117706-32-8] $C_{17}H_{25}NO_3$, HCl mol.wt. 327.85



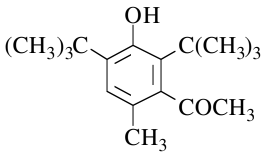
Synthesis

-Obtained by reaction of hydrogen chloride with the corresponding base in ethanol, then adding ethyl ether to the mixture [777].

m.p. 88-90° [777].

1-[2,4-Bis(1,1-dimethylethyl)-3-hydroxy-6-methylphenyl]ethanone

[175438-44-5] $C_{17}H_{26}O_2$ mol.wt. 262.39



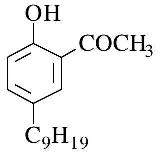
Synthesis

-Refer to: Chem. Abstr., **124**, 260501q (1995).

N.B.: this ketone is erroneously referenced in the Chemical Abstracts (Vol. **124**, 1996, Formula Index, 2675F). The compound actually obtained by reaction between acetic anhydride and 2,6-di-tert-butyl-6-methylphenol in the presence of various Metal Bis(trifluoromethylsulfonyl)-amides such as a titanium and ytterbium bistrifylamides in methylene chloride or acetonitrile at r.t. is the phenolic ester, i.e. the 2,6-di-tert-butyl-6-methylphenyl acetate (90-99%), which has been unambiguously characterized [1232] (personal communication from professor Koichi MIKAMI).

1-(2-Hydroxy-5-nonylphenyl)ethanone

[115851-77-9] $C_{17}H_{26}O_2$ mol.wt. 262.39



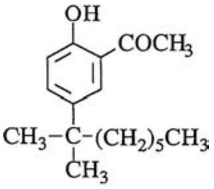
Synthesis

-Preparation by reaction of acetyl chloride on 4-nonylphenol with aluminium chloride in ethylene dichloride at 110-120° (63%) [1033].

b.p.$_4$ 178-182° [1033].

1-(2-Hydroxy-5-tert-nonylphenyl)ethanone

[57375-45-8] $C_{17}H_{26}O_2$ mol.wt. 262.39

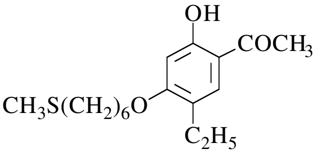


Synthesis

-Preparation by Fries rearrangement of 4-tert-nonylphenyl acetate with aluminium chloride under nitrogen in tetrachloroethane or in tetrachloroethylene at 120-125° (77-79%) [1842] or in refluxing chlorobenzene (46%) [1842].

1-[5-Ethyl-2-hydroxy-4-[[6-(methylthio)hexyl]oxy]phenyl]ethanone

[117706-37-3] $C_{17}H_{26}O_3S$ mol.wt. 310.46



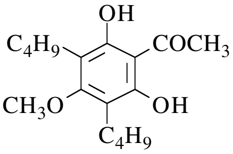
Synthesis

-Preparation by adding a DMF solution of 4-(6-bromohexyloxy)-5-ethyl-2-hydroxy acetophenone to a DMF solution of methanethiol previously treated with sodium hydride (78%) [256] [257] [777].

m.p. 52-53° [256] [257], 47-48° [777]; ^{1}H NMR [256] [257] [777], MS [777].

1-(3,5-Dibutyl-2,6-dihydroxy-4-methoxyphenyl)ethanone

[175785-88-3] $C_{17}H_{26}O_4$ mol.wt. 294.39

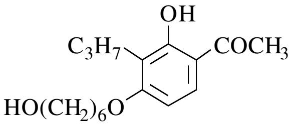


Synthesis

-Refer to: [1737] (Japanese patent).

1-[2-Hydroxy-4-[(6-hydroxyhexyl)oxy]-3-propylphenyl]ethanone

[106627-20-7] $C_{17}H_{26}O_4$ mol.wt. 294.39



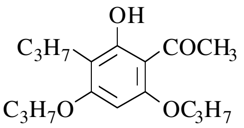
Synthesis

-Preparation by reaction of 6-chlorohexanol with 2,4-dihydroxy-3-propylacetophenone in the presence of potassium carbonate in refluxing methyl ethyl ketone (20%) [1156].

oily solid [1156]; MS [1156].

1-[2-Hydroxy-3-propyl-4,6-bis(propyloxy)phenyl]ethanone

$C_{17}H_{26}O_4$ mol.wt. 294.39



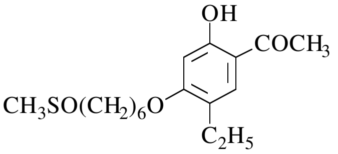
Synthesis

-Preparation by catalytic hydrogenation of 2-hydroxy-3-(2-propynyl)-4,6-bis(2-propynyloxy)acetophenone in the presence of 10% Pd/C in ethanol (77%) [427].

m.p. 78-80° [427].

1-[5-Ethyl-2-hydroxy-4-[[6-(methylsulfinyl)hexyl]oxy]phenyl]ethanone

[117706-38-4] $C_{17}H_{26}O_4S$ mol.wt. 326.46



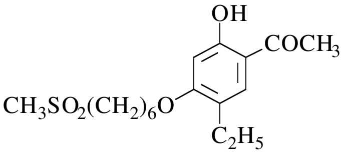
Synthesis

-Obtained (by-product) by reaction of m-chloroperbenzoic acid on 2-hydroxy-4-[6-(methylthio)-hexyloxy]-5-ethylacetophenone in methylene chloride, first at 0°, then at r.t. (17%) [256] [257] [777].

m.p. 87-90° [256] [257], 87-89° [777].

1-[5-Ethyl-2-hydroxy-4-[[6-(methylsulfonyl)hexyl]oxy]phenyl]ethanone

[117690-76-3] $C_{17}H_{26}O_5S$ mol.wt. 342.46



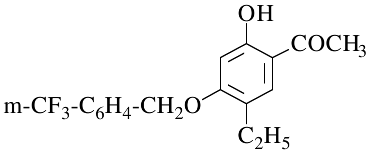
Synthesis

-Preparation by reaction of m-chloroperbenzoic acid on 5-ethyl-2-hydroxy-4-[6-(methylthio)hexyloxy]-acetophenone in methylene chloride, first at 0°, then at r.t. (70-76%) [256] [257] [777].

m.p. 124-126° [256] [257] [777].

1-[5-Ethyl-2-hydroxy-4-[[3-(trifluoromethyl)phenyl]methoxy]phenyl]ethanone

[117706-51-1] $C_{18}H_{17}F_3O_3$ mol.wt. 338.33

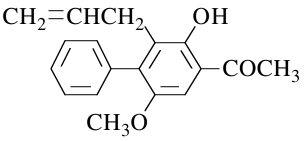


Synthesis

-Preparation by reaction of 3-(trifluoromethyl)benzyl bromide with 5-ethyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide (11%) [256] [257].

1-[3-Hydroxy-6-methoxy-2-(2-propenyl)[1,1'-biphenyl]-4-yl]ethanone

[43037-65-6] $C_{18}H_{18}O_3$ mol.wt. 282.34

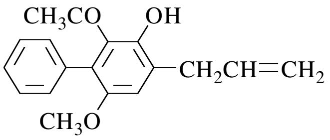


Synthesis

-Obtained by thermal Claisen rearrangement of 1-[2-methoxy-5-(2-propenyloxy)[1,1'-biphenyl]-4-yl]-ethanone in N,N-dimethylaniline at 170° (52%) [581].

1-[3-Hydroxy-6-methoxy-4-(2-propenyl)[1,1'-biphenyl]-2-yl]ethanone

[43037-67-8] $C_{18}H_{18}O_3$ mol.wt. 282.34

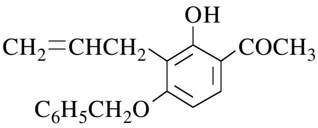


Synthesis

-Obtained by thermal Claisen rearrangement of 1-[2-methoxy-5-(2-propenyloxy)[1,1'-biphenyl]-4-yl]-ethanone in N,N-dimethylaniline at 170° (33%) [581]. The formation of this ketone is rationalised as involving a [1,5] acetyl shift.

1-[2-Hydroxy-4-(phenylmethoxy)-3-(2-propenyl)phenyl]ethanone

[137170-49-1] $C_{18}H_{18}O_3$ mol.wt. 282.34

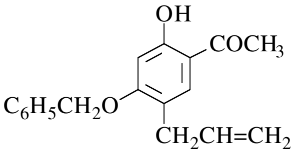


Syntheses

-Refer to: [423] [1367] (patents).

1-[2-Hydroxy-4-(phenylmethoxy)-5-(2-propenyl)phenyl]ethanone

[117690-55-8] $C_{18}H_{18}O_3$ mol.wt. 282.34



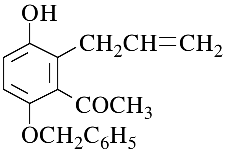
Synthesis

-Preparation by reaction of benzyl bromide on 5-allyl-2,4-dihydroxyacetophenone with potassium carbonate and potassium iodide (60%) [256] [257].

m.p. 86° [256] [257].

1-[3-Hydroxy-6-(phenylmethoxy)-2-(2-propenyl)phenyl]ethanone

$C_{18}H_{18}O_3$ mol.wt. 282.34

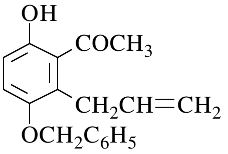


Synthesis

-Obtained (by-product) by reaction of benzyl bromide with 2-allyl-3,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 5.5 h under nitrogen atmosphere (3%) [699].

1-[6-Hydroxy-3-(phenylmethoxy)-2-(2-propenyl)phenyl]ethanone

[263138-72-3] $C_{18}H_{18}O_3$ mol.wt. 282.34



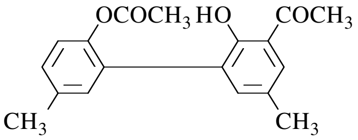
Synthesis

-Obtained by reaction of benzyl bromide with 2-allyl-3,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 5.5 h under nitrogen atmosphere (54%) [699].

m.p. 92-93° [699]; ^{1}H NMR [699], ^{13}C NMR [699], IR [699], MS [699].

1-(2'-Acetoxy-2-hydroxy-5,5'-dimethyl[1,1'-biphenyl]-3-yl)ethanone

[24046-01-3] $C_{18}H_{18}O_4$ mol.wt. 298.34



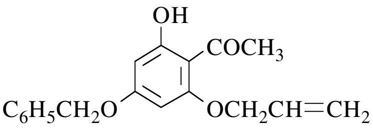
Synthesis

-Obtained by stirring a solution of 1-(2,2'-dihydroxy-5,5'-dimethyl[1,1'-biphenyl]-3-yl)ethanone in pyridine with freshly fused sodium acetate for 1 h (95%) [1816].

pale yellow oil [1816]; b.p.$_{10^{-5}}$ 120° [1816].

1-[2-Hydroxy-4-(phenylmethoxy)-6-(2-propenyloxy)phenyl]ethanone

[76609-36-4] $C_{18}H_{18}O_4$ mol.wt. 298.34



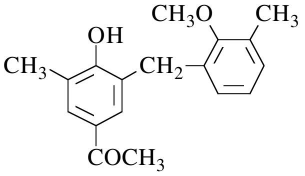
Synthesis

-Obtained by partial benzylation of 6-(allyloxy)-2,4-dihydroxyacetophenone [13].

m.p. 64-65° [13].

1-[4-Hydroxy-3-[(2-methoxy-3-methylphenyl)methyl]-5-methylphenyl]ethanone

[38778-41-5] $C_{18}H_{20}O_3$ mol.wt. 284.36



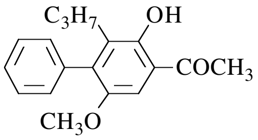
Synthesis

-Preparation by Fries rearrangement of 2-acetoxy-2'-methoxy-3,3'-dimethyldiphenylmethane with aluminium chloride in nitrobenzene at 40° for 3 h (50%) [1327].

m.p. 124-125° [1327];
^{1}H NMR [1327], IR [1327], UV [1327].

1-(3-Hydroxy-6-methoxy-2-propyl[1,1'-biphenyl]-4-yl)ethanone

[43037-69-0] $C_{18}H_{20}O_3$ mol.wt. 284.36

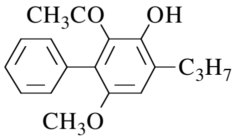


Synthesis

-Obtained by catalytic hydrogenation of 1-[3-hydroxy-6-methoxy-2-(2-propenyl)[1,1'-biphenyl]-4-yl]ethanone or by thermal Fries rearrangement of 3-(acetyloxy)-6-methoxy-2-propyl [1,1'-biphenyl] with aluminium chloride [581].

1-(3-Hydroxy-6-methoxy-4-propyl[1,1'-biphenyl]-2-yl)ethanone

[43037-70-3] $C_{18}H_{20}O_3$ mol.wt. 284.36

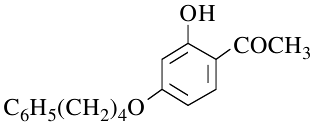


Synthesis

-Obtained by catalytic hydrogenation of 1-[3-hydroxy-6-methoxy-4-(2-propenyl)[1,1'-biphenyl]-2-yl]ethanone or by thermal Fries rearrangement of 5-(acetyloxy)-2-methoxy-4-propyl[1,1'-biphenyl] with aluminium chloride [581].

1-[2-Hydroxy-4-(4-phenylbutoxy)phenyl]ethanone

[63359-88-6] $C_{18}H_{20}O_3$ mol.wt. 284.36



Synthesis

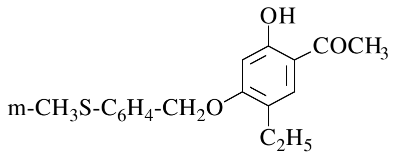
-Obtained by reaction of 1-bromo-4-phenylbutane with resacetophenone in the presence of potassium carbonate in refluxing acetone for 24 h. The 1-chloro derivative and the butanone can also be used instead of the mentioned starting material and solvent (59%) [314].

-Also refer to: [312].

m.p. 55° [314].

1-[5-Ethyl-2-hydroxy-4-[[3-(methylthio)phenyl]methoxy]phenyl]ethanone

[117706-52-2] $C_{18}H_{20}O_3S$ mol.wt. 316.42



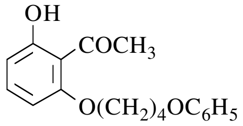
Synthesis

-Preparation by reaction of 3-methylmercaptobenzyl bromide with 2,4-dihydroxy-5-ethylacetophenone in the presence of potassium carbonate and potassium iodide (18%) [256] [257].

m.p. 89° [256] [257]; ^1H NMR [256] [257].

1-[2-Hydroxy-6-(4-phenoxybutoxy)phenyl]ethanone

[69079-91-0] $C_{18}H_{20}O_4$ mol.wt. 300.35



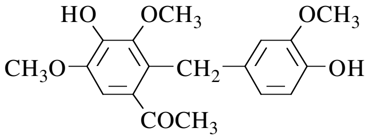
Synthesis

-Obtained by reaction of 1-bromo-4-phenoxybutane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 24 h (91%). The 1-chloro derivative and butanone can also be used instead of the mentioned starting material and solvent [314].

m.p. 81° [314].

1-[4-Hydroxy-2-[(4-hydroxy-3-methoxyphenyl)methyl]-3,5-dimethoxyphenyl]ethanone

[147904-71-0] $C_{18}H_{20}O_6$ mol.wt. 332.35



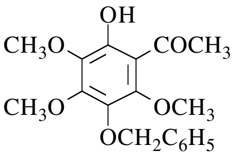
Synthesis

-Obtained by alkaline CuO oxidation of lignin (compound Vm2Sn) named 2-vanillylacetosyringone [689].

GC [689], GC-MS [689].

1-[2-Hydroxy-3,4,6-trimethoxy-5-(phenylmethoxy)phenyl]ethanone

[76844-54-7] $C_{18}H_{20}O_6$ mol.wt. 332.35

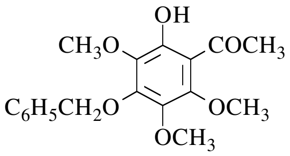


Syntheses

-Preparation by [796] according to [800] (Japanese paper).
-Also obtained by benzylation of 2,5-dihydroxy-3,4,6-trimethoxyacetophenone with benzyl chloride [1465].

1-[2-Hydroxy-3,5,6-trimethoxy-4-(phenylmethoxy)phenyl]ethanone

[3162-49-0] $C_{18}H_{20}O_6$ mol.wt. 332.35



Syntheses

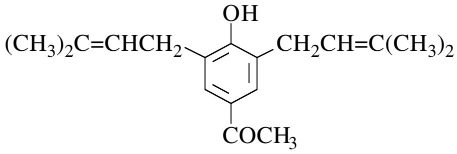
-Preparation by partial methylation of 4-benzyloxy-2,5-dihydroxy-3,6-dimethoxyacetophenone with dimethyl sulfate in the presence of potassium carbonate in petroleum ether (b.p. 40-60°) (70%) [1072].

-Also refer to: [584] [1073].

m.p. 35-36° [1072]; IR [1072], UV [1072].

1-[4-Hydroxy-3,5-bis(3-methyl-2-butenyl)phenyl]ethanone

[41607-43-6] $C_{18}H_{24}O_2$ mol.wt. 272.39



Synthesis

-Preparation by thermal Claisen rearrangement of 3-(3,3-dimethylallyl)-4-(3,3-dimethylallyloxy)acetophenone in N,N-diethylaniline at 170-175° (84%) [246].

Isolation from natural sources

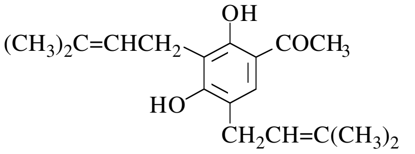
-From the roots of several *Gerbera* species (Tribus *Arctotideae*, Fam. Compositae): *Gerbera asplenifolia* (1.5%) [252], *Gerbera crocea* (1%) [252] and as a trace in *Gerbera cordata* Less. (0.008%) [243].

-From the roots of several *Ageratina* species (Compositae): *Ageratina aschenbornia* (0.017%) [249] and *Ageratina altissima* (0.005%) [249].

m.p. 93°6 [252], 92°3 [246]; ^1H NMR [252], IR [252], UV [252].

1-[2,4-Dihydroxy-3,5-bis-(3-methyl-2-butenyl)phenyl]ethanone

[24672-82-0] $C_{18}H_{24}O_3$ mol.wt. 288.39



Syntheses

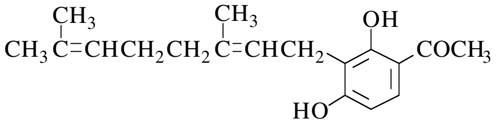
-Obtained (poor yield) by reaction of 2-methyl-but-3-en-2-ol on resacetophenone with boron trifluoride etherate [43] [884] in dioxane at r.t. (6%) [884].

-Also obtained [1056] (poor yield) [882] by reaction of prenyl bromide with resacetophenone in potassium hydroxide solution at r.t. (3%) [882].

m.p. 117° [1056], 109-114° [882], 109-110° [884];
^1H NMR [43] [44] [882] [1056], IR [882] [1056], UV [43] [882].

1-[3-(3,7-Dimethyl-2,6-octadienyl)-2,4-dihydroxyphenyl]ethanone

[88661-97-6] $C_{18}H_{24}O_3$ mol.wt. 288.39



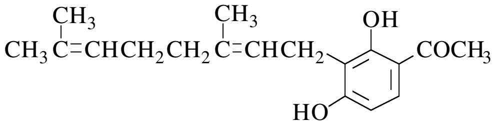
Synthesis

-Preparation by condensation of resacetophenone with 3,7-dimethyl-3-hydroxy-1,6-octadiene in the presence of boron trifluoride etherate in dioxane at r.t. (compound **14**) [865].

^{1}H NMR [865], IR [865].

1-[3-(3,7-Dimethyl-2,6-octadienyl)-2,4-dihydroxyphenyl]ethanone

[18296-19-0] *(Z)* $C_{18}H_{24}O_3$ mol.wt. 288.39
[20212-67-3] *(E)*



Syntheses

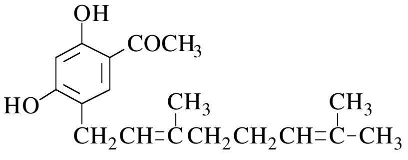
-Preparation by alkylation of 2,4-dihydroxyacetophenone lithium salt with geranyl bromide in refluxing benzene (23%) [354] (no specification).

-Also obtained by treatment of 6-acetyl-2-methyl-2-(4-methylpent-3-enyl)-3-phenylthiochroman-5-ol with potassium naphthalenide in tetrahydrofuran at -78°; then, the mixture was allowed to warm to -30° (48%) (2*E*, 6*Z*) [1252].

m.p. 120-121° [354]; ^{1}H NMR [354], UV [354] (compound **XX**);
(no specification) (*E* isomer ?).
m.p. 93-96° [1252]; ^{1}H NMR [1252], MS [1252] (compound **29**);
(as a 1:1 mixture of *E* and *Z* isomers by ^{13}C NMR) [1252].

1-[5-(3,7-Dimethyl-2,6-octadienyl)-2,4-dihydroxyphenyl]ethanone

[146954-92-9] $C_{18}H_{24}O_3$ mol.wt. 288.39

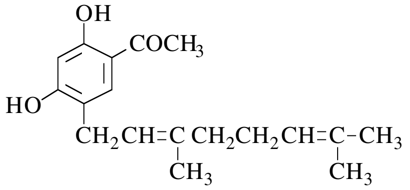


Synthesis

-Preparation by condensation of resacetophenone with 3,7-dimethyl-3-hydroxy-1,6-octadiene in the presence of boron trifluoride etherate in dioxane at r.t. (compound **15**) [865].

1-[5-(3,7-Dimethyl-2,6-octadienyl)-2,4-dihydroxyphenyl]ethanone *(E)*

[20212-68-4] $C_{18}H_{24}O_3$ mol.wt. 288.39



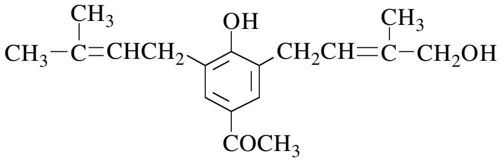
Synthesis

-Obtained (poor yield) by alkylation of 2,4-dihydroxyacetophenone lithium salt with geranyl bromide in benzene (< 2%) [354].

m.p. 88° [354];
^{1}H NMR [354], UV [354].

1-[4-Hydroxy-3-(4-hydroxy-3-methyl-2-butenyl)-5-(3-methyl-2-butenyl)phenyl]-ethanone *(E)*

[81053-02-3] $C_{18}H_{24}O_3$ mol.wt. 288.39



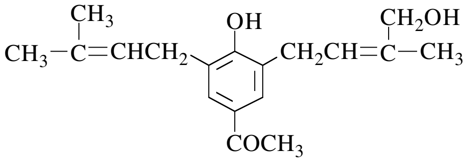
Isolation from natural sources

-From the aerial parts of *Artemisia campestris* L. subsp. glutinosa (Gay ex Besser) Batt. (Compositae) (1.8%) [489].

m.p. 83° [489]; ^{1}H NMR [489], IR [489], UV [489], MS [489].

1-[4-Hydroxy-3-(4-hydroxy-3-methyl-2-butenyl)-5-(3-methyl-2-butenyl)phenyl]-ethanone *(Z)*

[77370-28-6] $C_{18}H_{24}O_3$ mol.wt. 288.39



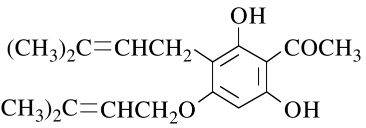
Isolation from natural sources

-From *Artemisia campestris* L. ssp. glutinosa (Gay ex Besser) Batt,
*compound (7) (12%) (from the aerial parts) [489];
*compound (2) [488].

m.p. 109-110° [488]; ^{1}H NMR [488] [489], IR [488], UV [488], MS [488] [489].

1-[2,6-Dihydroxy-3-(3-methyl-2-butenyl)-4-[(3-methyl-2-butenyl)oxy]phenyl]ethanone

[158499-98-0] $C_{18}H_{24}O_4$ mol.wt. 304.39



Synthesis

-Obtained by reaction of 4,6-dihydroxy-3-prenyl-2-tosyloxyacetophenone with prenyl bromide in the presence of potassium carbonate in acetone at 20° for 2 h, followed by hydrolysis of the resulting 6-hydroxy-3-prenyl-4-prenyloxy-2-tosyloxyacetophenone with 30% potassium hydroxide in refluxing ethanol under nitrogen atmosphere for 1 h [1823].

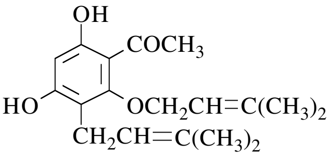
Isolation from natural sources

-From the fruit of *Evodia merrillii* [1823].

m.p. 108-110° [1823]; ^{1}H NMR [1823], IR [1823].

1-[4,6-Dihydroxy-3-(3-methyl-2-butenyl)-2-[(3-methyl-2-butenyl)oxy]phenyl]ethanone

[153399-38-3] $C_{18}H_{24}O_4$ mol.wt. 304.39



Syntheses

-Obtained by hydrolysis of 4',6'-bis(benzoyloxy)-2'-(3-methyl-2-butenyloxy)-3'-(3-methyl-2-butenyl)-acetophenone with dilute sodium hydroxide under nitrogen atmosphere at 50° [1824].
-Also refer to: [1823].

Isolation from natural sources

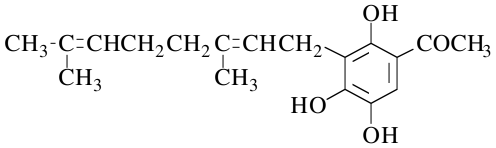
-From the root bark of *Euodia lunu-ankenda* (Rutaceae) [1045].

m.p. 73-75° [1045], 71-72° [1824]; TLC [1045];
^{1}H NMR [1045] [1824], IR [1045] [1824], UV [1045],
MS [1045], HRMS [1045].

N.B.: The synthetic works [1824] [1823] have suggested that the prenylphenol of natural products isolated by [1045] had an incorrectly assigned structure. This compound [1045] is identical with 1-[2,6-dihydroxy-3-(3-methyl-2-butenyl)-4-[(3-methyl-2-butenyl)oxy]phenyl]ethanone [158499-98-0].

1-[3-(3,7-Dimethyl-2,6-octadienyl)-2,4,5-trihydroxyphenyl]ethanone

[18296-18-9] *(Z)* $C_{18}H_{24}O_4$ mol.wt. 304.39
[20212-66-2] *(E)*



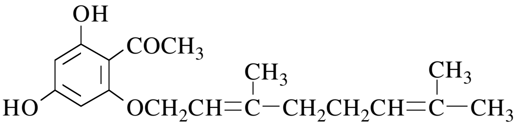
Syntheses

-Preparation by reaction of geraniol of 2,4,5-trihydroxyacetophenone in refluxing decalin [354] (no specification).
-Also obtained by reaction of potassium naphthalenide with 6-acetyl-2-methyl-2-(4-methylpent-3-enyl)-3-phenylthiochroman-5,8-diol in tetrahydrofuran at r.t. (11%) (*E*, *Z*) [1252].

m.p. 127-130° [354]; UV [354]; (compound **XVIII**);
(no specification) (*E* isomer ?).
unstable oil [1252]; ^{1}H NMR [1252], MS [1252]; (compound **30**);
(as a 1:1 mixture of *E* and *Z* isomers by ^{13}C NMR) [1252].

1-[2-[(3,7-Dimethyl-2,6-octadienyl)oxy]-4,6-dihydroxyphenyl]ethanone *(E)*

[142905-39-3] $C_{18}H_{24}O_4$ mol.wt. 304.39



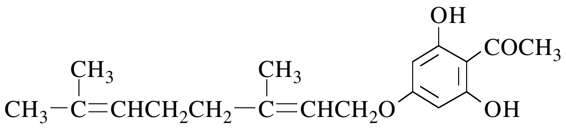
Isolation from natural sources

-From the fruit of *Evodia Merrillii* Kanehira & Sasaki ex Kanehira (Rutaceae) [408].

m.p. 147-150° [408]; column chromatography [408];
^{1}H NMR [408], ^{13}C NMR [408], IR [408], UV [408], MS [408].

1-[4-[(3,7-Dimethyl-2,6-octadienyl)oxy]-2,6-dihydroxyphenyl]ethanone *(E)*

[142905-40-6] $C_{18}H_{24}O_4$ mol.wt. 304.39



Synthesis

-Obtained by hydrolysis of 2-toluenesulfonyloxy-6-hydroxy-4-(1'-geranyloxy)-acetophenone with 30% potassium hydroxide in refluxing ethanol for 1.5 h (75%) [825].

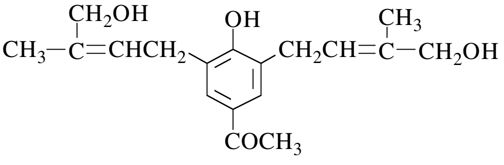
Isolation from natural sources

-From the fruit of *Evodia Merrillii* Kanehira & Sasaki ex Kanehira (Rutaceae) [408].

waxy substance [408]; m.p. 147-148° [825];
^{1}H NMR [408] [825], ^{13}C NMR [408], IR [408] [825], UV [408],
MS [408], EIMS [825], HREIMS [825];
column chromatography [408].

1-[4-Hydroxy-3,5-bis(4-hydroxy-3-methyl-2-butenyl)phenyl]ethanone *(E,Z)*

[81053-03-4] $C_{18}H_{24}O_4$ mol.wt. 304.39



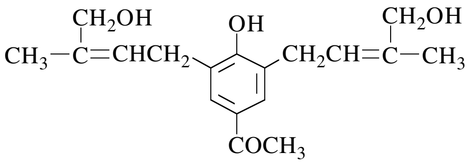
Isolation from natural sources

-From the aerial parts of *Artemisia campestris* L. subsp. glutinosa (Gay ex Besser) Batt. (Compositae) (2%) [489].

m.p. 97° [489]; ^{1}H NMR [489], IR [489], UV [489], MS [489].

1-[4-Hydroxy-3,5-bis(4-hydroxy-3-methyl-2-butenyl)phenyl]ethanone *(Z,Z)*

[77370-30-0] $C_{18}H_{24}O_4$ mol.wt. 304.39



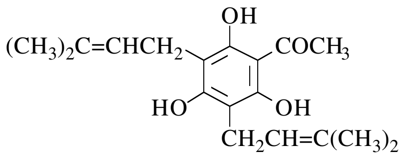
Isolation from natural sources

-From *Artemisia camprstris* L. ssp. glutinosa (Gay ex Besser) Batt,
*compound (10) (0.6%) (from the aerial parts) [489];
*compound (3) (12%) [488].

m.p. 120° [488]; ^{1}H NMR [488] [489], IR [488], UV [488], MS [488] [489].

1-[2,4,6-Trihydroxy-3,5-bis(3-methyl-2-butenyl)phenyl]ethanone

[35458-19-6] $C_{18}H_{24}O_4$ mol.wt. 304.39



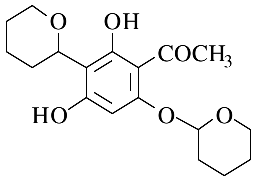
Syntheses

-Preparation by reaction of 2-methylbut-3-en-2-ol with phloroacetophenone in the presence of boron trifluoride etherate in dioxane at 20° [426] [1611], (21%) [426] or at 50° [428].
-Also obtained by reaction of prenyl bromide with phloroacetophenone in the presence of potassium hydroxide in 80% aqueous methanol (15%) [1489].

m.p. 78-79° [426] [428] [1489] [1611], 68-72° [350]; b.p.$_1$ 135-140° [1489]; ^{1}H NMR [350]; UV [426] [1489].

1-[2,4-Dihydroxy-3-(tetrahydro-2*H*-pyran-2-yl)-6-[(tetrahydro-2*H*-pyran-2-yl)-oxy]phenyl]ethanone

[136257-83-5] $C_{18}H_{24}O_6$ mol.wt. 336.38



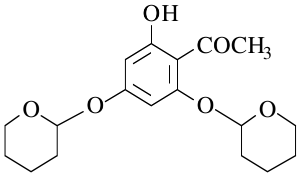
Synthesis

-Obtained (by-product) by reaction of 3,4-dihydro-2*H*-pyran on phloroacetophenone with p-toluenesulfonic acid in dioxane at r.t. (8%) [5].

m.p. 118-121° [5]; ^{1}H NMR [5], ^{13}C NMR [5].

1-[2-Hydroxy-4,6-bis[(tetrahydro-2*H*-pyran-2-yl)oxy]phenyl]ethanone

[130600-90-7] $C_{18}H_{24}O_6$ mol.wt. 336.38



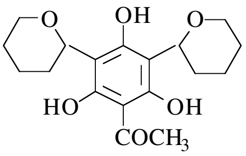
Synthesis

-Obtained (by-product) by reaction of 3,4-dihydro-2*H*-pyran on phloroacetophenone with p-toluenesulfonic acid in dioxane at r.t. (7%) [5].

^1H NMR [5], ^{13}C NMR [5].

1-[2,4,6-Trihydroxy-3,5-bis(tetrahydro-2*H*-pyran-2-yl)phenyl]ethanone

[136257-82-4] $C_{18}H_{24}O_6$ mol.wt. 336.38



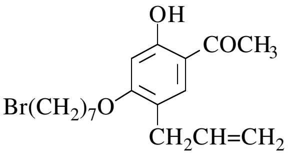
Synthesis

-Obtained (by-product) by reaction of 3,4-dihydro-2*H*-pyran on phloroacetophenone with p-toluenesulfonic acid in dioxane at r.t. (1%) [5].

^1H NMR [5], ^{13}C NMR [5].

1-[4-[(7-Bromoheptyl)oxy]-2-hydroxy-5-(2-propenyl)phenyl]ethanone

[117706-40-8] $C_{18}H_{25}BrO_3$ mol.wt. 369.30



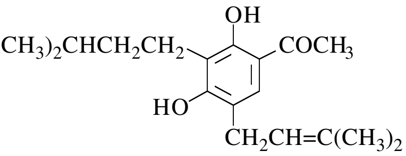
Synthesis

-Preparation by reaction of 1,7-dibromoheptane with 5-allyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (70%) [256] [257] [777].

oil [256] [257] [777].

1-[2,4-Dihydroxy-5-(3-methyl-2-butenyl)-3-(3-methylbutyl)phenyl]ethanone

[50773-38-1] $C_{18}H_{26}O_3$ mol.wt. 290.40



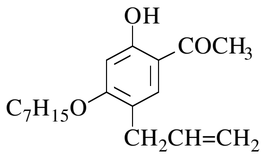
Synthesis

-Preparation by reaction of prenyl bromide with 2,4-dihydroxy-3-isopentylacetophenone in aqueous potassium hydroxide solution at r.t. [1056].

m.p. 113°5 [1056];
^1H NMR [1056], IR [1056].

1-[4-(Heptyloxy)-2-hydroxy-5-(2-propenyl)phenyl]ethanone

[117706-56-6] $C_{18}H_{26}O_3$ mol.wt. 290.40



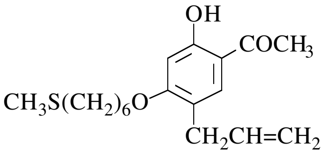
Synthesis

-Preparation by reaction of heptyl bromide with 5-allyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing methyl ethyl ketone (77%) [777], (40%) [256] [257].

oil [256] [257] [777].

1-[2-Hydroxy-4-[[6-(methylthio)hexyl]oxy]-5-(2-propenyl)phenyl]ethanone

[117706-34-0] $C_{18}H_{26}O_3S$ mol.wt. 322.47



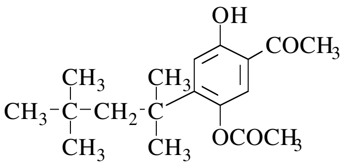
Synthesis

-Preparation by adding a DMF solution of 5-allyl-4-(6-bromohexyloxy)-2-hydroxyacetophenone to a DMF solution of methanethiol previously treated with sodium hydride (54%) [256] [257].

m.p. 42° [256] [257].

1-[5-(Acetyloxy)-2-hydroxy-4-(1,1,3,3-tetramethylbutyl)phenyl]ethanone

[107188-54-5] $C_{18}H_{26}O_4$ mol.wt. 306.40

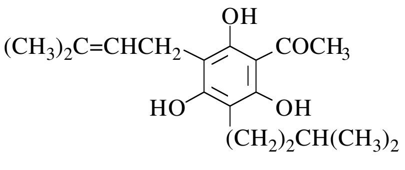


Synthesis

-Refer to: [1928].

1-[2,4,6-Trihydroxy-3-(3-methyl-2-butenyl)-5-(3-methylbutyl)phenyl]ethanone

[57744-70-4] $C_{18}H_{26}O_4$ mol.wt. 306.40



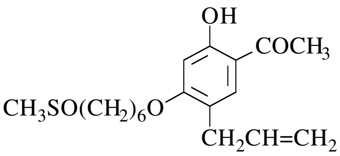
Synthesis

-Obtained by reaction of 2-methyl-3-buten-2-ol with isopentylphloroacetophenone in the presence of boron trifluoride etherate in dioxane at 20° (13%) [1611].

m.p. 92°5-93°5 [350], 92-93°5 [1611];
^1H NMR [350].

1-[2-Hydroxy-4-[[6-(methylsulfinyl)hexyl]oxy]-5-(2-propenyl)phenyl]ethanone

[117706-35-1] $C_{18}H_{26}O_4S$ mol.wt. 338.47

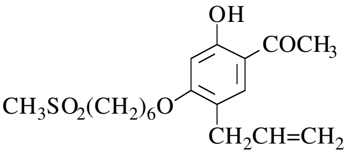


Synthesis

-Obtained (by-product) by reaction of m-chloroperbenzoic acid with 5-allyl-2-hydroxy-4-[6-(methylthio)hexyloxy]acetophenone in methylene chloride, first at 0°, then at r.t. (9%) [256] [257].

1-[2-Hydroxy-4-[[6-(methylsulfonyl)hexyl]oxy]-5-(2-propenyl)phenyl]ethanone

[117706-36-2] $C_{18}H_{26}O_5S$ mol.wt. 354.47

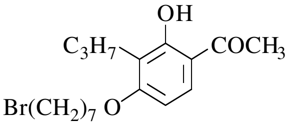


Synthesis

-Obtained by reaction of m-chloroperbenzoic acid with 5-allyl-2-hydroxy-4-[6-(methylthio)hexyloxy]acetophenone in methylene chloride, first at 0°, then at r.t. (20%) [256] [257].

1-[4-[(7-Bromoheptyl)oxy]-2-hydroxy-3-propylphenyl]ethanone

[106627-33-2] $C_{18}H_{27}BrO_3$ mol.wt. 371.31

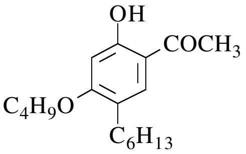


Synthesis

-Preparation by reaction of 1,7-dibromoheptane with 2,4-dihydroxy-3-propylacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (21%) [1156].

1-(4-Butoxy-5-hexyl-2-hydroxyphenyl)ethanone

[101002-31-7] $C_{18}H_{28}O_3$ mol.wt. 292.42



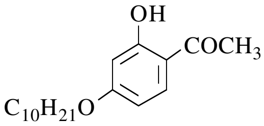
Synthesis

-Obtained by partial alkylation of 2,4-dihydroxy-5-hexylacetophenone with butyl bromide in the presence of potassium carbonate in refluxing acetone for 20 h [183].

m.p. 37° [183].

1-[4-(Decyloxy)-2-hydroxyphenyl]ethanone

[143286-86-6] $C_{18}H_{28}O_3$ mol.wt. 292.42



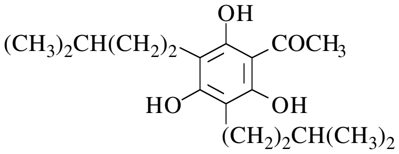
Syntheses

-Preparation by partial alkylation of resacetophenone with decyl bromide in the presence of potassium carbonate in refluxing acetone for 20 h [183].
-Also refer to: [1733].

m.p. 35° [183] [1733].

1-[2,4,6-Trihydroxy-3,5-bis(3-methylbutyl)phenyl]ethanone

[55380-57-9] $C_{18}H_{28}O_4$ mol.wt. 308.42



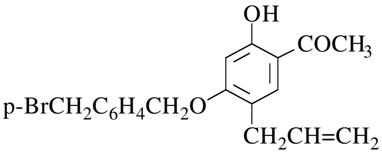
Synthesis

-Preparation by catalytic hydrogenation of deoxyacetohumulone [2,4,6-trihydroxy-3,5-(dimethylallyl)acetophenone] in the presence of 10% Pd/C in ethanol [428].

^{1}H NMR [428], UV [428], MS [428].

1-[4-[[4-(Bromomethyl)phenyl]methoxy]-2-hydroxy-5-(2-propenyl)phenyl]ethanone

[117706-46-4] $C_{19}H_{19}BrO_3$ mol.wt. 375.26



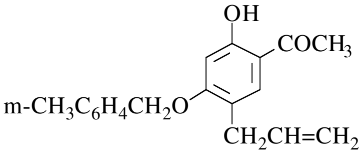
Synthesis

-Preparation by reaction of 4-(bromomethyl)benzyl bromide with 5-allyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide (18%) [256] [257].

oil [256] [257].

1-[2-Hydroxy-4-[(3-methylphenyl)methoxy]-5-(2-propenyl)phenyl]ethanone

[117706-45-3] $C_{19}H_{20}O_3$ mol.wt. 296.37



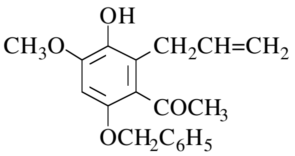
Synthesis

-Preparation by reaction of 3-methylbenzyl bromide on 5-allyl-2,4-dihydroxyacetophenone with potassium carbonate and potassium iodide (50%) [256] [257].

m.p. 87-88° [256] [257].

1-[3-Hydroxy-4-methoxy-6-(phenylmethoxy)-2-(2-propenyl)phenyl]ethanone

$C_{19}H_{20}O_4$ mol.wt. 312.37



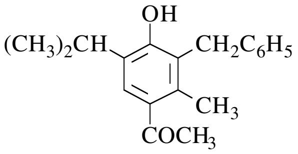
Synthesis

-Preparation by thermal Claisen rearrangement of 3-(allyloxy)-6-(benzyloxy)-4-methoxyacetophenone in boiling carbitol (diethylene glycol monoethyl ether) (89%) [498].

m.p. 116° [498].

1-[4-Hydroxy-2-methyl-5-(1-methylethyl)-3-(phenylmethyl)phenyl]ethanone

$C_{19}H_{22}O_2$ mol.wt. 282.38



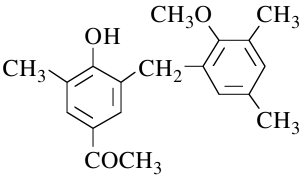
Synthesis

-Obtained (poor yield) by reaction of benzyl chloride with 4-hydroxy-2-methyl-5-isopropylacetophenone in the presence of zinc chloride in boiling chloroform (4%) [1522].

m.p. 88° [1522]; b.p.$_{14}$ 243-245° [1522].

1-[4-Hydroxy-3-[(2-methoxy-3,5-dimethylphenyl)methyl]-5-methylphenyl]ethanone

[38778-48-2] $C_{19}H_{22}O_3$ mol.wt. 298.38



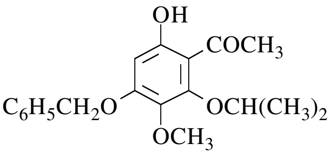
Synthesis

-Obtained by Fries rearrangement of 2-acetoxy-2'-methoxy-3,3',5-trimethyldiphenylmethane with aluminium chloride in nitrobenzene at 55° for 3 h (23%) [1327].

m.p. 128° [1327];
^{1}H NMR [1327], IR [1327], UV [1327].

1-[6-Hydroxy-3-methoxy-2-(1-methylethoxy)-4-(phenylmethoxy)phenyl]ethanone

[188927-31-3] $C_{19}H_{22}O_5$ mol.wt. 330.38



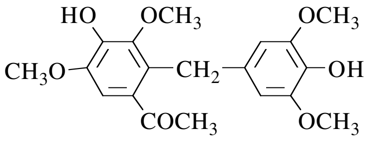
Synthesis

-Preparation by treatment of 4-(benzyloxy)-3,6-dimethoxy-2-isopropoxyacetophenone (m.p. 74-75°) with aluminium bromide in acetonitrile at 0° for 10-15 min (75%) [804].

m.p. 69-70° [804].

1-[4-Hydroxy-2-[(4-hydroxy-3,5-dimethoxyphenyl)methyl]-3,5-dimethoxyphenyl]-ethanone

[147904-74-3] $C_{19}H_{22}O_7$ mol.wt. 362.38



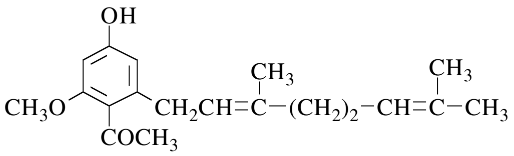
Synthesis

-Obtained by upon alkaline CuO oxidation of lignin (compound Sm2Sn) named 2-syringylaceto-syringone [689].

GC [689], GC-MS [689].

1-[2-(3,7-Dimethyl-2,6-octadienyl)-4-hydroxy-6-methoxyphenyl]ethanone

[121379-44-0] $C_{19}H_{26}O_3$ mol.wt. 302.41

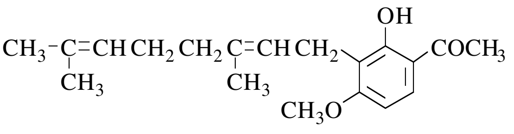


Isolation from natural sources

-From the bulbs of *Dioscorea bulbifera* [715].

1-[2-Hydroxy-4-methoxy-3-(3,7-dimethyl-2,6-octadienyl)phenyl]ethanone *(E)*

$C_{19}H_{26}O_3$ mol.wt. 302.41



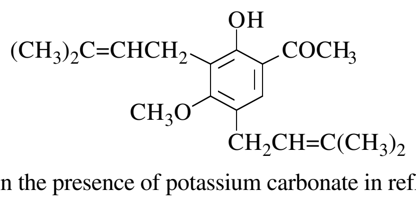
Synthesis

-Preparation by reaction of dimethyl sulfate on 3-geranyl-2,4-dihydroxyacetophenone with potassium carbonate in refluxing acetone [354].

${}^1H$ NMR [354]; UV [354].

1-[2-Hydroxy-4-methoxy-3,5-bis(3-methyl-2-butenyl)phenyl]ethanone

[50773-40-5] $C_{19}H_{26}O_3$ mol.wt. 302.41



Syntheses

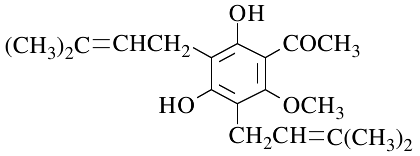
-Preparation by reaction of 2-methylbut-3-en-2-ol with 2-hydroxy-4-methoxyacetophenone in the presence of boron trifluoride etherate [43].

-Preparation by reaction of dimethyl sulfate with 2,4-dihydroxy-3,5-(dimethylallyl)acetophenone in the presence of potassium carbonate in refluxing acetone [1056].

${}^1H$ NMR [43] [44] [1056], UV [43].

1-[2,4-Dihydroxy-6-methoxy-3,5-bis(3-methyl-2-butenyl)phenyl]ethanone

[123999-38-2] $C_{19}H_{26}O_4$ mol.wt. 318.41



Isolation from natural sources

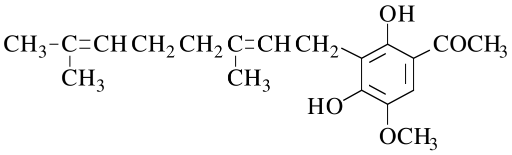
-From *Euodia lunu-ankenda* root bark (Rutaceae) [1045].
-From *Acronychia pedunculata* root bark (Rutaceae) [1044].

yellow oil [1044] [1045];

TLC [1044]; HPLC [1045];
^{1}H NMR [1044], IR [1044], HRMS [1044], MS [1044].

1-[2,4-Dihydroxy-5-methoxy-3-(3,7-dimethyl-2,6-octadienyl)phenyl]ethanone *(E)*

[20212-64-0] $C_{19}H_{26}O_4$ mol.wt. 318.41



Synthesis

-Obtained by alkylation of 2,4-dihydroxy-5-methoxyacetophenone lithium salt with geranyl bromide in benzene (7%) [353] [354].

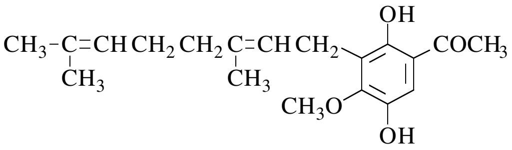
Isolation from natural sources

-Also obtained on barium hydroxide degradation of homoflemingin, a chalkone isolated from the seed pods of *Flemingia rhodocarpa* Baker (Leguminosae) [353] [354].

m.p. 107° [354]; ^{1}H NMR [354], UV [354], MS [354].

1-[2,5-Dihydroxy-4-methoxy-3-(3,7-dimethyl-2,6-octadienyl)phenyl]ethanone *(E)*

[20180-88-5] $C_{19}H_{26}O_4$ mol.wt. 318.41



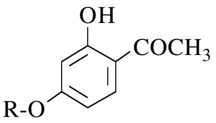
Synthesis

-Obtained by Elbs persulfate oxidation of 3-geranyl-2-hydroxy-4-methoxyacetophenone (10%) [354].

m.p. 69-70° [354]; ^{1}H NMR [354], UV [354].

1-[2-Hydroxy-4-[(6-O-β-D-xylopyranosyl-β-D-glucopyranosyl)oxy]phenyl]ethanone
(Bungeiside D)

[149475-54-7] $C_{19}H_{26}O_{12}$ mol.wt. 446.41



R = β-D-xyl (1→ 6) β-D-glc

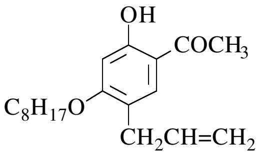
Isolation from natural sources

-From the roots of *Cynanchum bungei* DECNE (Asclepiadaceae) [1088].

colourless needles [1088]; m.p. 238-240° [1088]; $(\alpha)_D$ = -68°3 (c = 0.5, methanol) [1088]; MS [1088], ^{1}H NMR [1088], ^{13}C NMR [1088], IR [1088].

1-[2-Hydroxy-4-(octyloxy)-5-(2-propenyl)phenyl]ethanone

[117690-46-7] $C_{19}H_{28}O_3$ mol.wt. 304.43



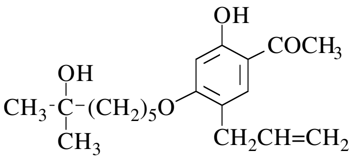
Synthesis

-Preparation by reaction of n-octyl bromide with 5-allyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide (21%) [256] [257].

oil [256] [257].

1-[2-Hydroxy-4-[(6-hydroxy-6-methylheptyl)oxy]-5-(2-propenyl)phenyl]ethanone

[117706-02-2] $C_{19}H_{28}O_4$ mol.wt. 320.43



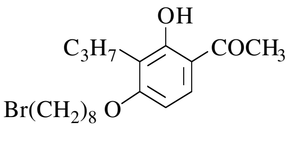
Synthesis

-Obtained by reaction of 7-(4-acetyl-2-allyl-5-hydroxyphenoxy)heptanoyl chloride on methyl lithium in ether at -98°; the reaction mixture was allowed to warm up to -50° and then poured into dilute hydrochloric acid (8%) [777].

oil [777].

1-[4-[(8-Bromooctyl)oxy]-2-hydroxy-3-propylphenyl]ethanone

[106627-34-3] $C_{19}H_{29}BrO_3$ mol.wt. 343.26



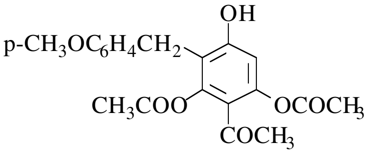
Synthesis

-Preparation by reaction of 1,8-dibromooctane with 2,4-dihydroxy-3-propylacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (63%) [1156].

pale green oil [1156]; ^{1}H NMR [1156].

1-[2,6-Bis(acetyloxy)-4-hydroxy-3-[(4-methoxyphenyl)methyl]phenyl]ethanone

[145747-40-6] $C_{20}H_{20}O_7$ mol.wt. 372.37

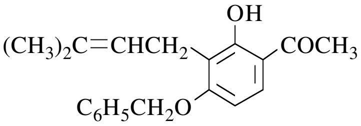


Synthesis

-Obtained by enzymatic hydrolysis of 2,4,6-triacetoxy-3-(4-methoxy)benzylacetophenone in the presence of porcine pancreas lipase in tetrahydrofuran at 42-45° (65%) [1381].

1-[2-Hydroxy-3-(3-methyl-2-butenyl)-4-(phenylmethoxy)phenyl]ethanone

$C_{20}H_{22}O_3$ mol.wt. 310.39



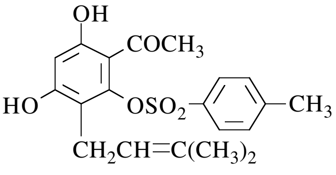
Synthesis

-Obtained by reaction of benzyl bromide with 3-prenylresacetophenone in the presence of potassium carbonate in refluxing acetone for 8 h (64%) [1719].

m.p. 70-71° [1719]; ^1H NMR [1719], IR [1719].

1-[4,6-Dihydroxy-3-(3-methyl-2-butenyl)-2-[[(4-methylphenyl)sulfonyl]oxy]phenyl]-ethanone

[158499-95-7] $C_{20}H_{22}O_6S$ mol.wt. 390.46



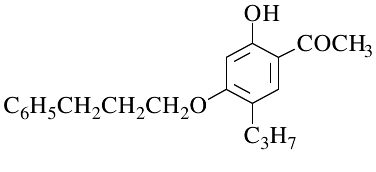
Synthesis

-Obtained by hydrolysis of 4,6-bis(benzoyloxy)-3-prenyl-2-(tosyloxy)acetophenone with aqueous methanolic sodium hydroxide solution under nitrogen at 50° [1823].

paste [1823].

1-[2-Hydroxy-4-(3-phenylpropoxy)-5-propylphenyl]ethanone

[117706-47-5] $C_{20}H_{24}O_3$ mol.wt. 312.41



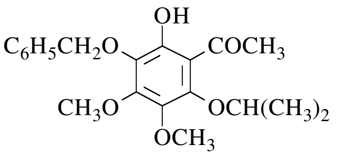
Synthesis

-Preparation by reaction of 3-phenylpropyl bromide on 2,4-dihydroxy-5-propylacetophenone with potassium carbonate and potassium iodide (26%) [256] [257].

m.p. 60° [256] [257].

1-[2-Hydroxy-4,5-dimethoxy-6-(1-methylethoxy)-3-(phenylmethoxy)phenyl]ethanone

[169130-27-2] $C_{20}H_{24}O_6$ mol.wt. 360.41



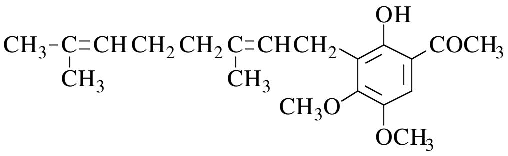
Synthesis

-Obtained by selective demethylation of 3-benzyloxy-6-isopropoxy-2,4,5-trimethoxyacetophenone with aluminium bromide in acetonitrile, first at 0° for 15 min, then at 50-60° for 15-20 min after dilution with *ca* 3% hydrochloric acid (68%) [796].

m.p. 76-77° [796]; ^{1}H NMR [796].

1-[2-Hydroxy-4,5-dimethoxy-3-(3,7-dimethyl-2,6-octadienyl)phenyl]ethanone *(E)*

[20212-65-1] $C_{20}H_{28}O_4$ mol.wt. 332.44



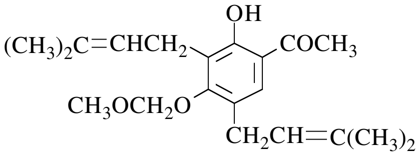
Synthesis

-Preparation by methylation of 3-geranyl-2,4-dihydroxy-5-methoxyacetophenone or of 3-geranyl-2,4,5-trihydroxyacetophenone with diazomethane [354].

oil [354]; ^{1}H NMR [354], IR [354], UV [354].

1-[2-Hydroxy-4-(methoxymethoxy)-3,5-bis(3-methyl-2-butenyl)phenyl]ethanone

[217442-59-6] $C_{20}H_{28}O_4$ mol.wt. 332.44



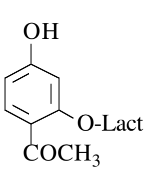
Synthesis

-Obtained by reaction of chloromethyl methyl ether with 3,5-diprenylresacetophenone in acetone in the presence of potassium carbonate [1713] at r.t. for 3 h (83%) [709].

m.p. 67-68° [709]; ^{1}H NMR [709].

1-[2-[(4-O-β-D-Galactopyranosyl-β-D-glucopyranosyl)oxy]-4-hydroxyphenyl]ethanone

$C_{20}H_{28}O_{13}$ mol.wt. 476.41



Lact = β-D-Lactosid rest

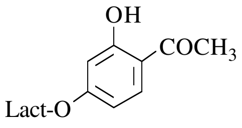
Synthesis

-Preparation by reaction of 0.2 M sodium methoxide with 4-acetylresacetophenone-2-heptaacetyl-β-D-lactosid in boiling methanol for 3 min (40%) [1861].

monohydrate [1861]; m.p. 165-168° [1861]; $(\alpha)_D^{21}$ = -45° (c = 1, water) [1861].

1-[4-[(4-O-β-D-Galactopyranosyl-β-D-glucopyranosyl)oxy]-2-hydroxyphenyl]ethanone

$C_{20}H_{28}O_{13}$ mol.wt. 476.43



Lact = β-D-Lactosid rest

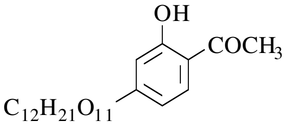
Synthesis

-Preparation by reaction of 0.2 M sodium methoxide with resacetophenone-4-heptaacetyl-b-D-lactosid in boiling methanol for 3 min (50%) [1861].

m.p. 255-258° [1861]; $(\alpha)_D^{21}$ = -62°6 (c = 1, water) [1861].

1-[4-[(4-o-b-D-Glucopyranosyl-b-D-glucopyranosyl)oxy]-2-hydroxyphenyl]ethanone

[54918-30-8] C20H28O13 mol.wt. 476.43



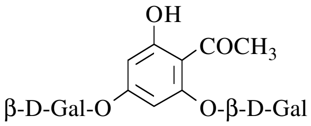
Synthesis

-Preparation by reaction of sodium on 2',4'-dihydroxy-acetophenone-4-β-hepta-O-acetyl-D-cellobioside in methanol (67%) [1480].

m.p. 212° [1480]; $(\alpha)_D^{17}$ = -60° (pyridine) [1480].

1-[2,4-Bis-(β–D-galactopyranosyloxy)-6-hydroxyphenyl]ethanone

[88087-01-8] $C_{20}H_{28}O_{14}$ mol.wt. 492.43



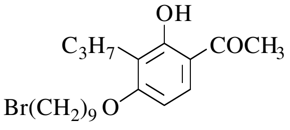
Synthesis

-Preparation by deacetylation of phloracetophenone 2,4-di-O-(2,3,4,6-tetra-O-acetyl)-β-D-galactopyranoside with 0.1 N methanolic sodium methoxide (87%) [1008].

m.p. 183-185° [1008]; ^{1}H NMR [1008].

1-[4-[(9-Bromononyl)oxy]-2-hydroxy-3-propylphenyl]ethanone

[79557-82-7] $C_{20}H_{31}BrO_3$ mol.wt. 399.37

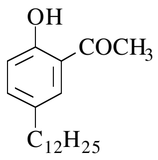


Synthesis

-Preparation by reaction of 1,9-dibromononane with 2,4-dihydroxy-3-propylacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (63%) [1156].

1-(5-Dodecyl-2-hydroxyphenyl)ethanone

[84744-37-6] $C_{20}H_{32}O_2$ mol.wt. 304.47



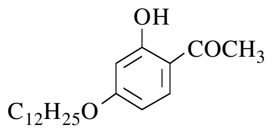
Synthesis

-Preparation by reaction of acetyl chloride on 4-dodecylphenol with aluminium chloride in ethylene dichloride at 110-120° (46%) [1033].

b.p.$_4$ 198-203° [1033].

1-[4-(Dodecyloxy)-2-hydroxyphenyl]ethanone

[52122-72-2] $C_{20}H_{32}O_3$ mol.wt. 318.37



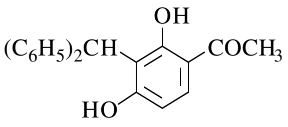
Syntheses

-Preparation by partial alkylation of resacetophenone with dodecyl bromide in the presence of potassium carbonate in refluxing acetone for 20 h [183].
-Also refer to: [1733].

m.p. 51° [183] [1733].

1-[3-(Diphenylmethyl)-2,4-dihydroxyphenyl]ethanone

[107114-32-9] $C_{21}H_{18}O_3$ mol.wt. 318.37



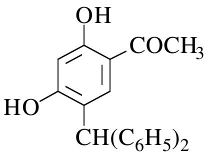
Synthesis

-Obtained by reaction of resacetophenone with diphenylcarbinol in the presence of boron trifluoride etherate in dioxane at r.t. (21%) [887].

m.p. 203-204° [887];
^{1}H NMR [887], IR [887], UV [887].

1-[5-(Diphenylmethyl)-2,4-dihydroxyphenyl]ethanone

[107114-35-2] $C_{21}H_{18}O_3$ mol.wt. 318.37



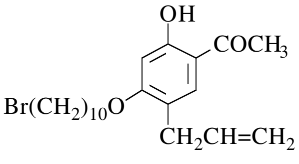
Synthesis

-Preparation by reaction of resacetophenone with diphenylcarbinol in the presence of boron trifluoride etherate in dioxane at r.t. (39%) [887].

m.p. 179-180° [887];
^{1}H NMR [887], IR [887], UV [887].

1-[4-[(10-Bromodecyl)oxy]-2-hydroxy-5-(2-propenyl)phenyl]ethanone

[117706-39-5] $C_{21}H_{31}BrO_3$ mol.wt. 411.38



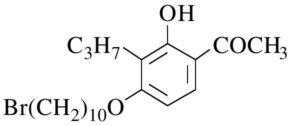
Synthesis

-Preparation by reaction of 1,10-dibromodecane with 5-allyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide (18%) [256] [257].

m.p. < 25° [256] [257]; ^{1}H NMR [256] [257].

1-[4-[(10-Bromodecyl)oxy]-2-hydroxy-3-propylphenyl]ethanone

[106627-35-4] $C_{21}H_{33}BrO_3$ mol.wt. 413.40

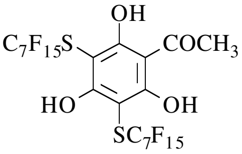


Synthesis

-Preparation by reaction of 1,10-dibromodecane with 2,4-dihydroxy-3-propylacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (60%) [1156].

1-[2,4,6-Trihydroxy-3,5-bis[(pentadecafluoroheptyl)thio]phenyl]ethanone

$C_{22}H_6F_{30}O_4S_2$ mol.wt. 968.37



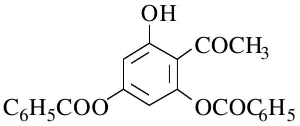
Synthesis

-Preparation by reaction of perfluoroheptanesulfenyl chloride with phloroacetophenone in chloroform in the presence of a slight excess of pyridine and a little quantity of iron powder, first at -40°, then at 60° for 3 h (39%) [456].

m.p. 106-108° [456]; ^{1}H NMR [456], IR [456].

1-[2,4-Bis(benzoyloxy)-6-hydroxyphenyl]ethanone

$C_{22}H_{16}O_6$ mol.wt. 376.37



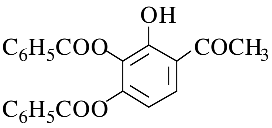
Synthesis

-Preparation by reaction of benzoyl chloride on phloroacetophenone in dilute aqueous sodium hydroxide [1673].

m.p. 109-110° [1673].

1-[3,4-Bis(benzoyloxy)-2-hydroxyphenyl]ethanone

[27865-59-4] $C_{22}H_{16}O_6$ mol.wt. 367.37



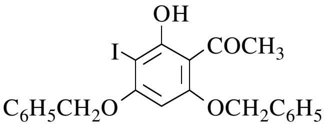
Synthesis

-Preparation by partial esterification of gallacetophenone with benzoyl chloride in pyridine at 100° (21%) [1053].

m.p. 108-109° [1053]; ^{1}H NMR [1053], IR [1053].

1-[2-Hydroxy-3-iodo-4,6-bis(phenylmethoxy)phenyl]ethanone

[95165-66-5] $C_{22}H_{19}IO_4$ mol.wt. 474.29



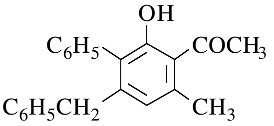
Syntheses

-Obtained by reaction of 2-hydroxy-4,6-bis(benzyloxy)-acetophenone with iodine in the presence of silver trifluoroacetate in chloroform at r.t. (83%) [1824].
-Also refer to: [1823].

m.p. 204-206° [1824]; ^1H NMR [1824].

1-[2-Hydroxy-6-methyl-3-phenyl-4-(phenylmethyl)phenyl]ethanone

[64648-09-5] $C_{22}H_{20}O_2$ mol.wt. 316.40



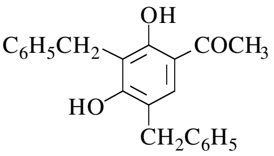
Synthesis

-Obtained by a potassium fluoride catalyzed self-condensation of 1-phenyl-2,4-pentanedione in DMF solution [414] [1753], (52%) [414]; also refer to: "ERRATUM" [415].

m.p. 124° [414] [415];
^1H NMR [414] [415] [1753], ^{13}C NMR [414] [415], IR [414] [415], MS [414] [415].

1-[2,4-Dihydroxy-3,5-bis(phenylmethyl)phenyl]ethanone

[95832-44-3] $C_{22}H_{20}O_3$ mol.wt. 332.40



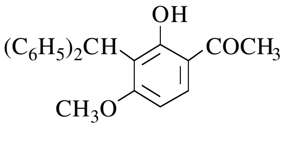
Syntheses

-Obtained by reaction of benzyl alcohol with resacetophenone in the presence of boron trifluoride etherate and dioxane at 60-70° (9%) [878].
-Also obtained (poor yield) by reaction of benzyl bromide with resacetophenone in the presence of potassium hydroxide in methanol at r.t. (< 2%) [885].

m.p. 159-160° [885], 157-158° [878]; ^1H NMR [878], IR [878], UV [878].

1-[3-(Diphenylmethyl)-2-hydroxy-4-methoxyphenyl]ethanone

[107114-34-1] $C_{22}H_{20}O_3$ mol.wt. 332.40



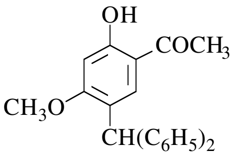
Synthesis

-Preparation by partial methylation of 3-(diphenylmethyl)resacetophenone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone (90%) [887].

m.p. 161-162° [887]; ^1H NMR [887].

1-[5-(Diphenylmethyl)-2-hydroxy-4-methoxyphenyl]ethanone

[107114-37-4] $C_{22}H_{20}O_3$ mol.wt. 332.40



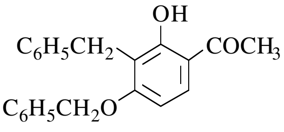
Synthesis

-Preparation by partial methylation of 5-(diphenylmethyl)resacetophenone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone (90%) [887].

m.p. 145-146° [887]; ^{1}H NMR [887].

1-[2-Hydroxy-4-(phenylmethoxy)-3-(phenylmethyl)phenyl]ethanone

[105485-45-8] $C_{22}H_{20}O_3$ mol.wt. 332.40



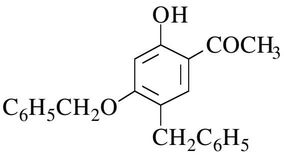
Synthesis

-Obtained by reaction of benzyl chloride [1274] or benzyl bromide [885] with resacetophenone in the presence of potassium hydroxide in refluxing methanol (10%) [1274], (< 1%) [885].

m.p. 120-121° [1274], 118-120° [885]; ^{1}H NMR [885], IR [885], UV [885].

1-[2-Hydroxy-4-(phenylmethoxy)-5-(phenylmethyl)phenyl]ethanone

[105485-48-1] $C_{22}H_{20}O_3$ mol.wt. 332.40



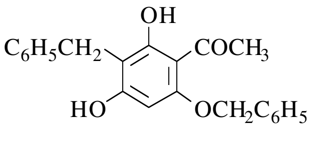
Synthesis

-Preparation by reaction of benzyl chloride with 5-benzyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone [885].

m.p. 100-102° [885]; ^{1}H NMR [885], UV [885].

1-[2,4-Dihydroxy-6-(phenylmethoxy)-3-(phenylmethyl)phenyl]ethanone

[39548-85-1] $C_{22}H_{20}O_4$ mol.wt. 348.40



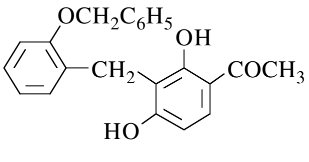
Synthesis

-Obtained (poor yield) by reaction of benzyl chloride with phloroacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (6%) [880].

m.p. 166-167° [880]; UV [880].

1-[2,4-Dihydroxy-3-[[2-(phenylmethoxy)phenyl]methyl]phenyl]ethanone

[103633-36-9] $C_{22}H_{20}O_4$ mol.wt. 348.40



Syntheses

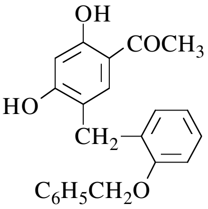
-Obtained by reaction of o-benzyloxybenzyl alcohol with resacetophenone in dioxane in the presence of boron trifluoride etherate at 60-70° for 3 h (10%) [873].

-Also obtained by reaction of o-benzyloxybenzyl bromide with resacetophenone in methanol in the presence of potassium hydroxide at r.t. for 24 h (14%) [873].

m.p. 155-156° [873]; ^{1}H NMR [873], IR [873], UV [873].

1-[2,4-Dihydroxy-5-[[2-(phenylmethoxy)phenyl]methyl]phenyl]ethanone

[103633-37-0] $C_{22}H_{20}O_4$ mol.wt. 348.40



Syntheses

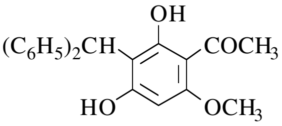
-Obtained by reaction of o-benzyloxybenzyl alcohol with resacetophenone in dioxane in the presence of boron trifluoride etherate at 60-70° for 3 h (18%) [873].

-Also obtained by reaction of o-benzyloxybenzyl bromide with resacetophenone in methanol in the presence of potassium hydroxide at r.t. for 24 h (7%) [873].

m.p. 127-128° [873]; ^{1}H NMR [873], IR [873], UV [873].

1-[3-(Diphenylmethyl)-2,4-dihydroxy-6-methoxyphenyl]ethanone

[101161-94-8] $C_{22}H_{20}O_4$ mol.wt. 348.40



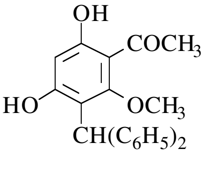
Synthesis

-Obtained by reaction of diphenylcarbinol with 2,4-dihydroxy-6-methoxyacetophenone in the presence of boron trifluoride etherate in dioxane at r.t. (15%) [879].

m.p. 150-151° [879]; ^{1}H NMR [879], IR [879], UV [879].

1-[3-(Diphenylmethyl)-4,6-dihydroxy-2-methoxyphenyl]ethanone

[101161-95-9] $C_{22}H_{20}O_4$ mol.wt. 348.40



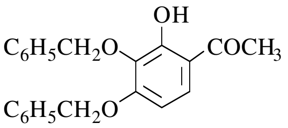
Synthesis

-Obtained by reaction of diphenylcarbinol with 2,4-dihydroxy-6-methoxyacetophenone in the presence of boron trifluoride etherate in dioxane at r.t. (20%) [879].

m.p. 148-149° [879]; ^{1}H NMR [879], IR [879], UV [879].

1-[2-Hydroxy-3,4-bis(phenylmethoxy)phenyl]ethanone

[2652-27-9] $C_{22}H_{20}O_4$ mol.wt. 348.40



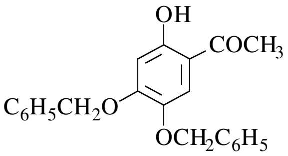
Syntheses

-Obtained by reaction of benzyl chloride with gallacetophenone in the presence of sodium bicarbonate and sodium iodide in refluxing mixture of acetone and ethanol [589] [972] [1053], (48%) [1053], (< 2%) [972].
-Also refer to: [973].

m.p. 114-115° [1053], 113-114° [972]; ^1H NMR [1053], IR [1053].

1-[2-Hydroxy-4,5-bis(phenylmethoxy)phenyl]ethanone

[7298-39-7] $C_{22}H_{20}O_4$ mol.wt. 348.40



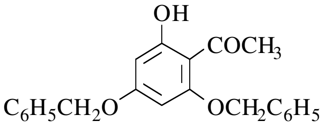
Syntheses

-Preparation by reaction of benzyl halide with 2,4,5-trihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone (69%) [1900].
-Preparation by reaction of benzyl chloride with 5-acetoxy-2,4-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone (52%) [703].

m.p. 96-97° [703], 94-95° [1900]; ^1H NMR [703], IR [703].

1-[2-Hydroxy-4,6-bis(phenylmethoxy)phenyl]ethanone

[18065-05-9] $C_{22}H_{20}O_4$ mol.wt. 348.40



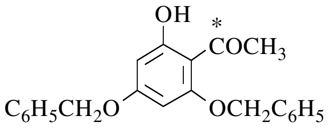
Synthesis

-Preparation by reaction of benzyl chloride on phloroacetophenone with potassium carbonate in refluxing acetone (29%) [1281], (20%) [880], in DMF at 100° (54%) [841] and at 150-153° (26%) [1820] or in HMPA at 90-93° (80%) [1822].

m.p. 119-120°5 [841], 101-102° [880], 100-102° [1822], 98-100° [1281], 96-98° [1820]. One of the reported melting points is obviously wrong.
^1H NMR [841], IR [841], UV [880], MS [841].

1-[2-Hydroxy-4,6-bis(phenylmethoxy)phenyl]ethanone-*1*-^{13}C

[332900-03-5] $C_{22}H_{20}O_4$ mol.wt. 349.40



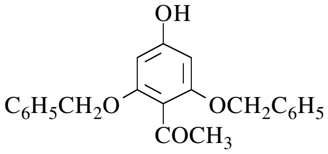
Syntheses

-Preparation by selective deprotection of tri-O-benzylphloroacetophenone labelled at the carbonyl group with titanium tetrachloride in methylene chloride for 160 min at 0° (80%) [1314].
-Also refer to: [961] [1313].

m.p. 104° [1314], 103° [961];
^{1}H NMR [1314], ^{13}C NMR [1314], IR [1314], UV [1314], MS [1314].

1-[4-Hydroxy-2,6-bis(phenylmethoxy)phenyl]ethanone

[76799-38-7] $C_{22}H_{20}O_4$ mol.wt. 348.40

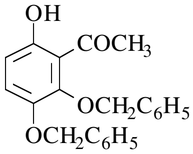


Synthesis

-Refer to: [1046] (compound 7) (45%).

1-[6-Hydroxy-2,3-bis(phenylmethoxy)phenyl]ethanone

$C_{22}H_{20}O_4$ mol.wt. 348.40



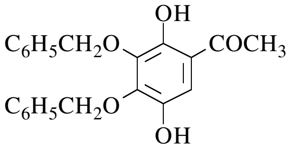
Synthesis

-Preparation by reaction of benzyl chloride on 2-(benzyloxy)-3,6-dihydroxyacetophenone with potassium carbonate in refluxing acetone (10%) [130].

m.p. 57°5 [130].

1-[2,5-Dihydroxy-3,4-bis(phenylmethoxy)phenyl]ethanone

[151148-87-9] $C_{22}H_{20}O_5$ mol.wt. 364.40



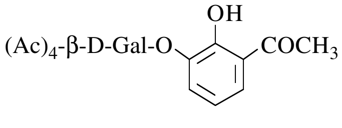
Synthesis

-Obtained by persulfate oxidation of 3,4-bis(benzyloxy)-2-hydroxyacetophenone (Elbs reaction) (10%) [886].

m.p. 121° [886];
^{1}H NMR [886], UV [886]; TLC [886].

1-[2-Hydroxy-3-[(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)oxy]phenyl]ethanone

[88086-96-8] $C_{22}H_{26}O_{12}$ mol.wt. 482.44



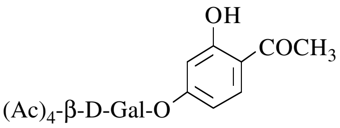
Syntheses

-Obtained by reaction of acetobromo-α-D-galactose with 2,3-dihydroxyacetophenone,
*in the presence of silver carbonate in quinoline at r.t., according to the Koenigs-Knorr method [1008];
*in the presence of 10% aqueous potassium hydroxide in acetone at r.t. for 24 h, according to the Fischer method (14%) [1008].

m.p. 152-153° [1008]; $(\alpha)_D^{20}$ = -47° (c = 1 in chloroform) [1008];
^{1}H NMR [1008].

1-[2-Hydroxy-4-[(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)oxy]phenyl]ethanone

[54918-27-3] $C_{22}H_{26}O_{12}$ mol.wt. 482.44



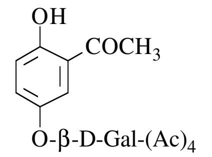
Syntheses

-Preparation by reaction of acetobromo-α-D-galactose (m.p. 79-81°) with resacetophenone,
*in the presence of silver oxide in quinoline at r.t. for 2 h (30%) [1861];
*in the presence of 10% aqueous potassium hydroxide in acetone at r.t. for 24 h (12%) [1008].

m.p. 115-117° [1861], 115° [1008]; $(\alpha)_D^{22}$ = -2°6 (c = 4 in chloroform) [1861].

1-[2-Hydroxy-5-[(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)oxy]phenyl]ethanone

[88086-98-0] $C_{22}H_{26}O_{12}$ mol.wt. 482.44



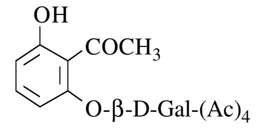
Syntheses

-Preparation by reaction of acetobromo-α-D-galactose,
*with 2-benzoyloxy-5-hydroxyacetophenone in the presence of silver carbonate in dry quinoline at r.t. for 3 h according to the Koenigs-Knorr method (quantitative yield) [1008];
*with quinacetophenone in the presence of 10% aqueous sodium hydroxide in acetone at r.t. for 24 h according to the Fischer method (14%) [1008].

m.p. 69-73° [1008]; ^{1}H NMR [1008].

1-[2-Hydroxy-6-[(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)oxy]phenyl]ethanone

$C_{22}H_{26}O_{12}$ mol.wt. 482.44

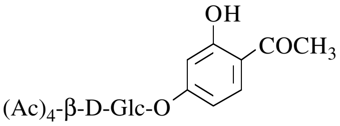


Synthesis

-Preparation by reaction of acetobromo-α-D-galactose with 2,6-dihydroxyacetophenone in the presence of silver carbonate in quinoline at r.t. for 3 h [1008], according to Koenigs-Knorr method [1004].

1-[2-Hydroxy-4-[(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)oxy]phenyl]ethanone

$C_{22}H_{26}O_{12}$ mol.wt. 482.44



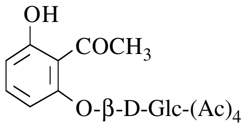
Syntheses

-Obtained by reaction of acetobromo-α-D-glucose with resacetophenone,
*in acetone in the presence of 10% sodium hydroxide at r.t. for 4 days (30%) [1478];
*in acetone in the presence of aqueous potassium hydroxide solution at r.t. for 24-40 h (20-45%) [549];
*in quinoline in the presence of silver oxide during 15 min (11%) [1201].

m.p. 131-132° [1201], 130-131° [1478]; $(\alpha)_D^{20}$ = -29°7 (in acetone) [1478].

1-[2-Hydroxy-6-[(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)oxy]phenyl]ethanone

[23141-00-6] $C_{22}H_{26}O_{12}$ mol.wt. 482.44



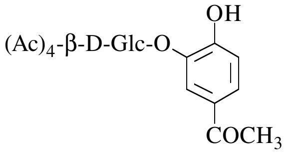
Syntheses

-Preparation by glycosation of 2,6-dihydroxyacetophenone with acetobromo-α-D-glucose,
*in the presence of cadmium carbonate in refluxing toluene for 20 h, with removal of generated water (71%) [1818], according to Dick's method [524];
*in the presence of benzyltributylammonium chloride and potassium carbonate in chloroform at r.t. for 24 h (93%) [792];
*in the presence of potassium hydroxide in aqueous acetone (38%) [1818], (32%) [525].

m.p. 201-203° [525], 200°5-201°5 [1818], 197-200° [792];
^{1}H NMR [792] [1818], IR [792] [1818], MS [1818], FAB-MS [792].

1-[4-Hydroxy-3-[(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)oxy]phenyl]ethanone
(Tetraacetylpungenin)

[101140-11-8] $C_{22}H_{26}O_{12}$ mol.wt. 482.44



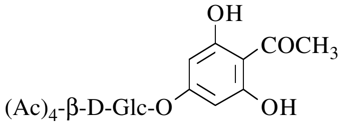
Synthesis

-Preparation by treatment of 3-(β-tetraacetylglucopyranosyloxy)-4-(2-methoxyethoxy)methoxyacetophenone (SM) with zinc bromide in methylene chloride at r.t. under nitrogen atmosphere (76%). SM was obtained by action of acetobromo-α-D-glucose with 3-hydroxy-4-(2-methoxyethoxy)-methoxyacetophenone in the presence of silver oxide in dry quinoline at r.t. under nitrogen atmosphere [1700].

m.p. 106-112° [1700]; ^{1}H NMR [1700], IR [1700], MS [1700].

1-[2,6-Dihydroxy-4-[(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)oxy]phenyl]ethanone

$C_{22}H_{26}O_{13}$ mol.wt. 498.42



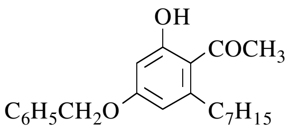
Synthesis

-Obtained by reaction of acetobromo-α-D-glucose with phloracetophenone in the presence of 2.25 N aqueous sodium hydroxide in acetone at 0° (9-12%) [1943].

m.p. 215-216° [1943]; $(\alpha)_D^{20}$ = -52°7 (pyridine) [1943].

1-[2-Heptyl-6-hydroxy-4-(phenylmethoxy)phenyl]ethanone

[96864-14-1] $C_{22}H_{28}O_3$ mol.wt. 340.46



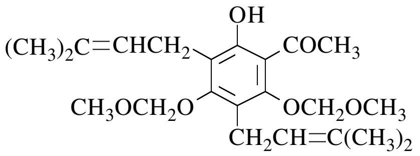
Synthesis

-Preparation by reaction of benzyl bromide with 2,4-dihydroxy-6-heptylacetophenone in the presence of potassium carbonate in refluxing acetone for 1.5 h (42%) [987].

m.p. 45° [987]; ^{1}H NMR [987], MS [987].

1-[2-Hydroxy-4,6-bis(methoxymethoxy)-3,5-bis(3-methyl-2-butenyl)phenyl]ethanone

[131303-37-2] $C_{22}H_{32}O_6$ mol.wt. 392.49



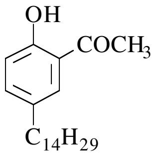
Syntheses

-Obtained by reaction of methoxymethyl chloride with 3,5-diprenyl-2,4,6-trihydroxyacetophenone (57%) [1953].

-Also refer to: [1948] [1949] [1952].

1-(2-Hydroxy-5-tetradecylphenyl)ethanone

[118469-76-4] $C_{22}H_{36}O_2$ mol.wt. 332.53



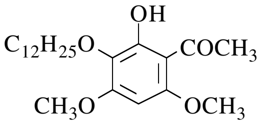
Synthesis

-Preparation by Fries rearrangement of 4-tetradecylphenyl acetate with aluminium chloride without solvent at 120° (94%) [1890].

m.p. 39-40° [1890]; ^{1}H NMR [1890], IR [1890].

1-[3-(Dodecyloxy)-2-hydroxy-4,6-dimethoxyphenyl]ethanone

[103777-47-5] $C_{22}H_{36}O_5$ mol.wt. 380.52



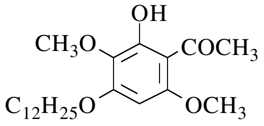
Synthesis

-Preparation by partial demethylation of 3-(dodecyloxy)-2,4,6-trimethoxyacetophenone (SM) with aluminium chloride in acetonitrile at 60° for 1.5 h (83%). SM was obtained by alkylation of 3-hydroxy-2,4,6-trimethoxyacetophenone with dodecyl iodide in the presence of potassium carbonate in refluxing acetone for 12 h [807].

m.p. 53-54° [807].

1-[4-(Dodecyloxy)-2-hydroxy-3,6-dimethoxyphenyl]ethanone

[103777-44-2] $C_{22}H_{36}O_5$ mol.wt. 380.52



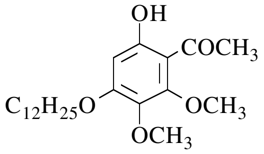
Synthesis

-Preparation by partial alkylation of 4,6-dihydroxy-2,5-dimethoxyacetophenone with dodecyl iodide (92%) [807].

m.p. 55-56° [807].

1-[4-(Dodecyloxy)-6-hydroxy-2,3-dimethoxyphenyl]ethanone

[103777-43-1] $C_{22}H_{36}O_5$ mol.wt. 380.52



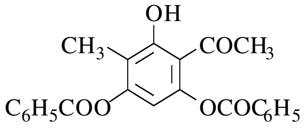
Synthesis

-Preparation by partial alkylation of 4,6-dihydroxy-2,3-dimethoxyacetophenone with dodecyl iodide [807].

oil [807].

1-[4,6-Bis(benzoyloxy)-2-hydroxy-3-methylphenyl]ethanone

$C_{23}H_{18}O_6$ mol.wt. 390.39



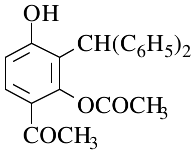
Synthesis

-Obtained by reaction of benzoyl chloride on 2,4,6-trihydroxy-3-methylacetophenone with 2% sodium hydroxide solution at 0° (9-12%) [1883].

m.p. 149° [1883].

1-[2-(Acetyloxy)-3-(diphenylmethyl)-4-hydroxyphenyl]ethanone

[145747-37-1] $C_{23}H_{20}O_4$ mol.wt. 360.41

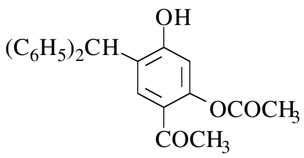


Synthesis

-Obtained by enzymatic hydrolysis of 2,4-diacetoxy-3-(diphenylmethyl)acetophenone in the presence of porcine pancreas lipase in tetrahydrofuran at 42-45° (70%) [1381].

1-[2-(Acetyloxy)-5-(diphenylmethyl)-4-hydroxyphenyl]ethanone

[145747-38-2] $C_{23}H_{20}O_4$ mol.wt. 360.41

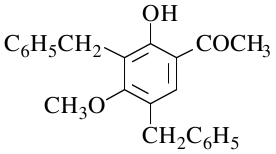


Synthesis

-Obtained by enzymatic hydrolysis of 2,4-diacetoxy-5-(diphenylmethyl)acetophenone in the presence of porcine pancreas lipase in tetrahydrofuran at 42-45° (68%) [1381].

1-[2-Hydroxy-4-methoxy-3,5-bis(phenylmethyl)phenyl]ethanone

[95832-46-5] $C_{23}H_{22}O_3$ mol.wt. 346.43



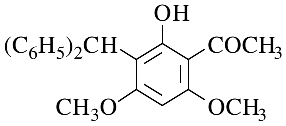
Synthesis

-Preparation by reaction of dimethyl sulfate with 3,5-dibenzyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone (90%) [887].

oil [887]; ^1H NMR [887].

1-[3-(Diphenylmethyl)-2-hydroxy-4,6-dimethoxyphenyl]ethanone

[101161-96-0] $C_{23}H_{22}O_4$ mol.wt. 362.42



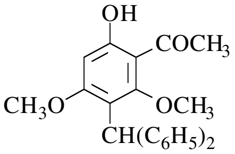
Synthesis

-Preparation by reaction of dimethyl sulfate with 2,4-dihydroxy-6-methoxy-3-(diphenylmethyl)acetophenone in the presence of potassium carbonate in refluxing acetone (82%) [879].

m.p. 173-174° [879]; ^1H NMR [879], UV [879].

1-[3-(Diphenylmethyl)-6-hydroxy-2,4-dimethoxyphenyl]ethanone

[101161-97-1] $C_{23}H_{22}O_4$ mol.wt. 362.42



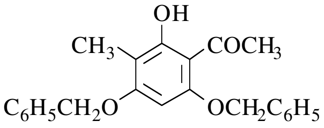
Synthesis

-Preparation by reaction of dimethyl sulfate with 2,4-dihydroxy-6-methoxy-5-(diphenylmethyl)acetophenone in the presence of potassium carbonate in refluxing acetone (69%) [879].

m.p. 167-168° [879]; ^1H NMR [879], UV [879].

1-[2-Hydroxy-3-methyl-4,6-bis(phenylmethoxy)phenyl]ethanone

[39548-92-0] $C_{23}H_{22}O_4$ mol.wt. 362.42



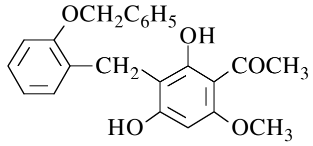
Syntheses

-Preparation by reaction of benzyl chloride on 3-methylphloracetophenone with potassium carbonate in refluxing acetone (27-31%) [1186] [1883], (18%) [880].
-Also refer to: [1184].

m.p. 145° [218] [880] [1883], 142° [1186].

1-[2,4-Dihydroxy-6-methoxy-3-[[2-(phenylmethoxy)phenyl]methyl]phenyl]ethanone

[103633-31-4] $C_{23}H_{22}O_5$ mol.wt. 378.42



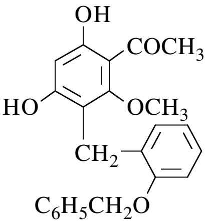
Syntheses

-Obtained by reaction of o-(benzyloxy)benzyl bromide with 2,4-dihydroxy-6-methoxyacetophenone in the presence of potassium hydroxide in methanol at r.t. for 24 h (18%) [873].
-Also obtained by reaction of o-(benzyloxy)benzyl alcohol with 2,4-dihydroxy-6-methoxyacetophenone in the presence of boron trifluoride etherate in dioxane (7%) [873].

m.p. 152-153° [873]; TLC [873];
^{1}H NMR [873], IR [873], UV [873].

1-[4,6-Dihydroxy-2-methoxy-3-[[2-(phenylmethoxy)phenyl]methyl]phenyl]ethanone

[103633-32-5] $C_{23}H_{22}O_5$ mol.wt. 378.42



Syntheses

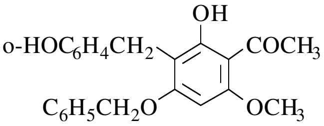
-Obtained by reaction of o-(benzyloxy)benzyl alcohol with 2,4-dihydroxy-6-methoxyacetophenone in the presence of boron trifluoride etherate in dioxane at 60-70° for 3 h (< 15%) [873].
-Also obtained by reaction of o-(benzyloxy)benzyl bromide with 2,4-dihydroxy-6-methoxyacetophenone in the presence of potassium hydroxide in methanol at r.t. for 24 h (7%) [873].

m.p. 145-146° [873]; TLC [873]; ^{1}H NMR [873], IR [873], UV [873].

1-[2-Hydroxy-3-[(2-hydroxyphenyl)methyl]-6-methoxy-4-(phenylmethoxy)-phenyl]ethanone

1-[2,4-Dihydroxy-3-[(2-hydroxyphenyl)methyl]-6-methoxyphenyl]ethanone, monoether with benzenemethanol

[102056-83-7] $C_{23}H_{22}O_5$ mol.wt. 378.42

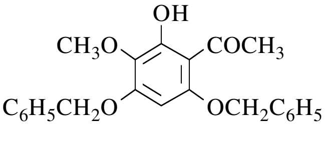


Synthesis

-Obtained by reaction of benzyl chloride with 2',4'-dihydroxy-3'-(2-hydroxybenzyl)-6'-methoxyacetophenone in the presence of potassium carbonate in refluxing acetone (10%) [1140].

1-[2-Hydroxy-3-methoxy-4,6-bis(phenylmethoxy)phenyl]ethanone

[24126-73-6] $C_{23}H_{22}O_5$ mol.wt. 378.42



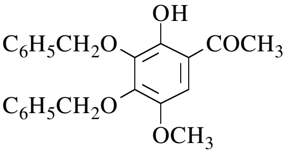
Syntheses

-Preparation by selective cleavage of 2-benzyloxy group of 2,4,6-tris(benzyloxy)-3-methoxyacetophenone (SM) with concentrated hydrochloric acid in acetic acid at r.t. for 50 min (82%). SM (oily material) was obtained by reaction of benzyl chloride with 4-benzyloxy-2,6-dihydroxy-3-methoxyacetophenone in the presence of potassium carbonate in DMF at 150-160° for 10 min [803].
-Also obtained by partial benzylation of 3-methoxy-2,4,6-trihydroxyacetophenone [809], with benzyl chloride in the presence of potassium carbonate in refluxing acetone for 16 h (6%) [642].

m.p. 140-141° [642] [809], 137-138° [803]; ^{1}H NMR [809]; UV [642] [809].

1-[2-Hydroxy-5-methoxy-3,4-bis(phenylmethoxy)phenyl]ethanone

[158148-88-0] $C_{23}H_{22}O_5$ mol.wt. 378.42



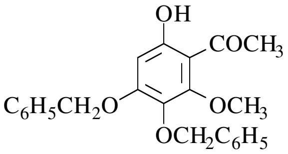
Synthesis

-Preparation by reaction of dimethyl sulfate with 3,4-bis(benzyloxy)-2,5-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 8 h (79%) [886].

m.p. 131° [886]; TLC [886];
^{1}H NMR [886], IR [886], UV [886].

1-[6-Hydroxy-2-methoxy-3,4-bis(phenylmethoxy)phenyl]ethanone

[73239-53-9] $C_{23}H_{22}O_5$ mol.wt. 378.42



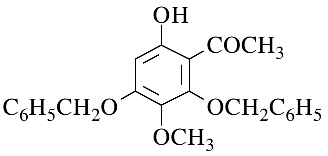
Synthesis not yet described

-Refer to: [379].

TLC [379].

1-[6-Hydroxy-3-methoxy-2,4-bis(phenylmethoxy)phenyl]ethanone

$C_{23}H_{22}O_5$ mol.wt. 378.42



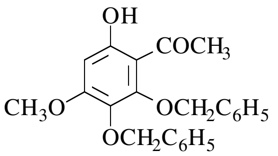
Syntheses

-Obtained by partial benzylation of 3-methoxy-2,4,6-trihydroxyacetophenone [809], with benzyl chloride in the presence of potassium carbonate in refluxing acetone for 16 h (31%) [642].
-Also refer to: [643] [804].

oil [642]; m.p. 70-71° [809]; ^{1}H NMR [809].

1-[6-Hydroxy-4-methoxy-2,3-bis(phenylmethoxy)phenyl]ethanone

[54299-56-8] $C_{23}H_{22}O_5$ mol.wt. 378.42



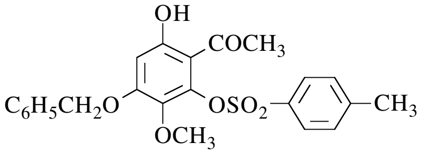
Synthesis

-Preparation by reaction of benzyl chloride with 6-(benzyloxy)-2,5-dihydroxy-4-methoxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (71%) [215].

m.p. 95-97° [215].

1-[6-Hydroxy-3-methoxy-2-[[(4-methylphenyl)sulfonyl]oxy]-4-(phenylmethoxy)phenyl]-ethanone

[188927-30-2] $C_{23}H_{22}O_7S$ mol.wt. 442.49



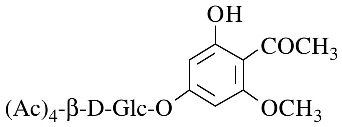
Synthesis

-Preparation by treatment of 4-(benzyloxy)-3,6-dimethoxy-2-(tosyloxy)acetophenone (m.p. 106-108°) with aluminium bromide in acetonitrile at 0° for 1 h (quantitative yield) [804].

m.p. 94-95° [804].

1-[2-Hydroxy-6-methoxy-4-[(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)oxy]phenyl]-ethanone

[139545-92-9] $C_{23}H_{28}O_{13}$ mol.wt. 512.47



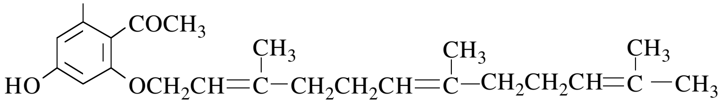
Syntheses

-Obtained by treatment of 2,4-dihydroxy-6-methoxyacetophenone with acetobromo-α-D-glucose,
*in acetone in the presence of 10% aqueous sodium hydroxide at r.t. for 4.5 h (48%) [1007];
*in quinoline or in acetone in the presence of silver oxide at r.t. for 20 min (22 and 30% yields, respectively) [1944].

m.p. 169-171° [1007], 168° [1944]; $(\alpha)_D^{25}$ = -39°7 to -42°3 (pyridine) [1944];
^{1}H NMR [1007], IR [1007], MS [1007]; TLC [1007].

1-[2,4-Dihydroxy-6-[(3,7,11-trimethyl-2,6,10-dodecatrienyl)oxy]phenyl]ethanone *(E,E)*

[200129-18-6] $C_{23}H_{32}O_4$ mol.wt. 372.50

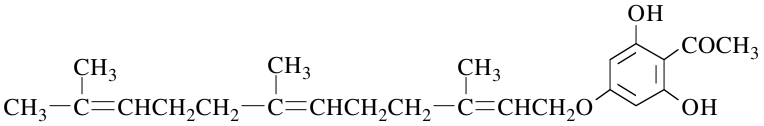


Synthesis

-Refer to: [823] (Chinese paper).

1-[2,6-Dihydroxy-4-[(3,7,11-trimethyl-2,6,10-dodecatrienyl)oxy]phenyl]ethanone

[156499-52-4] $C_{23}H_{32}O_4$ mol.wt. 372.50



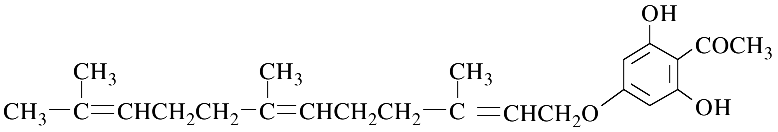
Isolation from natural sources

-From the aerial parts of *Boronia Ramosa* (Rutaceae) [24].

gum [24];
^{1}H NMR [24], ^{13}C NMR [24], IR [24], UV [24], MS [24].

1-[2,6-Dihydroxy-4-[(3,7,11-trimethyl-2,6,10-dodecatrienyl)oxy]phenyl]ethanone *(E,E)*

[183143-91-1] $C_{23}H_{32}O_4$ mol.wt. 372.50



Syntheses

-Preparation by hydrolysis of 2-p-toluenesulfonyloxy-6-hydroxy-4-(1'-farnesyloxy)acetophenone with 30% potassium hydroxide in refluxing ethanol for 1.5 h (89%) [825].
-Obtained (poor yield) by reaction of farnesyl bromide with phloroacetophenone in the presence of potassium carbonate in refluxing acetone for 4 h (7%) [822] [823].

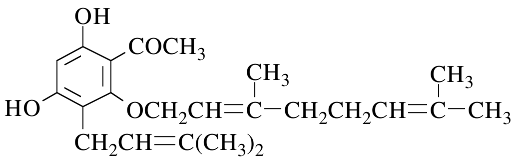
Isolation from natural sources

-From the aerial parts of *Boronia ramosa* in Australian genus *Boronia* (Rutaceae) [24] [823].

white gum [24] [825];
^{1}H NMR [24] [825], ^{13}C NMR [24], IR [24] [825], UV [24], EIMS [24] [825].

1-[2-[(3,7-Dimethyl-2,6-octadienyl)oxy]-4,6-dihydroxy-3-(3-methyl-2-butenyl)phenyl]-ethanone *(E)*

[126259-76-5] $C_{23}H_{32}O_4$ mol.wt. 372.50



Synthesis

-Obtained by hydrolysis of 4',6'-bis (benzoyloxy)-2'-geranyloxy-3'-prenylacetophenone with dilute sodium hydroxide under nitrogen atmosphere at 50° (good yield) [1824].

Isolation from natural sources

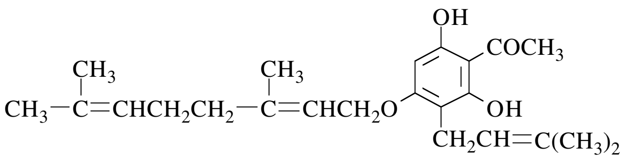
-From the *Euodia Lunu-Ankenda* root bark (Rutaceae) [1045].

N.B.: The synthetic works [1823] [1824] have suggested that the natural product ketone isolated by [1045] had an incorrectly assigned structure. This compound [1045] will be identical with 1-[4-[(3,7-dimethyl-2,6-octadienyl)oxy]-2,6-dihydro-3-(3-methyl-2-butenyl)phenyl]ethanone [142905-38-2].

m.p. 88-90° [1045], 71-73° [1824]. One of the reported melting points is obviously wrong.
^{1}H NMR [1045] [1824], IR [1045][1824], UV [1045], MS [1045],
HRMS [1045]; TLC [1045];

1-[4-[(3,7-Dimethyl-2,6-octadienyl)oxy]-2,6-dihydroxy-3-(3-methyl-2-butenyl)phenyl]-ethanone *(E)*

[142905-38-2] $C_{23}H_{32}O_4$ mol.wt. 372.50



Synthesis

-Obtained *via* a nine-step synthesis from the 4',6'-bis(benzyloxy)-2'-hydroxyacetophenone [1823].

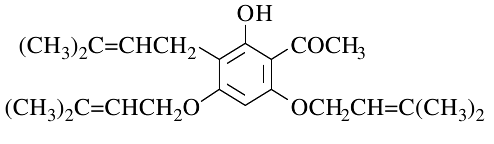
Isolation from natural sources

-From the fruit of *Evodia Merrillii* Kanehira & Sasaki ex Kanehira (Rutaceae) [408] [1099].

m.p. 98-101° [408] [1099], 98-100° [1823]; column chromatography [408];
^{1}H NMR [408] [1099] [1823], ^{13}C NMR [408],
IR [408] [1099] [1823], UV [408], MS [408].

1-[2-Hydroxy-3-(3-methyl-2-butenyl)-4,6-bis[(3-methyl-2-butenyl)oxy]phenyl]ethanone

$C_{23}H_{32}O_4$ mol.wt. 372.50



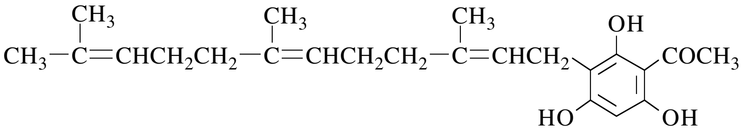
Synthesis

-Obtained (poor yield) by reaction of prenyl bromide with phloroacetophenone in the presence of aqueous potassium hydroxide solution (3%) [1489].

b.p.$_{0.2}$ 135-150° [1489].

1-[2,4,6-Trihydroxy-3-(3,7,11-trimethyl-2,6,10-dodecatrienyl)phenyl]ethanone

[156499-51-3] $C_{23}H_{32}O_4$ mol.wt. 372.50



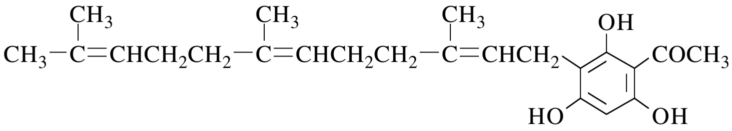
Isolation from natural sources

-From the aerial parts of *Boronia Ramosa* (Rutaceae) [24].

m.p. 112-115° [24];
^{1}H NMR [24], ^{13}C NMR [24], IR [24], UV [24], MS [24].

1-[2,4,6-Trihydroxy-3-(3,7,11-trimethyl-2,6,10-dodecatrienyl)phenyl]ethanone *(E,E)*

[183143-90-0] $C_{23}H_{32}O_4$ mol.wt. 372.50



Synthesis

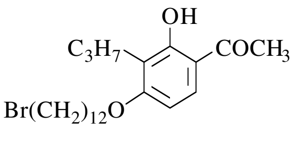
-Obtained by reaction of farnesyl bromide with phloroacetophenone in the presence of potassium carbonate in refluxing acetone for 4 h (52%) [822] [823].

Isolation from natural sources

-From the aerial parts of *Boronia ramosa* in Australia [823].

1-[4-[(12-Bromododecyl)oxy]-2-hydroxy-3-propylphenyl]ethanone

[106627-36-5] $C_{23}H_{37}BrO_3$ mol.wt. 441.45

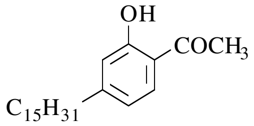


Synthesis

-Preparation by reaction of 1,12-dibromododecane with 2,4-dihydroxy-3-propylacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (45%) [1156].

1-(2-Hydroxy-4-pentadecylphenyl)ethanone

[52122-69-7] $C_{23}H_{38}O_2$ mol.wt. 346.55



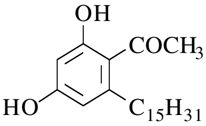
Synthesis

-Preparation by Fries rearrangement of 3-pentadecylphenyl acetate with aluminium chloride without solvent at 140-150° [550].

m.p. 50° [550]; b.p.$_2$ 212-214° [550].

1-(2,4-Dihydroxy-6-pentadecylphenyl)ethanone

$C_{23}H_{38}O_3$ mol.wt. 362.55



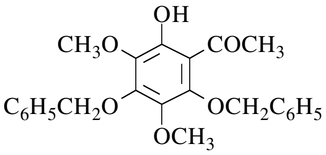
Synthesis

-Preparation by reaction of acetic acid on 5-pentadecylresorcinol with boron trifluoride and hydrofluoric acid in xylene at 50-60° (75%) [332].

m.p. 63° [332].

1-[2-Hydroxy-3,5-dimethoxy-4,6-bis(phenylmethoxy)phenyl]ethanone

[3162-54-7] $C_{24}H_{24}O_6$ mol.wt. 408.45



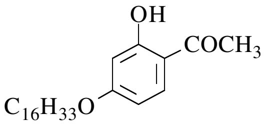
Synthesis

-Obtained by alkaline degradation of *Lucidin dibenzyl ether* by refluxing with 10% aqueous ethanolic potassium hydroxide under nitrogen atmosphere for 17 h [1072].

b.p.$_{0.2}$ 160-180° [1072]; m.p. 86-87° [1072].

1-[4-(Hexadecyloxy)-2-hydroxyphenyl]ethanone

[143286-87-7] $C_{24}H_{40}O_3$ mol.wt. 376.58



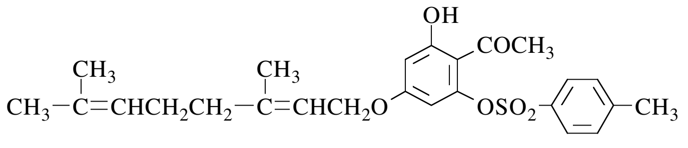
Synthesis

-Preparation by partial alkylation of resacetophenone with hexadecyl bromide in the presence of potassium carbonate in refluxing acetone for 20 h [183].

m.p. 56° [183].

1-[4-[[(2*E*)-3,7-Dimethyl-2,6-octadienyl]oxy]-2-hydroxy-6-[[(4-methylphenyl)sulfonyl]-oxy]phenyl]ethanone

[225088-73-3] $C_{25}H_{30}O_6S$ mol.wt. 458.58



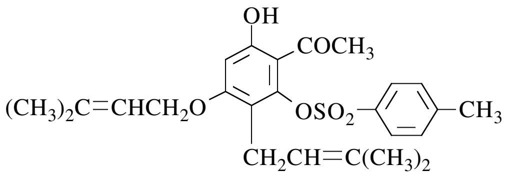
Synthesis

-Preparation by treatment of 2-toluenesulfonyloxy-4,6-dihydroxyacetophenone with geranyl bromide in acetone in the presence of potassium carbonate at r.t. for 2 h (84%) [825].

colourless gum [825];
^{1}H NMR [825], IR [825], EIMS [825], HREIMS [825].

1-[6-Hydroxy-3-(3-methyl-2-butenyl)-4-[(3-methyl-2-butenyl)oxy]-2-[[(4-methylphenyl)-sulfonyl]oxy]phenyl]ethanone

[158499-97-9] $C_{25}H_{30}O_6S$ mol.wt. 458.58



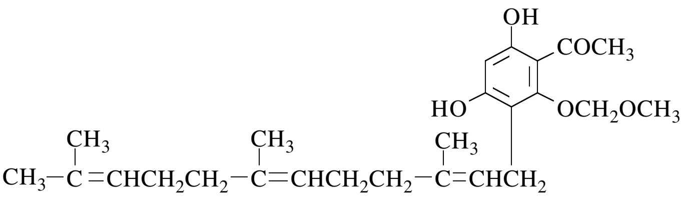
Synthesis

-Obtained by reaction of prenyl bromide with 4',6'-dihydroxy-3'-prenyl-2'-tosyloxyacetophenone in the presence of potassium carbonate in acetone at 20° for 2 h [1823].

^{1}H NMR [1823].

1-[4,6-Dihydroxy-3-(methoxymethoxy)-3-(3,7,11-trimethyl-2,6,10-dodecatrienyl)phenyl]-ethanone

$C_{25}H_{36}O_5$ mol.wt. 416.56

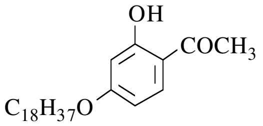


Synthesis

-Obtained by reaction of chloromethyl methyl ether with 3-farnesyl-2,4,6-trihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 5 h (82%) [822].

1-[2-Hydroxy-4-(octadecyloxy)phenyl]ethanone

[99283-88-2] $C_{26}H_{44}O_3$ mol.wt. 404.63



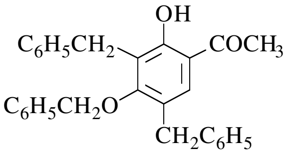
Syntheses

-Preparation by partial alkylation of resacetophenone with octadecyl bromide in the presence of potassium carbonate in refluxing acetone for 20 h [183].
-Also refer to: [1733].

m.p. 61° [183] [1733]; GC [1732].

1-[2-Hydroxy-4-(phenylmethoxy)-3,5-bis(phenylmethyl)phenyl]ethanone

[105485-47-0] $C_{29}H_{26}O_3$ mol.wt. 422.52



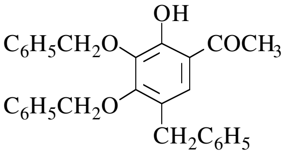
Synthesis

-Obtained by reaction of benzyl chloride with 3,5-dibenzyl-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone [885].

m.p. 87-89° [885]; ^{1}H NMR [885], IR [885], UV [885].

1-[2-Hydroxy-3,4-bis(phenylmethoxy)-5-(phenylmethyl)phenyl]ethanone

[105485-46-9] $C_{29}H_{26}O_4$ mol.wt. 438.52



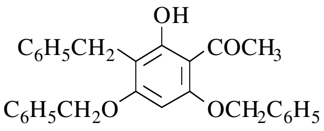
Synthesis

-Preparation by reaction of benzyl chloride with 5-benzyl-2,3,4-trihydroxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone (64%) [885].

m.p. 56-58° [885]; ^{1}H NMR [885], IR [885], UV [885].

1-[2-Hydroxy-4,6-bis(phenylmethoxy)-3-(phenylmethyl)phenyl]ethanone

[18065-06-0] $C_{29}H_{26}O_4$ mol.wt. 438.52



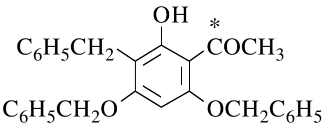
Synthesis

-Obtained by reaction of benzyl chloride with phloroacetophenone in the presence of potassium carbonate in DMF at 150-153° (31%) [1820] or in refluxing acetone [406] [880], (2%) [880].

m.p. 123-124° [406] [880], 111-112° [1820];
^{1}H NMR [880], IR [406], UV [406] [880].

1-[2-Hydroxy-4,6-bis(phenylmethoxy)-3-(phenylmethyl)phenyl]ethanone-*1*-^{13}C

[357409-15-5] $C_{29}H_{26}O_4$ mol.wt. 439.52



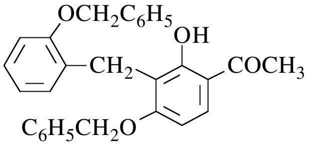
Syntheses

-Obtained (by-product) by selective deprotection of tri-O-benzylphloroacetophenone labelled at the carbonyl group with titanium tetrachloride in methylene chloride for 160 min at 0° (7%) [1314].
-Also refer to: [1313].

m.p. 117° [1314];
^1H NMR [1314], ^{13}C NMR [1314], IR [1314], UV [1314], MS [1314].

1-[2-Hydroxy-4-(phenylmethoxy)-3-[[2-(phenylmethoxy)phenyl]methyl]phenyl]ethanone

[103633-40-5] $C_{29}H_{26}O_4$ mol.wt. 438.52



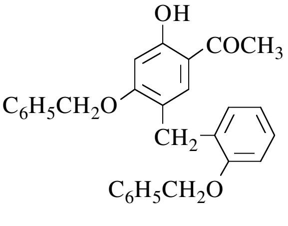
Synthesis

-Preparation by reaction of benzyl chloride with 3-(o-benzyloxybenzyl)-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone for 6 h (73%) [873].

m.p. 135-136° [873]; TLC [873]; ^1H NMR [873], IR [873], UV [873].

1-[2-Hydroxy-4-(phenylmethoxy)-5-[[2-(phenylmethoxy)phenyl]methyl]phenyl]ethanone

[103633-43-8] $C_{29}H_{26}O_4$ mol.wt. 438.52



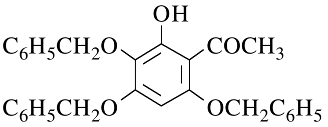
Synthesis

-Preparation by reaction of benzyl chloride with 5-(o-benzyloxybenzyl)-2,4-dihydroxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone for 6 h (75%) [873].

m.p. 113-114° [873]; TLC [873];
^1H NMR [873], IR [873], UV [873].

1-[2-Hydroxy-3,4,6-tris(phenylmethoxy)phenyl]ethanone

[60840-18-8] $C_{29}H_{26}O_5$ mol.wt. 454.52



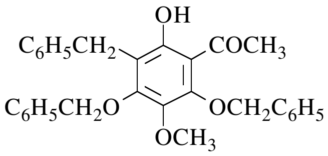
Synthesis

-Preparation from 2,3,4,6-tetrakis(benzyloxy)acetophenone on refluxing with 90% aqueous acetic acid (91%) [756], (78%) [757] [758]. There is a selective hydrolysis of the 2-(benzyloxy) group [756].

m.p. 141-142° [757] [758];
^1H NMR [756] [757] [758], IR [756] [757] [758], MS [756].

1-[2-Hydroxy-5-methoxy-4,6-bis(phenylmethoxy)-3-(phenylmethyl)phenyl]ethanone

$C_{30}H_{28}O_5$ mol.wt. 468.55



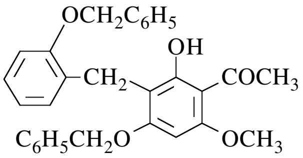
Synthesis

-Obtained (by-product) by partial benzylation of 3-methoxy-2,4,6-trihydroxyacetophenone [809].

oil [809]; ^{1}H NMR [809].

1-[2-Hydroxy-6-methoxy-4-(phenylmethoxy)-3-[[2-(phenylmethoxy)phenyl]methyl]-phenyl]ethanone

[102104-05-2] $C_{30}H_{28}O_5$ mol.wt. 468.55



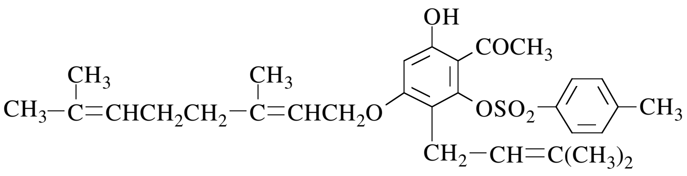
Synthesis

-Preparation by reaction of benzyl chloride with 3-(o-benzyloxybenzyl)-2,4-dihydroxy-6-methoxy-acetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone for 6 h (73%) [873].

m.p. 167-168° [873]; TLC [873];
^{1}H NMR [873], IR [873], UV [873].

1-[4-[(3,7-Dimethyl-2,6-octadienyl)oxy]-6-hydroxy-3-(3-methyl-2-butenyl)-2-[[(4-methyl-phenyl)sulfonyl]oxy]phenyl]ethanone *(E)*

[158499-96-8] $C_{30}H_{38}O_6S$ mol.wt. 526.69



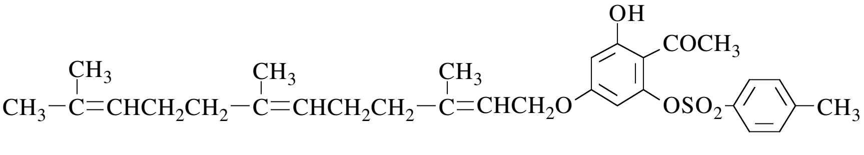
Synthesis

-Obtained by reaction of geranyl bromide with 4',6'-dihydroxy-3'-prenyl-2'-tosyloxyacetophenone in the presence of potassium carbonate in acetone at 20° for 2 h [1823].

^{1}H NMR [1823].

1-[2-Hydroxy-6-[[(4-methylphenyl)sulfonyl]oxy]-4-[[*(2E,6E)*-3,7,11-trimethyl-2,6,10-dodecatrienyl]oxy]phenyl]ethanone

[225088-74-4] $C_{30}H_{38}O_6S$ mol.wt. 526.69



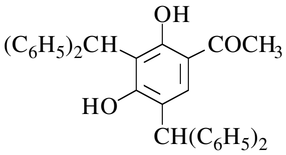
Synthesis

-Obtained by reaction of 2-toluenesulfonyloxy-4,6-dihydroxyacetophenone with farnesyl bromide in acetone in the presence of potassium carbonate at r.t. for 2 h (60%) [825].

colourless gum [825];
^{1}H NMR [825], IR [825], EIMS [825].

1-[3,5-Bis(diphenylmethyl)-2,4-dihydroxyphenyl]ethanone

[107114-29-4] $C_{34}H_{28}O_3$ mol.wt. 484.59



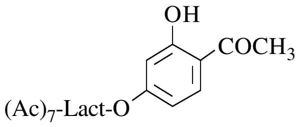
Synthesis

-Obtained by reaction of resacetophenone with diphenylcarbinol in the presence of boron trifluoride etherate in dioxane at r.t. (14%) [887].

m.p. 144-145° [887];
^{1}H NMR [887], IR [887], UV [887].

1-[2-Hydroxy-4-[(per-O-acetyl-β-D-galactopyranosyl-β-D-glucopyranosyl)oxy]phenyl]-ethanone

$C_{34}H_{42}O_{20}$ mol.wt. 770.70



$(Ac)_7$-Lact = heptaacetyllactosid rest

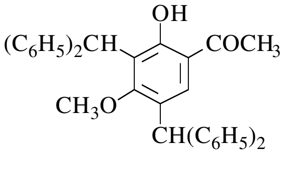
Synthesis

-Preparation by reaction of α-acetobromolactose with resacetophenone in the presence of silver oxide in quinoline at r.t. for 2 h (40%) [1861].

m.p. 195-197° [1861];
$(\alpha)^{21}_{D}$ = -32°3 (c = 2 in chloroform) [1861].

1-[3,5-Bis(diphenylmethyl)-2-hydroxy-4-methoxyphenyl]ethanone

[107114-31-8] $C_{35}H_{30}O_3$ mol.wt. 498.62



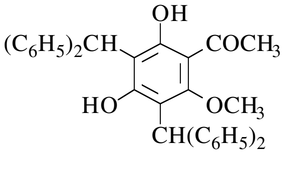
Synthesis

-Preparation by reaction of dimethyl sulfate with 3,5-bis-(diphenylmethyl)-2,4-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone (81%) [887].

m.p. 152-153° [887]; ^{1}H NMR [887].

1-[3,5-Bis(diphenylmethyl)-2,4-dihydroxy-6-methoxyphenyl]ethanone

[101161-93-7] $C_{35}H_{30}O_4$ mol.wt. 514.62



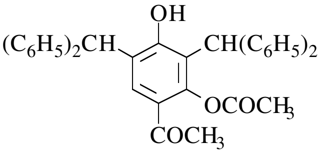
Synthesis

-Obtained (poor yield) by reaction of diphenylcarbinol with 2,4-dihydroxy-6-methoxyacetophenone in dioxane at r.t. in the presence of boron trifluoride etherate (7%) [879].

m.p. 122-123° [879]; ^{1}H NMR [879], IR [879], UV [879].

1-[2-(Acetyloxy)-3,5-bis(diphenylmethyl)-4-hydroxyphenyl]ethanone

[145747-39-3] $C_{36}H_{30}O_4$ mol.wt. 526.63

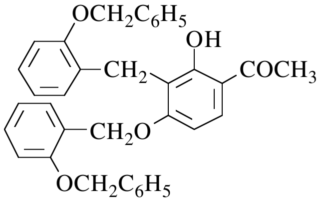


Synthesis

-Obtained by partial deacylation of 2,4-diacetoxy-3,5-bis-(diphenylmethyl)acetophenone by porcine pancreatic lipase in tetrahydrofuran at 42-45° (63%) [1381] [1382].

1-[2-Hydroxy-4-[[2-(phenylmethoxy)phenyl]methoxy]-3-[[2-(phenylmethoxy)phenyl]-methyl]phenyl]ethanone

[103633-46-1] $C_{36}H_{32}O_5$ mol.wt. 544.65



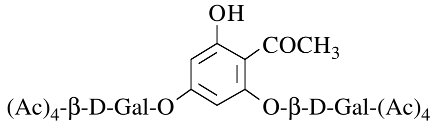
Synthesis

-Obtained (poor yield) by reaction of o-benzyloxybenzyl bromide with resacetophenone in methanol in the presence of potassium hydroxide at r.t. for 24 h (< 2%) [873].

m.p. 135-136° [873]; TLC [873];
^{1}H NMR [873], IR [873], UV [873].

1-[2-Hydroxy-4,6-bis[(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)oxy]phenyl]ethanone

[88087-00-7] $C_{36}H_{44}O_{22}$ mol.wt. 828.73



Synthesis

-Obtained by reaction of 2,3,4,6-tetra-O-acetyl-$_\alpha$-D-galactopyranosyl bromide with phloracetophenone in the presence of 30% aqueous sodium hydroxide in acetone (17%) [1008], according to Zemplen's procedure [1943].

m.p. 184-186° [1008]; ^{1}H NMR [1008].

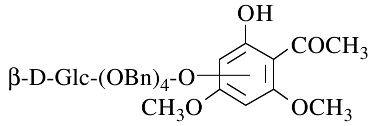
1-[2-Hydroxy-4,6-dimethoxy-3-[2,3,4,6-tetrakis-O-(phenylmethyl)-β-D-glucopyranosyl]-phenyl]ethanone

[115130-46-6] $C_{44}H_{46}O_9$ mol.wt. 718.84

and

1-[6-Hydroxy-2,4-dimethoxy-3-[2,3,4,6-tetrakis-O-(phenylmethyl)-β-D-glucopyranosyl]-phenyl]ethanone

[169566-54-5] $C_{44}H_{46}O_9$ mol.wt. 718.84



Synthesis

-Obtained (*via* O → C glycoside rearrangement) by adding boron trifluoride etherate to a mixture of 2-hydroxy-4,6-dimethoxyacetophenone, 2,3,4,6-tetra-O-benzyl-$_\alpha$-D-glucopyranosyl fluoride (R) and powdered molecular sieves 4 Å in methylene chloride and stirring at -78° for 2 h under an argon atmosphere; after the disappearance of R on TLC, the reaction temperature was raised from -78° to r.t. and the mixture stirred for 45 min (92%) [1046].

N.B.: The *3-isomer* was obtained by selective glycosylation of 2-hydroxy-4,6-dimethoxy-acetophenone with O-(2,3,4,6-tetra-O-benzyl-$_\alpha$-D-glucopyranosyl)trichloroacetimidate and trimethylsilyl triflate as promoter in methylene chloride first at -25°, then heating up to r.t. [407] [1132].

^{1}H NMR [1046], IR [1046], MS [1046].

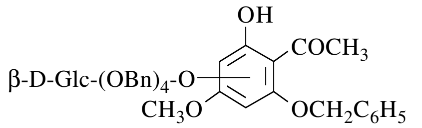
1-[2-Hydroxy-4-methoxy-6-(phenylmethoxy)-3-[2,3,4,6-tetrakis-O-(phenylmethyl)-β-D-glucopyranosyl]phenyl]ethanone

[169566-44-3] $C_{50}H_{50}O_9$ mol.wt. 794.94

and

1-[6-Hydroxy-4-methoxy-2-(phenylmethoxy)-3-[2,3,4,6-tetrakis-O-(phenylmethyl)-β-D-glucopyranosyl]phenyl]ethanone

[169566-55-6] $C_{50}H_{50}O_9$ mol.wt. 794.94



Synthesis

-Obtained (*via* O → C glycoside rearrangement) by adding boron trifluoride etherate to a mixture of 2-(benzyloxy)-6-hydroxy-4-methoxy-acetophenone, 2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl fluoride (R) and powdered molecular sieves 4 Å in methylene chloride and stirring at -78° for 2 h under an argon atmosphere; after the disappearance of (R) on TLC, the reaction temperature was raised from -78° to r.t. and the mixture stirred for 45 min (78%) [1046].

^{1}H NMR [1046], IR [1046], MS [1046].

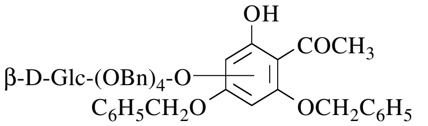
1-[2-Hydroxy-4,6-bis(phenylmethoxy)-3-[2,3,4,6-tetrakis-O-(phenylmethyl)-β-D-glucopyranosyl]phenyl]ethanone

[169566-46-5] $C_{56}H_{54}O_9$ mol.wt. 871.04

and

1-[6-Hydroxy-2,4-bis(phenylmethoxy)-3-[2,3,4,6-tetrakis-O-(phenylmethyl)-β-D-glucopyranosyl]phenyl]ethanone

[169566-56-7] $C_{56}H_{54}O_9$ mol.wt. 871.04



Synthesis

-Obtained (*via* O → C glycoside rearrangement) by adding boron trifluoride etherate to a mixture of 2-acetylphloroglucinol 3,5-bis-(benzyl ether), 2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl fluoride (R) and powdered molecular sieves 4 Å in methylene chloride and stirring at -20° for 2 h under an argon atmosphere; after the disappearance of (R) on TLC, the reaction temperature was raised from -20° to r.t. and the mixture stirred for 45 min (92%) [1046].

colourless syrup [1046]; ^{1}H NMR [1046], IR [1046], MS [1046].

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COMMON ABBREVIATIONS

Common abbreviations used in the dictionary for organic chemistry

Å	Angström units
$(\alpha)_D^{20}$	Specific optical rotation at 20°C for D (sodium) line
b.p.	Boiling point (for example, b.p.$_{0.1}$ 100° means boils at 100° if the pressure is 0.1 mm Hg)
d	Density (for example, d_4^{20} specific gravity at 20°C referred to water at 4°C)
20°	20 degrees Celsius
DEAD	Diethyl azodicarboxylate
dl	Racemic
DME	1,2-Dimethoxyethane (glyme)
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
EIMS	Electron impact mass spectra
GC	Gas chromatography
GLC	Gas liquid chromatography
HMPA	Hexamethylphosphoramide (hexamethylphosphoric triamide),
HMPT	Hexamethylphosphorous triamide
HPLC	High performance (pressure, power) liquid chromatography
^{13}C NMR	Nuclear magnetic resonance relative to carbon 13
(E)	Geometric stereodescriptor used for compounds having achiral elements resulting from double bonds where the groups of highest priority are on the opposite sides of the vertical reference plane
^{19}F NMR	Nuclear magnetic resonance relative to fluorine 19
h	Hour
HREIMS	High resolution electron impact mass spectra
HRMS	High resolution mass spectra
^{1}H NMR	Nuclear magnetic resonance relative to proton
IR	Infrared spectra

iso-	Aliphatic hydrocarbon having two methyl groups on the terminal carbon atom of the chain (for example, isoamyl $(CH_3)_2CH\text{-}CH_2\text{-}CH_2\text{-}$)
m-	Meta-
M	Molar (concentration)
min	Minute
mol	Molecule
mol. equiv.	Molecular equivalent
mol.wt.	Molecular weight
m.p.	Melting point
MS	Mass spectra
n-	Normal (as n-butyl)
N	Normal (equivalents per liter, as applied to concentration)
NA	Not available
N.B.:	Nota bene
NBS	N-Bromosuccinimide
n_D^{20} =	Index of refraction (n_D^{20} for 20°C and sodium light)
o-	Ortho-
p-	Para-
Pd/C	Palladium on charcoal
$PdCl_2$/C	Palladium chloride on charcoal
PdO/C	Palladium oxide on charcoal
pH	Log of reciprocal of hydrogen ion concentration
pK_a	Log of the reciprocal of the dissociation constant, 1/log K_a
Pt/C	Platinum on charcoal
r.t.	Room temperature
sec-	Secondary (as sec-butyl)
SM	Starting material
TBAI	Tetrabutylammonium iodide

tert-	Tertiary (as tert-butyl)
TFE	2,2,2-Trifluoroethanol
THF	Tetrahydrofuran
TLC	Thin layer chromatography
UV	Ultraviolet spectra
(Z)	Opposite of *(E)*

PART 1 MONOKETONES

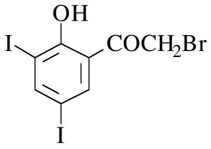
Chapter 2. Compounds derived from halogenoacetic acids

2.1. *Compounds derived from bromoacetic acids*

2.1.1. From monobromoacetic acid

2-Bromo-1-(2-hydroxy-3,5-diiodophenyl)ethanone

[32559-04-9] $C_8H_5BrI_2O_2$ mol.wt. 466.84



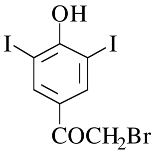
Synthesis

-Preparation by bromination of 2-hydroxy-3,5-diiodoacetophenone in acetic acid at 70-80°, under light irradiation (84%) [332].

m.p. 150-151° [332].

2-Bromo-1-(4-hydroxy-3,5-diiodophenyl)ethanone

[31827-97-1] $C_8H_5BrI_2O_2$ mol.wt. 466.84



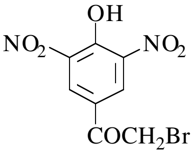
Synthesis

-Preparation by reaction of bromine on 4-hydroxy-3,5-diiodoacetophenone in boiling chloroform under light irradiation (81-83%) [330] [331].

m.p. 171-172° [330] [331]; UV [330].

2-Bromo-1-(4-hydroxy-3,5-dinitrophenyl)ethanone

[120388-18-3] $C_8H_5BrN_2O_6$ mol.wt. 305.04



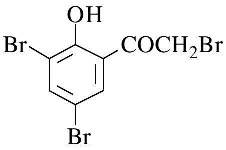
Synthesis

-Preparation by bromination of 4-hydroxy-3,5-dinitroacetophenone with cupric bromide in refluxing ethyl acetate (60%) [210].

m.p. 92-94° [210]; Crystal Data [210].

2-Bromo-1-(3,5-dibromo-2-hydroxyphenyl)ethanone

[194226-52-3] $C_8H_5Br_3O_2$ mol.wt. 372.84



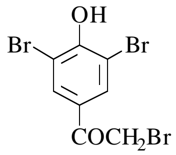
Syntheses

-Preparation by action of bromine with 3,5-dibromo-2-hydroxyacetophenone in refluxing acetic acid for 2.5 h (55%) [490].
-Also obtained by reaction of bromine with 2-hydroxyacetophenone in chloroform in an ice bath for 2 h [1308].

m.p. 107-108° [490]; ^1H NMR [490], IR [490].

2-Bromo-1-(3,5-dibromo-4-hydroxyphenyl)ethanone

[34969-79-4] $C_8H_5Br_3O_2$ mol.wt. 372.84



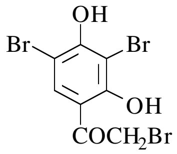
Synthesis

-Preparation by bromination of 3,5-dibromo-4-hydroxyacetophenone in chloroform [1108] [1201] [1246], (79%) [1246].

m.p. 137° [1246], 128° [1108] [1201].

2-Bromo-1-(3,5-dibromo-2,4-dihydroxyphenyl)ethanone

$C_8H_5Br_3O_3$ mol.wt. 388.84



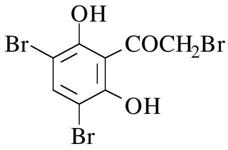
Synthesis

-Preparation by bromination of resacetophenone in acetic acid [1303].

m.p. 112-113° [1303].

2-Bromo-1-(3,5-dibromo-2,6-dihydroxyphenyl)ethanone

[74815-26-2] $C_8H_5Br_3O_3$ mol.wt. 388.84



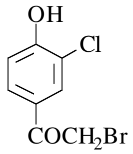
Synthesis

-Preparation by bromination of 2,6-dihydroxyacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture [109].

m.p. 150° [109].

2-Bromo-1-(3-chloro-4-hydroxyphenyl)ethanone

[41877-19-4] $C_8H_6BrClO_2$ mol.wt. 249.49



Syntheses

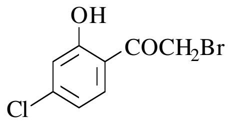
-Preparation by selective bromination of 3-chloro-4-hydroxyacetophenone with dioxane dibromide in dioxane-ethyl ether mixture at r.t. (85%) [1150].

-Preparation by selective bromination of 3-chloro-4-hydroxyacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture [807], (100%) [1340].

m.p. 128-130° [1150]; ^{1}H NMR [1150].

2-Bromo-1-(4-chloro-2-hydroxyphenyl)ethanone

[157068-00-3] $C_8H_6BrClO_2$ mol.wt. 249.49

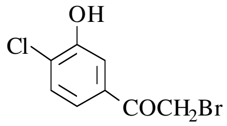


Synthesis

-Obtained by reaction of bromoacetyl bromide on 3-chloroanisole with aluminium chloride in carbon tetrachloride, first at 0°, then at r.t. (16%) [35].

2-Bromo-1-(4-chloro-3-hydroxyphenyl)ethanone

[73898-34-7] $C_8H_6BrClO_2$ mol.wt. 249.49

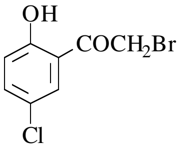


Synthesis

-Preparation by reaction of dioxane dibromide on 4-chloro-3-hydroxyacetophenone in dioxane-ethyl ether mixture at r.t. (84%) [888].

2-Bromo-1-(5-chloro-2-hydroxyphenyl)ethanone

[52727-99-8] $C_8H_6BrClO_2$ mol.wt. 249.49



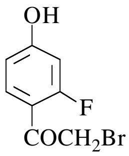
Syntheses

-Preparation by bromination of 5-chloro-2-hydroxyacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture (73%) [416].
-Also refer to: [1113] (compound 1b).

m.p. 64-65° [416]; ^{1}H NMR [416].

2-Bromo-1-(2-fluoro-4-hydroxyphenyl)ethanone

[220131-30-6] $C_8H_6BrFO_2$ mol.wt. 233.04

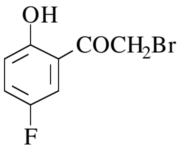


Synthesis

-Refer to: [1436].

2-Bromo-1-(5-fluoro-2-hydroxyphenyl)ethanone

[126581-65-5] $C_8H_6BrFO_2$ mol.wt. 233.04



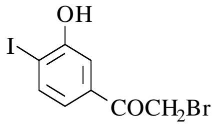
Synthesis

-Preparation by reaction of bromine on 5-fluoro-2-hydroxyacetophenone in dioxane-ethyl ether mixture (80%) [556] [557].

m.p. 86-87° [556] [557]; ^{1}H NMR [557].

2-Bromo-1-(3-hydroxy-4-iodophenyl)ethanone

[73898-36-9] $C_8H_6BrIO_2$ mol.wt. 340.94

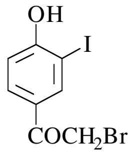


Synthesis

-Preparation by reaction of dioxane dibromide on 3-hydroxy-4-iodoacetophenone in dioxane-ethyl ether mixture at r.t. (75%) [888].

2-Bromo-1-(4-hydroxy-3-iodophenyl)ethanone

[73898-29-0] $C_8H_6BrIO_2$ mol.wt. 340.94

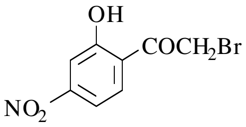


Synthesis

-Preparation by reaction of dioxane dibromide on 4-hydroxy-3-iodoacetophenone in dioxane-ethyl ether mixture at r.t. (87%) [888].

2-Bromo-1-(2-hydroxy-4-nitrophenyl)ethanone

$C_8H_6BrNO_4$ mol.wt. 260.04



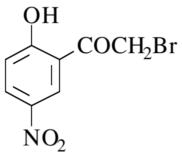
Synthesis

-Preparation by reaction of bromine on 2-hydroxy-4-nitroacetophenone in refluxing acetic acid (63%) [1367].

m.p. 112° [1367].

2-Bromo-1-(2-hydroxy-5-nitrophenyl)ethanone

[5037-70-7] $C_8H_6BrNO_4$ mol.wt. 260.04



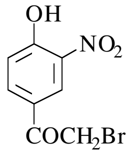
Synthesis

-Preparation by bromination of 2-hydroxy-5-nitroacetophenone in acetic acid (60%) [1367].

m.p. 127° [1367].

2-Bromo-1-(4-hydroxy-3-nitrophenyl)ethanone

[5029-61-8] $C_8H_6BrNO_4$ mol.wt. 260.04



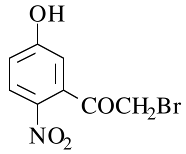
Syntheses

-Preparation by bromination of 4-hydroxy-3-nitroacetophenone in chloroform (74%) [537], (71%) [1367] or in acetic acid (58%) [275].
-Preparation by selective bromination of 4-hydroxy 3-nitroacetophenone with dioxane dibromide in dioxane-ethyl ether mixture at r.t. (94%) [1150].

m.p. 93° [275] [1367], 91°5-92° [537], 80-82° [1150]; b.p.$_{0.2}$ 150-155° [275].

2-Bromo-1-(5-hydroxy-2-nitrophenyl)ethanone

[50695-17-5] $C_8H_6BrNO_4$ mol.wt. 260.04



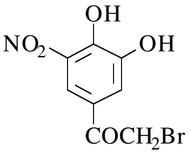
Synthesis

-Obtained by bromination of 5-hydroxy-2-nitroacetophenone in chloroform-carbon tetrachloride-ethyl acetate mixture at 61° (15%) [537].

m.p. 112°5-113° [537].

2-Bromo-1-(3,4-dihydroxy-5-nitrophenyl)ethanone

[134610-95-0] $C_8H_6BrNO_5$ mol.wt. 276.04



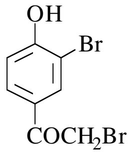
Synthesis

-Preparation by reaction of boron tribromide on 4-hydroxy-3-methoxy-5-nitro-α-bromoacetophenone in methylene chloride [163].

m.p. 138-140° [163].

2-Bromo-1-(3-bromo-4-hydroxyphenyl)ethanone

[41877-18-3] $C_8H_6Br_2O_2$ mol.wt. 293.94



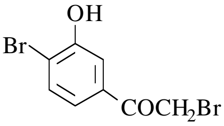
Syntheses

-Preparation by reaction of dioxane dibromide on 3-bromo-4-hydroxyacetophenone in dioxane-ethyl ether mixture at r.t. (82-85%) [888] [1150].
-Preparation by reaction of bromine on 4-hydroxyacetophenone in acetic acid at r.t. (37%) [1246].
-Preparation by reaction of phenyltrimethylammonium tribromide on 4-hydroxy-α-bromoacetophenone [977].
-Also refer to: [1202].

m.p. 143° [1246], 142-144° [1150], 140-142° [1298]; ^{1}H NMR [1150].

2-Bromo-1-(4-bromo-3-hydroxyphenyl)ethanone

[73898-35-8] $C_8H_6Br_2O_2$ mol.wt. 293.94

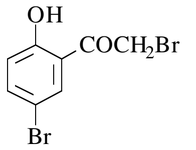


Synthesis

-Preparation by selective bromination of 4-bromo-3-hydroxyacetophenone with dioxane dibromide in dioxane-ethyl ether mixture at r.t. (79%) [888].

2-Bromo-1-(5-bromo-2-hydroxyphenyl)ethanone

[67029-74-7] $C_8H_6Br_2O_2$ mol.wt. 293.94



Syntheses

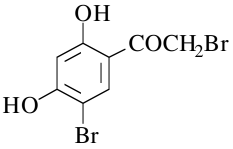
-Claimed to be prepared from 2-hydroxyacetophenone or 5-bromo-2-hydroxyacetophenone by reaction of bromine in glacial acetic acid and from 2-hydroxy-α-bromo-acetophenone by reaction of bromine in 50% aqueous acetic acid (quantitative yields) (m.p. 107°) [247]. No proof of structure was provided [146]. Actually, it probably concerns 3,5-dibromo-2-hydroxyacetophenone (m.p. 108° [105], 108-109° [1246]), as the use of acetic acid as solvent favours the aromatic ring bromination.

-Preparation by bromination of 5-bromo-2-hydroxyacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture [146] [807], (50%) [146].

m.p. 107° [247], 69° [146].
One of the reported melting points is obviously wrong.
^1H NMR [146], IR [146].

2-Bromo-1-(5-bromo-2,4-dihydroxyphenyl)ethanone

[99657-26-8] $C_8H_6Br_2O_3$ mol.wt. 309.94

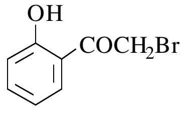


Synthesis

-Preparation by bromination of 5-bromo-2,4-dihydroxy-acetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture [334] [807].

2-Bromo-1-(2-hydroxyphenyl)ethanone

[2491-36-3] $C_8H_7BrO_2$ mol.wt. 215.05



Syntheses

-Preparation by bromination of 2-hydroxyacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture [293] [334] [807] [952] [1049] [1100] [1340], (100%) [293] [807], (56%) [1340], (36%) [952].

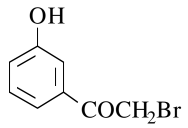
-Preparation by reaction of bromine on 2-hydroxyacetophenone in acetic acid at r.t. (47%) [247] or in a mixture of ethyl ether and chloroform [1100] according to [522].

-Preparation by Fries rearrangement of phenyl bromoacetate with aluminium chloride without solvent at 120-140° (45-50%) [1046] [1494].

m.p. 70-71° [1494], 45° [247], 44-45° [1340], 41-43° [1049], 40° [807], 39-41° [952].
One of the reported melting points is obviously wrong.
b.p.$_{7-10}$ 120-125° [1046], b.p.$_{18}$ 152-158° [247];
^1H NMR [952], UV [666].

2-Bromo-1-(3-hydroxyphenyl)ethanone

[2491-37-4] $C_8H_7BrO_2$ mol.wt. 215.05



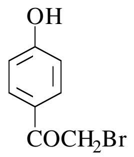
Syntheses

-Preparation by bromination of 3-hydroxyacetophenone,
*with cupric bromide in refluxing chloroform-ethyl acetate mixture [293] [807] [997] [1049] [1340], (quantitative yield) [293] [807] [1340];
*with dioxane dibromide in dioxane-ethyl ether mixture at r.t. (91%) [1150];
*in using silica gel coated with cupric bromide in refluxing ethyl acetate (94%) [927];
*with bromine in chloroform at 2° (96%) [244].

m.p. 74-75° [1150], 70-72° [244]; amorphous [927];
^{1}H NMR [927] [1150], IR [244] [927], UV [244], MS [927].

2-Bromo-1-(4-hydroxyphenyl)ethanone

[2491-38-5] $C_8H_7BrO_2$ mol.wt. 215.05



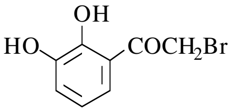
Syntheses

-Preparation by bromination of 4-hydroxyacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture [293] [807] [952] [997] [1048] [1049] [1100] [1340], (quantitative yield) [293] [807] [1340], (34-38%) [952] [997], (15%) [1048].
-Preparation by reaction of dioxane dibromide on 4-hydroxyacetophenone in dioxane-ethyl ether mixture at r.t. (86%) [1150].
-Preparation by bromination of 4-hydroxyacetophenone in acetic acid (63%) [251] or in a mixture of ethyl ether and chloroform [1100] according to [522].
-Preparation by Fries rearrangement of phenyl bromoacetate with aluminium chloride without solvent between 120-140° (40%) [1046], (30%) [1494].
-Preparation by reaction of tetrabutylammonium tribromide, benzyltrimethylammonium tribromide or phenyltrimethylammonium tribromide on 4-hydroxyacetophenone in tetrahydrofuran [977].
-Preparation by reaction of ammonium tribromide on 4-hydroxyacetophenone in methylene chloride-methanol mixture [977].
-Preparation by reaction of silica gel coated with cupric bromide on 4-hydroxyacetophenone in refluxing ethyl acetate (95%) [927].
-Preparation by sonochemical bromination of 4-hydroxyacetophenone using p-toluenesulfonic acid/N-bromosuccinimide in methanol for 6 h at 35-37°(97%) [8]. **N.B.**: In the absence of ultrasound the reaction takes place at the boiling point of methanol (65°) for 24 h (58%) [8].
-Also refer to: [80] [782] [854] [878] [1434].

m.p. 146° [1494], 132-133° [397], 130-131° [952], 130° [251], 129-131° [997], 128-130° [977], 128-129° [1046], 126-127° [1048], 125-129° [8], 124-126° [807] [1150], 121-122° [927], 105-108° [1414];
^{1}H NMR [8] [397] [927] [952] [1048] [1150], IR [8] [927], UV [1048], MS [397] [927].

2-Bromo-1-(2,3-dihydroxyphenyl)ethanone

[19278-79-6] $C_8H_7BrO_3$ mol.wt. 231.05



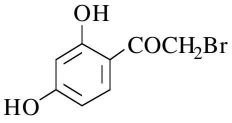
Synthesis

-Obtained by reaction of hydrobromic acid on 2,3-diacetoxy-α-bromoacetophenone in refluxing ethanol [1294].

m.p. 75-76° [1294]; UV [666].

2-Bromo-1-(2,4-dihydroxyphenyl)ethanone

[2491-39-6] $C_8H_7BrO_3$ mol.wt. 231.05



Syntheses

-Preparation by bromination of resacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture (quantitative yield) [293] [807], (3%) [952].

-Also obtained by reaction of bromoacetonitrile on resorcinol with zinc chloride and hydrobromic acid in ethyl ether (Hoesch reaction) [1380] [1382].

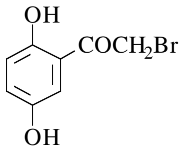
-Also obtained by reaction of bromoacetyl chloride on resorcinol with aluminium bromide or aluminium chloride in carbon disulfide [1048] [1062], (80%) [1062], (12%) [1048].

-Also obtained (poor yield) by reaction of bromoacetic acid on resorcinol with zinc chloride or phosphorous oxychloride [436] [516].

m.p. 144-145° [807], 127° [1380] [1382], 126-128° [1048], 118-119° [952].
There is discrepancy between the different melting points.
^{1}H NMR [952] [1048], UV [1048].

2-Bromo-1-(2,5-dihydroxyphenyl)ethanone

[25015-91-2] $C_8H_7BrO_3$ mol.wt. 231.05



Syntheses

-Preparation by bromination of 2,5-dihydroxyacetophenone,
*with cupric bromide in refluxing chloroform-ethyl acetate mixture (74-87%) [293] [807] [1193], (70%) [1277], (37%) [952];
*with bromine in acetic acid at 55-58° (16%) [137].

-Preparation by reaction of hydrobromic acid on 5-α-bromoacetoxy-2-hydroxy-α-bromoacetophenone in methanol at r.t. (87%) [819].

-Preparation by reaction of aluminium bromide on 2-hydroxy-5-methoxy-α-bromo-acetophenone in carbon disulfide at r.t. (87%) [819].

-Also obtained by action of acetic acid saturated with hydrobromic acid (10 min, r.t.) on 2,5-diacetoxy-α-diazoacetophenone, reduced pressure elimination of acetic acid, then action (overnight, r.t.) of a methanolic solution of hydrobromic acid (59%) [819].

-Also obtained by reaction of aluminium bromide on 2,5-dimethoxy-α-chloroacetophenone in refluxing carbon disulfide (28%) [819].

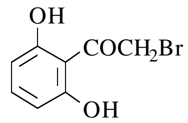
-Also obtained by reaction of bromoacetyl bromide on 1,4-dimethoxybenzene with aluminium bromide at r.t. (11%) [1048], (2%) [819].

-Also obtained by reaction of phenyltrimethylammonium bromide tribromide with 2,5-dihydroxyacetophenone in THF at r.t. overnight (63%) [216], according to [217].

m.p. 120-121° [137], 117°5-119° [819], 117-119° [1048], 114-116° [1277], 113-115° [952] [1193], 112-113° [807];
TLC [216]; flash chromatography [216];
^{1}H NMR [137] [216] [819] [952] [1048] [1277], IR [216] [1277], UV [137] [216] [666] [1048], MS [216] [1277].

2-Bromo-1-(2,6-dihydroxyphenyl)ethanone

[2491-40-9] $C_8H_7BrO_3$ mol.wt. 231.05



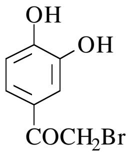
Syntheses

-Preparation by bromination of 2,6-dihydroxyacetophenone with cupric bromide in refluxing ethyl acetate (quantitative yield) [1340].
-Preparation by reaction of 40% hydrobromic acid on 2,6-diacetoxy-α-bromoacetophenone in refluxing 60% ethanol (73%) [1356].
-Refer to: [1287] (Japanese patent).

m.p. 143° [1356]; UV [666].

2-Bromo-1-(3,4-dihydroxyphenyl)ethanone

[40131-99-5] $C_8H_7BrO_3$ mol.wt. 231.05



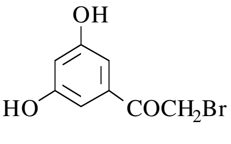
Syntheses

-Preparation by reaction of bromoacetic acid on pyrocatechol with phosphorous oxychloride [437].
-Preparation by reaction of bromoacetyl bromide on pyrocatechol with aluminium bromide in carbon disulfide at r.t. (63%) [827].
-Preparation by reaction of bromine on 3,4-dihydroxyacetophenone in chloroform at r.t. [975] [1054].
-Also refer to: [27] [521] [606] [946] [1181] [1202] and [1064] (Japanese patent).

m.p. 167° [437], 61° [827]. One of the reported melting points is obviously wrong.
^{1}H NMR [827], IR [827], UV [827], MS [827].

2-Bromo-1-(3,5-dihydroxyphenyl)ethanone

[62932-92-7] $C_8H_7BrO_3$ mol.wt. 231.05

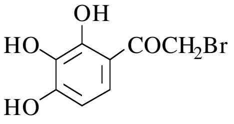


Syntheses

-Preparation by reaction of bromine on 3,5-dihydroxyacetophenone in chloroform at r.t. [975].
-Also refer to: [521] [1202].

2-Bromo-1-(2,3,4-trihydroxyphenyl)ethanone

[105190-52-1] $C_8H_7BrO_4$ mol.wt. 247.05



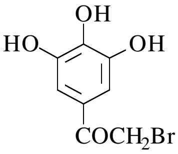
Syntheses

-Preparation by reaction of bromoacetyl bromide on pyrogallol with aluminium bromide in carbon disulfide at r.t. (42%) [827].
-Also obtained by reaction of bromoacetic acid on pyrogallol with phosphorous oxychloride [1083], (poor yield) [436] [516] or with zinc chloride (poor yield) [436] [516].

m.p. 159° [1083], 138° [827]. One of the reported melting points is obviously wrong.
^{1}H NMR [827], IR [827], UV [827], MS [827].

2-Bromo-1-(3,4,5-trihydroxyphenyl)ethanone

[111011-09-7] $C_8H_7BrO_4$ mol.wt. 247.05

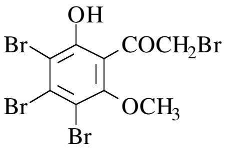


Synthesis

-Refer to: [1566].

2-Bromo-1-(3,4,5-tribromo-2-hydroxy-6-methoxyphenyl)ethanone

[98592-28-0] $C_9H_6Br_4O_3$ mol.wt. 481.76

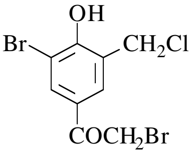


Synthesis not yet described

-Only one reference dealing with 2,3',4',5'-tetrabromo-2'-hydroxy-6'-methoxyacetophenone does exist. This reference [Chem. Abstr., Formula Index, page 112F, **52**, 2796h (1958)] is obviously erroneous. The described product is actually 2,2,3',5'-tetrabromo-2'-hydroxy-6'-methoxyacetophenone, since in the original paper [358] it is specified that two labile bromine atoms are present in the molecule.

2-Bromo-1-[3-bromo-5-(chloromethyl)-4-hydroxyphenyl]ethanone

[107700-04-9] $C_9H_7Br_2ClO_2$ mol.wt. 342.41



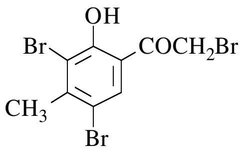
Synthesis

-Preparation by adding a methylene chloride solution of bromine to a methanol/methylene chloride solution of 3-(chloromethyl)-4-hydroxyacetophenone at r.t. (80%) [214].

m.p. 95° [214]; ^{1}H NMR [214], IR [214], MS [214].

2-Bromo-1-(3,5-dibromo-2-hydroxy-4-methylphenyl)ethanone

[260435-53-8] $C_9H_7Br_3O_2$ mol.wt. 386.87



Syntheses

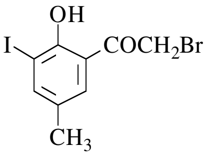
-Preparation by reaction of bromine with 2-hydroxy-4-methylacetophenone in chloroform/ethylene dichloride mixture, first in an ice-water bath, then for 2 h at r.t. (50%) [1307].

-Preparation by reaction of bromine with 3,5-dibromo-2-hydroxy-4-methylacetophenone in acetic acid first at r.t., then at reflux to discolouration (72%) [186].

m.p. 139-140° [1307], 136-137° [186];
^{1}H NMR [186] [1307], IR [186] [1307].

2-Bromo-1-(2-hydroxy-3-iodo-5-methylphenyl)ethanone

[194226-48-7] $C_9H_8BrIO_2$ mol.wt. 354.97

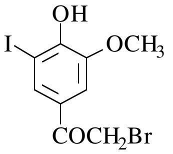


Synthesis

-Preparation [1279] (compound 1a) according to described procedure [270] (Romanian patent).

2-Bromo-1-(4-hydroxy-3-iodo-5-methoxyphenyl)ethanone

[144978-69-8] $C_9H_8BrIO_3$ mol.wt. 370.97



Syntheses

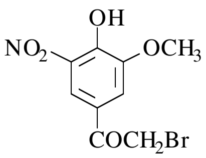
-Preparation by reaction of bromine with 5-iodoacetovanillone in chloroform (quantitative yield) [892].

-Preparation from 4-hydroxy-3-methoxy-α-bromoacetophenone by the oxidative procedure using chloramine T and sodium iodide in DMF, DMSO or acetonitrile [826] [892].

^{1}H NMR [892], ^{13}C NMR [892], MS [892].

2-Bromo-1-(4-hydroxy-3-methoxy-5-nitrophenyl)ethanone

[125629-36-9] $C_9H_8BrNO_5$ mol.wt. 290.07



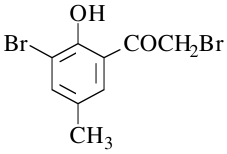
Synthesis

-Preparation by reaction of 96% nitric acid on 4-hydroxy-3-methoxy-α-bromoacetophenone in acetic acid at 20-25° [163] [211], (72%) [211].

m.p. 147-149° [163] [211]; ^{1}H NMR [211].

2-Bromo-1-(3-bromo-2-hydroxy-5-methylphenyl)ethanone

[194226-50-1] $C_9H_8Br_2O_2$ mol.wt. 307.97



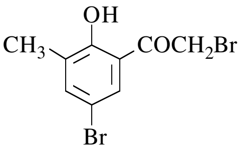
Syntheses

-Preparation by reaction of bromine on 2-hydroxy-5-methyl-α-bromoacetophenone in 50% aqueous acetic acid at 60° (75%) [247].
-Also obtained by reaction of bromine with 2-hydroxy-5-methylacetophenone in chloroform in an ice bath for 2 h [1308].

m.p. 106° [247].

2-Bromo-1-(5-bromo-2-hydroxy-3-methylphenyl)ethanone

[194226-51-2] $C_9H_8Br_2O_2$ mol.wt. 307.97



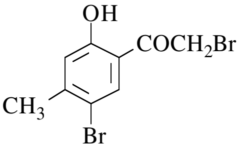
Synthesis

-Preparation by reaction of bromine (1 mol) with 5-bromo-2-hydroxy-3-methylacetophenone (1 mol) in acetic acid on a water bath for 20 min (47%) [185].

m.p. 72-73° [185]; ^1H NMR [185], IR [185].

2-Bromo-1-(5-bromo-2-hydroxy-4-methylphenyl)ethanone

[194226-49-8] $C_9H_8Br_2O_2$ mol.wt. 307.97

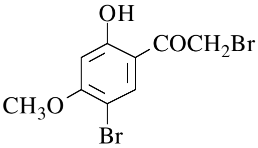


Synthesis

-Obtained by reaction of bromine with 2-hydroxy-4-methylacetophenone in chloroform in an ice bath for 2 h [1308].

2-Bromo-1-(5-bromo-2-hydroxy-4-methoxyphenyl)ethanone

$C_9H_8Br_2O_3$ mol.wt. 323.97



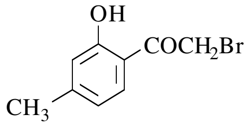
Syntheses

-Obtained by reaction of bromine with 3,3'-diacetyl-4,4'-dihydroxy-6,6'-dimethoxydiphenyl ether in acetic acid in the presence of a crystal of iodine, first at 90°, then at r.t. overnight [691].
-Also obtained (by-product) by reaction of bromine on 5-bromo-2-hydroxy-4-methoxyacetophenone in acetic acid [238].

m.p. 178-180° [238], 72-73° [691]. One of the reported melting points is obviously wrong.

2-Bromo-1-(2-hydroxy-4-methylphenyl)ethanone

[144219-74-9] $C_9H_9BrO_2$ mol.wt. 229.07



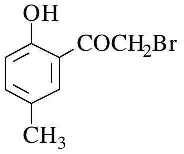
Synthesis

-Preparation by reaction of bromine with 2-acetoxy-4-methylacetophenone in refluxing chloroform (44%) [571].

colourless oil [571];
^{1}H NMR [571], IR [571], MS [571].

2-Bromo-1-(2-hydroxy-5-methylphenyl)ethanone

[51317-87-4] $C_9H_9BrO_2$ mol.wt. 229.07



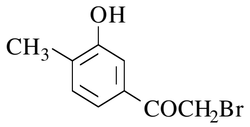
Syntheses

-Preparation by reaction of bromoacetic acid on p-cresol with boron trifluoride into an autoclave at 70° (90%) [1111].
-Preparation by Fries rearrangement of p-cresyl bromoacetate with aluminium chloride without solvent at 125° (47%) [1541].
-Preparation by reaction of bromine on 2-hydroxy-5-methylacetophenone in acetic acid at r.t. (39%) [247].

m.p. 45°5-46°5 [1541], 44-45° [1111].

2-Bromo-1-(3-hydroxy-4-methylphenyl)ethanone

[73898-30-3] $C_9H_9BrO_2$ mol.wt. 229.07

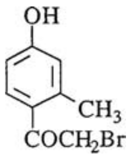


Synthesis

-Preparation by selective bromination of 3-hydroxy-4-methylacetophenone with dioxane dibromide in dioxane-ethyl ether mixture at r.t. (42%) [888].

2-Bromo-1-(4-hydroxy-2-methylphenyl)ethanone

[41877-16-1] $C_9H_9BrO_2$ mol.wt. 229.07



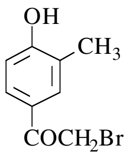
Synthesis

-Preparation by selective bromination of 4-hydroxy-2-methylacetophenone with dioxane dibromide in dioxane-ethyl ether mixture at r.t. (86%) [1150].

m.p. 122-124° [1150];
^{1}H NMR [1150].

2-Bromo-1-(4-hydroxy-3-methylphenyl)ethanone

[41877-17-2] $C_9H_9BrO_2$ mol.wt. 229.07



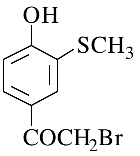
Syntheses

-Preparation by selective bromination of 4-hydroxy-3-methylacetophenone with dioxane dibromide in dioxane-ethyl ether mixture at r t. (98%) [1150], (78%) [888].
-Preparation by selective bromination of 4-hydroxy-3-methylacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture (quantitative yield) [1340].

m.p. 124-125° [1150]; ^{1}H NMR [1150].

2-Bromo-1-[4-hydroxy-3-(methylthio)phenyl]ethanone

[66265-63-2] $C_9H_9BrO_2S$ mol.wt. 261.14



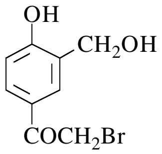
Synthesis

-Preparation by reaction of dioxane dibromide on 4-hydroxy-3-(methylthio)acetophenone in dioxane-ethyl ether mixture (75%) [1177] [1403].

solid [1177].

2-Bromo-1-[4-hydroxy-3-(hydroxymethyl)phenyl]ethanone

[62932-94-9] $C_9H_9BrO_3$ mol.wt. 245.07

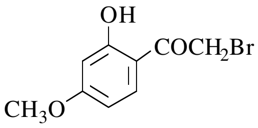


Syntheses

-Refer to: [142] [320] [491] [815] [816] [818] [939] [1203] [1368].

2-Bromo-1-(2-hydroxy-4-methoxyphenyl)ethanone

[60965-24-4] $C_9H_9BrO_3$ mol.wt. 245.07



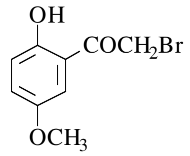
Syntheses

-Obtained by reaction of cupric bromide with 2-hydroxy-4-methoxyacetophenone, in refluxing chloroform-ethyl acetate mixture [1100] [1340], (quantitative yield) [1340] according to [807], (62%) [24] or in refluxing dioxane (44%) [405], (10%) [952].
-Preparation by reaction of bromine with 2-hydroxy-4-methoxyacetophenone in a mixture of ethyl ether and chloroform [1100] according to [522].
-Preparation from resorcinol dimethyl ether,
*by reaction of bromoacetyl bromide with aluminium bromide at r.t. [1438];
*by reaction of bromoacetyl chloride with aluminium chloride in carbon disulfide [96] [405], (23%) [405].
-Preparation by reaction of bromoacetonitrile on resorcinol dimethyl ether with hydrobromic acid gas in ethyl ether [1382].

m.p. 161° [405], 92° [1438], 90-92° [952], 70-72° [24].
There is discrepancy between the different melting points.
^{1}H NMR [24] [952], IR [24], MS [24].

2-Bromo-1-(2-hydroxy-5-methoxyphenyl)ethanone

[203524-87-2] $C_9H_9BrO_3$ mol.wt. 245.07



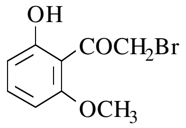
Syntheses

-Preparation by reaction of bromoacetyl bromide on 1,4-dimethoxybenzene with aluminium bromide at r.t. (18%) [819].
-Also refer to: [1480].

m.p. 65-66° [819].

2-Bromo-1-(2-hydroxy-6-methoxyphenyl)ethanone

[50879-47-5] $C_9H_9BrO_3$ mol.wt. 245.07



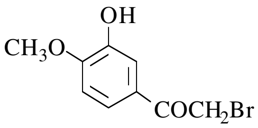
Synthesis

-Claimed to be prepared by bromination of 2-hydroxy-6-methoxyacetophenone in glacial acetic acid [1170].
N.B.: It has been observed that glacial acetic acid promotes side chain bromination of 2-hydroxyacetophenones [251]. However, actually, 3-bromo-2-hydroxy-6-methoxyacetophenone was obtained by bromination of 2-hydroxy-6-methoxyacetophenone in glacial acetic acid, dilute acetic acid (80%) or acetic anhydride [150] [414].

m.p. 106° [414] [1170].

2-Bromo-1-(3-hydroxy-4-methoxyphenyl)ethanone

[90971-90-7] $C_9H_9BrO_3$ mol.wt. 245.07

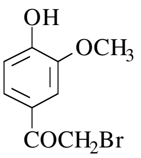


Synthesis

-Preparation by reaction of cupric bromide on 3-hydroxy-4-methoxyacetophenone in refluxing dioxane (80%) [1340].

2-Bromo-1-(4-hydroxy-3-methoxyphenyl)ethanone

[69638-06-8] $C_9H_9BrO_3$ mol.wt. 245.07



Syntheses

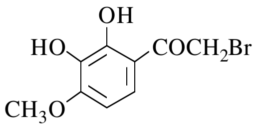
-Preparation by reaction of cupric bromide on 4-hydroxy-3-methoxyacetophenone in refluxing chloroform-ethyl acetate mixture (quantitative yield) [1340].
-Preparation by reaction of bromoacetyl bromide on guaiacol with aluminium chloride in carbon disulfide (75%) [1235].

-Preparation by reaction of bromine with 4-hydroxy-3-methoxyacetophenone [397] [399] in ice cooled solution of ethyl ether and dioxane (quantitative yield) [399].

m.p. 78-79° [1235]; ^{1}H NMR [399], IR [399], MS [399].

2-Bromo-1-(2,3-dihydroxy-4-methoxyphenyl)ethanone

[204648-67-9] $C_9H_9BrO_4$ mol.wt. 261.07

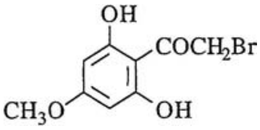


Synthesis

-Refer to: [862] (Japanese patent).

2-Bromo-1-(2,6-dihydroxy-4-methoxyphenyl)ethanone

$C_9H_9BrO_4$ mol.wt. 261.07



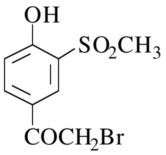
Synthesis

-Preparation by hydrolysis of 2,6-dihydroxy-4-methoxy-α-bromoacetophenone with 16% hydrobromic acid in refluxing ethanol (94%) [426].

m.p. 139°5-140°5 (d) [426].

2-Bromo-1-[4-hydroxy-3-(methylsulfonyl)phenyl]ethanone

[66264-67-3] $C_9H_9BrO_4S$ mol.wt. 293.14



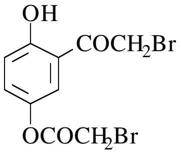
Synthesis

-Preparation by reaction of aluminium chloride on 4-methoxy-3-(methylsulfonyl)-α-bromoacetophenone in refluxing chlorobenzene (70%) [1403].

crystalline solid [1403].

2-Bromo-1-[5-(2-bromoacetyloxy)-2-hydroxyphenyl]ethanone

$C_{10}H_8Br_2O_4$ mol.wt. 352.00



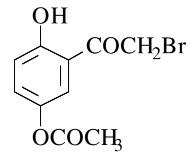
Synthesis

-Preparation by reaction of bromoacetyl bromide on hydroquinone dimethyl ether with aluminium bromide (13-16%) [819] [1048].

m.p. 106-107° [819], 105-107° [1048].

1-[5-(Acetyloxy)-2-hydroxyphenyl]-2-bromoethanone

$C_{10}H_9BrO_4$ mol.wt. 273.08



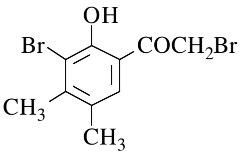
Synthesis

-Preparation from 2,5-dihydroxy-α-bromoacetophenone on heating with acetyl bromide (62%) [819].

m.p. 143°5-144° [819].

2-Bromo-1-(3-bromo-2-hydroxy-4,5-dimethylphenyl)ethanone

[319923-52-9] $C_{10}H_{10}Br_2O_2$ mol.wt. 322.00



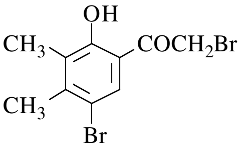
Synthesis

-Preparation by reaction of bromine with 3-bromo-2-hydroxy-4,5-dimethylacetophenone in acetic acid first at r.t., then at reflux to discolouration (2 min) (80%) [187].

m.p. 109-110° [187]; ^1H NMR [187], IR [187].

2-Bromo-1-(5-bromo-2-hydroxy-3,4-dimethylphenyl)ethanone

[260430-25-9] $C_{10}H_{10}Br_2O_2$ mol.wt. 322.00



Syntheses

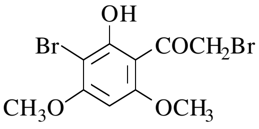
-Preparation by reaction of bromine with 2-hydroxy-3,4-dimethylacetophenone,
*in chloroform/ethylene dichloride mixture, first in an ice-water bath, then for 1 h at r.t. (68%) [1307];
*in chloroform in an ice-water bath for 2 h [1308].

-Preparation by reaction of bromine with 5-bromo-2-hydroxy-3,4-dimethylacetophenone in acetic acid first at r.t., then at reflux to discolouration (2 min) (68%) [187].

m.p. 97-98° [187] [1307]; ^1H NMR [187] [1307], IR [187] [1307].

2-Bromo-1-(3-bromo-2-hydroxy-4,6-dimethoxyphenyl)ethanone

[29784-35-8] $C_{10}H_{10}Br_2O_4$ mol.wt. 354.00



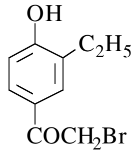
Synthesis

-Obtained by reaction of bromine on 2-hydroxy-4,6-dimethoxyacetophenone in chloroform (22%) [150].

m.p. 194-195° [150]; ^1H NMR [150].

2-Bromo-1-(3-ethyl-4-hydroxyphenyl)ethanone

[73898-24-5] $C_{10}H_{11}BrO_2$ mol.wt. 243.10

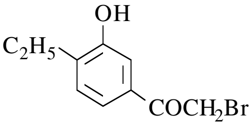


Syntheses

-Preparation by reaction of dioxane dibromide on 3-ethyl-4-hydroxyacetophenone in dioxane-ethyl ether mixture at r.t. (63%) [888].
-Also refer to: [955].

2-Bromo-1-(4-ethyl-3-hydroxyphenyl)ethanone

[73898-31-4] $C_{10}H_{11}BrO_2$ mol.wt. 243.10

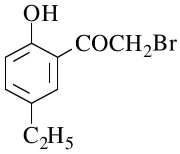


Synthesis

-Preparation by reaction of dioxane dibromide on 4-ethyl-3-hydroxyacetophenone in dioxane-ethyl ether mixture at r.t. (67%) [888].

2-Bromo-1-(5-ethyl-2-hydroxyphenyl)ethanone

[180154-50-1] $C_{10}H_{11}BrO_2$ mol.wt. 243.10

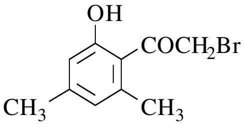


Synthesis

-Refer to: [903].

2-Bromo-1-(2-hydroxy-4,6-dimethylphenyl)ethanone

[67029-80-5] $C_{10}H_{11}BrO_2$ mol.wt. 243.10

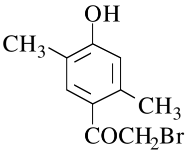


Synthesis

-Preparation by reaction of cupric bromide on 2-hydroxy-4,6-dimethylacetophenone in refluxing chloroform-ethyl acetate mixture [146].

2-Bromo-1-(4-hydroxy-2,5-dimethylphenyl)ethanone

[107584-78-1] $C_{10}H_{11}BrO_2$ mol.wt. 243.10



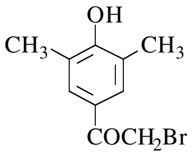
Synthesis

-Preparation from 4-hydroxy-2,5-dimethylacetophenone by standard bromination procedure according to [399], (62%) [397].

m.p. 129-131° [397]; ^1H NMR [397], MS [397].

2-Bromo-1-(4-hydroxy-3,5-dimethylphenyl)ethanone

[157014-27-2] $C_{10}H_{11}BrO_2$ mol.wt. 243.10



Syntheses

-Preparation by reaction of 4-hydroxy-3,5-dimethyl-α-chloroacetophenone in boiling methylene chloride with 46-48% aqueous hydrobromic acid in the presence of tetrabutylammonium bromide (0.3 M relative to the ketone) for 24 h, (87% yield) [171].

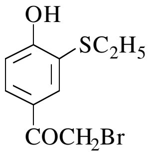
-Also obtained from 4-(benzyloxy)-3,5-dimethyl-α-bromoacetophenone by the former treatment (83%) [170].

-Also refer to: [104].

m.p. 131° [171], 130°6 [170]; ^{1}H NMR [170] [171], IR [170], MS [170] [171].

2-Bromo-1-[4-hydroxy-3-(ethylthio)phenyl]ethanone

$C_{10}H_{11}BrO_2S$ mol.wt. 275.17

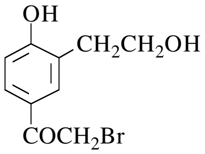


Synthesis

-Preparation by reaction of bromine on 3-(ethylthio)-4-hydroxyacetophenone in chloroform, in the presence of calcium carbonate at 25° [436] [1403].

2-Bromo-1-[4-hydroxy-3-(2-hydroxyethyl)phenyl]ethanone

[101386-50-9] $C_{10}H_{11}BrO_3$ mol.wt. 259.10

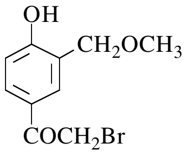


Syntheses

-Refer to: [492] [493].

2-Bromo-1-[4-hydroxy-3-(methoxymethyl)phenyl]ethanone

[91363-39-2] $C_{10}H_{11}BrO_3$ mol.wt. 259.10

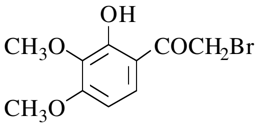


Synthesis

-Refer to: [494].

2-Bromo-1-(2-hydroxy-3,4-dimethoxyphenyl)ethanone

[18064-92-1] $C_{10}H_{11}BrO_4$ mol.wt. 275.10



Syntheses

-Preparation by reaction of cupric bromide on 2-hydroxy-3,4-dimethoxyacetophenone [353] or 2,3,4-trimethoxyacetophenone [729] in refluxing chloroform-ethyl acetate mixture (47%) [353], (26%) [729].

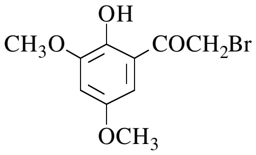
-Preparation by reaction of bromine on 2-hydroxy-3,4-dimethoxyacetophenone in chloroform-ethyl ether solution (44%) [522].

-Preparation by reaction of bromoacetyl chloride with 1,2,3-trimethoxybenzene in the presence of aluminium chloride in methylene chloride at 20° (42%) [1493].

m.p. 144-145° [522], 142° [1493], 140-142°5 [729], 140-141° [353];
^{1}H NMR [353] [522] [729], IR [522] [1492] [1493].

2-Bromo-1-(2-hydroxy-3,5-dimethoxyphenyl)ethanone

[204648-51-1] $C_{10}H_{11}BrO_4$ mol.wt. 275.10

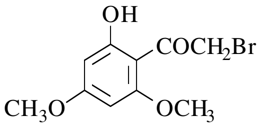


Synthesis

-Refer to: [862] (Japanese patent).

2-Bromo-1-(2-hydroxy-4,6-dimethoxyphenyl)ethanone

[18064-88-5] $C_{10}H_{11}BrO_4$ mol.wt. 275.10



Syntheses

-Preparation by reaction of aluminium bromide with 2,4,6-trimethoxy-α-bromoacetophenone at 120° [514].

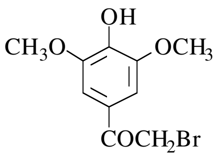
-Preparation by reaction of bromoacetyl bromide with phloroglucinol trimethyl ether according to [425], but using aluminium bromide instead of aluminium chloride in carbon disulfide at r.t. [514].

-Also obtained by reaction of cupric bromide on 2-hydroxy-4,6-dimethoxyacetophenone in refluxing chloroform-ethyl acetate mixture [293] [729], (2%) [729].

m.p. 130-131° [514], 125-126° [729]; ^{1}H NMR [293] [729], MS [293].

2-Bromo-1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone

[51149-28-1] $C_{10}H_{11}BrO_4$ mol.wt. 275.10



Syntheses

-Preparation by bromination of 4-hydroxy-3,5-dimethoxyacetophenone with,

*bromine in chloroform [640] [809] [892] [1005], (90%) [809], (27%) [1005];

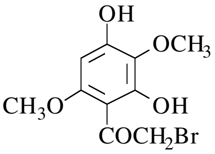
*cupric bromide in a refluxing mixture of ethyl acetate and chloroform [1477].

-Also refer to: [377].

m.p. 130° [809], 118-120° [1005]; ^{1}H NMR [809] [1005], IR [1005], MS [1477].

2-Bromo-1-(2,4-dihydroxy-3,6-dimethoxyphenyl)ethanone

$C_{10}H_{11}BrO_5$ mol.wt. 291.10



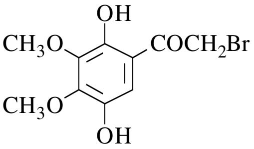
Synthesis

-Preparation by reaction of NBS on 2,4-dihydroxy-3,6-dimethoxyacetophenone in refluxing carbon tetrachloride (64%) [548].

m.p. 159-160° [548].

2-Bromo-1-(2,5-dihydroxy-3,4-dimethoxyphenyl)ethanone

[204648-54-4] $C_{10}H_{11}BrO_5$ mol.wt. 291.10

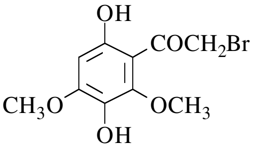


Synthesis

-Refer to: [862] (Japanese paper).

2-Bromo-1-(3,6-dihydroxy-2,4-dimethoxyphenyl)ethanone

[204648-57-7] $C_{10}H_{11}BrO_5$ mol.wt. 291.10

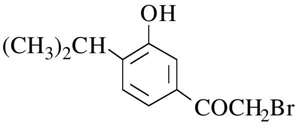


Synthesis

-Refer to: [862] (Japanese paper).

2-Bromo-1-[3-hydroxy-4-(1-methylethyl)phenyl]ethanone

[73898-32-5] $C_{11}H_{13}BrO_2$ mol.wt. 257.13

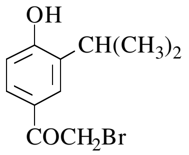


Synthesis

-Preparation by bromination of 3-hydroxy-4-isopropylacetophenone with dioxane dibromide in dioxane-ethyl ether mixture at r.t. (78%) [888].

2-Bromo-1-[4-hydroxy-3-(1-methylethyl)phenyl]ethanone

[73898-25-6] $C_{11}H_{13}BrO_2$ mol.wt. 257.13

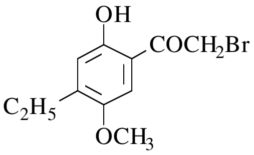


Synthesis

-Preparation by bromination of 4-hydroxy-3-isopropylacetophenone with dioxane dibromide in dioxane-ethyl ether mixture at r.t. (55%) [888].

2-Bromo-1-(4-ethyl-2-hydroxy-5-methoxyphenyl)ethanone

$C_{11}H_{13}BrO_3$ mol.wt. 273.13



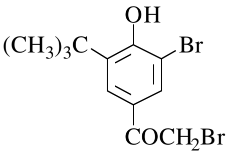
Synthesis

-Preparation by reaction of bromine on 4-ethyl-2-hydroxy-5-methoxyacetophenone in acetic acid at r.t. (59%) [1214].

m.p. 75-76° [1214].

2-Bromo-1-[3-bromo-5-(1,1-dimethylethyl)-4-hydroxyphenyl]ethanone

[153355-99-8] $C_{12}H_{14}Br_2O_2$ mol.wt. 350.05

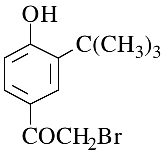


Synthesis

-Refer to: [1562] (Japanese patent).

2-Bromo-1-[3-(1,1-dimethylethyl)-4-hydroxyphenyl]ethanone

[118788-50-4] $C_{12}H_{15}BrO_2$ mol.wt. 271.15

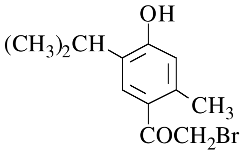


Synthesis

-Refer to: [1457].

2-Bromo-1-[4-hydroxy-2-methyl-5-(1-methylethyl)phenyl]ethanone

[205655-36-3] $C_{12}H_{15}BrO_2$ mol.wt. 271.15

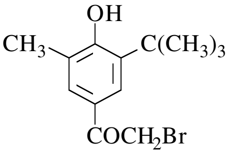


Synthesis

-Refer to: [1395].
N.B.: All reagents and starting materials were from commercial sources. This compound was called 4-hydroxy-3-isopropyl-6-methyl phenacyl bromide (p.185).

2-Bromo-1-[3-(1,1-dimethylethyl)-4-hydroxy-5-methylphenyl]ethanone

[18611-32-0] $C_{13}H_{17}BrO_2$ mol.wt. 285.18



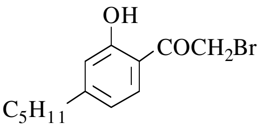
Syntheses

-Preparation by bromination of 3-tert-butyl-4-hydroxy-5-methylacetophenone in usual manner in benzene or chloroform [999].
-Preparation by reaction of cupric bromide with 3-tert-butyl-4-hydroxy-5-methylacetophenone in refluxing ethyl acetate (72%) [1457].

m.p. 95-97° [999], 90-92° [1457].

2-Bromo-1-(2-hydroxy-4-pentylphenyl)ethanone

[133301-45-8] $C_{13}H_{17}BrO_2$ mol.wt. 285.18



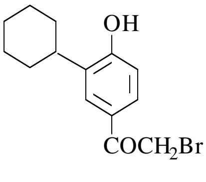
Synthesis

-Obtained by reaction of cupric bromide with 2-hydroxy-4-pentylacetophenone in refluxing ethyl acetate/chloroform mixture (1:1) for 4 h (18%) [1180].

^{1}H NMR [1180], IR [1180]; TLC [1180].

2-Bromo-1-(3-cyclohexyl-4-hydroxyphenyl)ethanone

[73898-26-7] $C_{14}H_{17}BrO_2$ mol.wt. 297.19

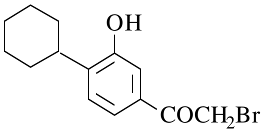


Synthesis

-Preparation by reaction of dioxane dibromide on 3-cyclohexyl-4-hydroxyacetophenone in dioxane and ethyl ether mixture at r.t. (95%) [888].

2-Bromo-1-(4-cyclohexyl-3-hydroxyphenyl)ethanone

[73898-33-6] $C_{14}H_{17}BrO_2$ mol.wt. 297.19

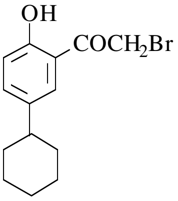


Synthesis

-Preparation by reaction of dioxane dibromide on 4-cyclohexyl-3-hydroxyacetophenone in dioxane and ethyl ether mixture at r.t. (51%) [888].

2-Bromo-1-(5-cyclohexyl-2-hydroxyphenyl)ethanone

[74815-30-8] $C_{14}H_{17}BrO_2$ mol.wt. 297.19



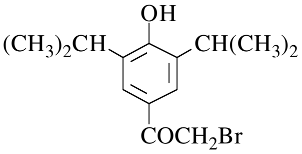
Synthesis

-Preparation by reaction of cupric bromide on 5-cyclohexyl-2-hydroxyacetophenone in refluxing ethyl acetate [109].

yellow oil [109].

2-Bromo-1-[4-hydroxy-3,5-bis(1-methylethyl)phenyl]ethanone

[157014-26-1] $C_{14}H_{19}BrO_2$ mol.wt. 299.21

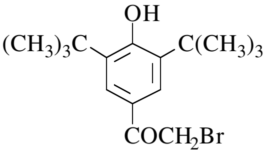


Synthesis

-Preparation by a Friedel-Crafts acylation of propofol (2,6-diisopropylphenol) using aluminium chloride and bromoacetyl bromide in methylene chloride (compound 6) [325].

1-[3,5-Bis(1,1-dimethylethyl)-4-hydroxyphenyl]-2-bromoethanone

[14386-64-2] $C_{16}H_{23}BrO_2$ mol.wt. 327.26



Synthesis

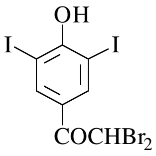
-Preparation by reaction of bromine with 3,5-di-tert-butyl-4-hydroxyacetophenone in ethanol under nitrogen bubbling for 2.5 h (73%) [1577] or in refluxing methylene chloride (67%) [1457].

m.p. 107°5-108°5 [1577], 105-108° [1457]; ^{1}H NMR [1577].

2.1.2. From dibromoacetic acid

2,2-Dibromo-1-(4-hydroxy-3,5-diiodophenyl)ethanone

$C_8H_4Br_2I_2O_2$ mol.wt. 545.74



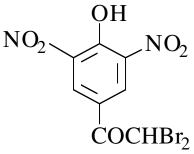
Synthesis

-Obtained by reaction of bromine on 4-hydroxy-3,5-diiodoacetophenone with sunlight in chloroform at 50-60° (83%) [333].

m.p. 132-133° [333].

2,2-Dibromo-1-(4-hydroxy-3,5-dinitrophenyl)ethanone

[120388-19-4] $C_8H_4Br_2N_2O_6$ mol.wt. 383.94



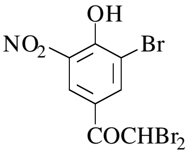
Synthesis

-Preparation by bromination of 4-hydroxy-3,5-dinitroacetophenone with excess cupric bromide in refluxing ethyl acetate (66%) [210].

m.p. 93-95° [210].

2,2-Dibromo-1-(3-bromo-4-hydroxy-5-nitrophenyl)ethanone

[35928-54-2] $C_8H_4Br_3NO_4$ mol.wt. 417.84



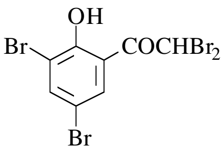
Synthesis

-Preparation by bromination of 3-bromo-4-hydroxy-5-nitroacetophenone in acetic acid-sulfuric acid solution at 25° (78%) [1428].

m.p. 121° [1428]; ^{1}H NMR [1428].

2,2-Dibromo-1-(3,5-dibromo-2-hydroxyphenyl)ethanone

[49619-83-2] $C_8H_4Br_4O_2$ mol.wt. 451.73



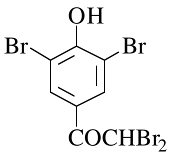
Syntheses

-Preparation by reaction of bromine on 2-hydroxyacetophenone in acetic acid [695] [1246], (62%) [1246].
-Also obtained by reaction of aqueous sodium hypobromite on chromone-3-carboxaldehyde in acetic acid (24-30%) [1096] [1097].
-Also obtained by reaction of sodium sulfite on 3,5-dibromo-2-hydroxy-α,α,α-tribromoacetophenone, in boiling acetic acid [513].
-Also obtained by reaction of bromine on 3,3'-diacetyl-4,4'-dihydroxydiphenyl thioether [692].

m.p. 124-125° [1096], 122-123° [513], 121-122° [1097], 120-121° [692] [695] [1246];
^{1}H NMR [1096] [1097], IR [1096] [1097], UV [1096], MS [1096] [1097].

2,2-Dibromo-1-(3,5-dibromo-4-hydroxyphenyl)ethanone

$C_8H_4Br_4O_2$ mol.wt. 451.73



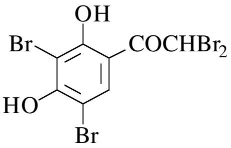
Syntheses

-Preparation by reaction of bromine on 3,5-dibromo-4-hydroxyacetophenone [1201] [1246].
-Preparation by reaction of bromine on 4-hydroxyacetophenone in acetic acid (60%) [1246].

m.p. 105-106° [1246], 105° [1201].

2,2-Dibromo-1-(3,5-dibromo-2,4-dihydroxyphenyl)ethanone

$C_8H_4Br_4O_3$ mol.wt. 467.73



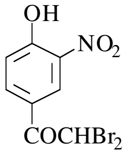
Synthesis

-Preparation by reaction of bromine on resacetophenone in acetic acid [231].

m.p. 110-110°5 [231].

2,2-Dibromo-1-(4-hydroxy-3-nitrophenyl)ethanone

[35928-53-1] $C_8H_5Br_2NO_4$ mol.wt. 338.94



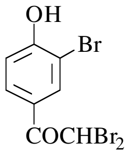
Syntheses

-Preparation by bromination of 4-hydroxy-3-nitroacetophenone with excess cupric bromide in refluxing ethyl acetate (56-82%) [210].
-Preparation by bromination of 4-hydroxy-3-nitroacetophenone in acetic acid-sulfuric acid mixture at 25° (49%) [1428].

m.p. 63° [1428]; ^{1}H NMR [1428].

2,2-Dibromo-1-(3-bromo-4-hydroxyphenyl)ethanone

$C_8H_5Br_3O_2$ mol.wt. 372.84



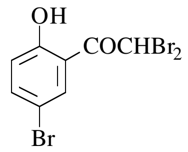
Synthesis

-Preparation by reaction of bromine on 4-hydroxyacetophenone in acetic acid or chloroform (65%) [1246].

m.p. 139° [1246].

2,2-Dibromo-1-(5-bromo-2-hydroxyphenyl)ethanone

$C_8H_5Br_3O_2$ mol.wt. 372.84



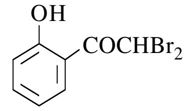
Synthesis

-Preparation by reaction of bromine on 2-hydroxyacetophenone in chloroform or acetic acid (quantitative yield) [1246].

m.p. 103-104° [1246].

2,2-Dibromo-1-(2-hydroxyphenyl)ethanone

[54735-43-2] $C_8H_6Br_2O_2$ mol.wt. 293.94



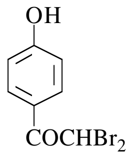
Syntheses

-Obtained by transformation of 4-hydroxycoumarin with tetrabutylammonium bromide promoted by hydrogen peroxide and vanadium pentoxide at 5° for 1 h (55%) [209].
-Also refer to: [79].

^{1}H NMR [209], ^{13}C NMR [209], UV [79]; TLC [209], GC [209].

2,2-Dibromo-1-(4-hydroxyphenyl)ethanone

[92596-96-8] $C_8H_6Br_2O_2$ mol.wt. 293.94



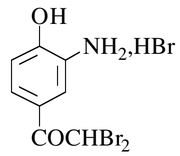
Syntheses

-Preparation by bromination of 4-hydroxyacetophenone with excess cupric bromide in refluxing ethyl acetate (56-82%) [210].
-Also obtained (by-product) by reaction of bromine with p-hydroxyacetophenone in dioxane at r.t. for 40 min (< 6%) [853].

m.p. 121-122° [853]; ^{1}H NMR [853], IR [853].

1-(3-Amino-4-hydroxyphenyl)-2,2-dibromoethanone *(Hydrobromide)*

$C_8H_7Br_2NO_2$, HBr mol.wt. 389.87



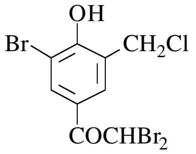
Synthesis

-Preparation by reaction of bromine on 3-amino-4-hydroxyacetophenone hydrobromide in acetic acid at 65° (60%) [275].

m.p. 215° [275].

2,2-Dibromo-1-[3-bromo-5-(chloromethyl)-4-hydroxyphenyl]ethanone

[107700-05-0] $C_9H_6Br_3ClO_2$ mol.wt. 421.31



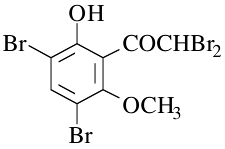
Synthesis

-Preparation by adding a methylene chloride solution of bromine to a methanol/methylene chloride solution of 3-(chloromethyl)-4-hydroxyacetophenone at r.t. (82%) [214].

m.p. 140° [214]; ^{1}H NMR [214], IR [214], MS [214].

2,2-Dibromo-1-(3,5-dibromo-2-hydroxy-6-methoxyphenyl)ethanone

$C_9H_6Br_4O_3$ mol.wt. 481.76



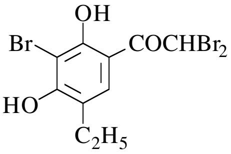
Synthesis

-Obtained by reaction of bromine on 3,3'-diacetyl-2,2'-dihydroxy-4,4'-dimethoxydiphenylsulfide in acetic acid, heated in a boiling water bath [358].

m.p. 101-102° [358].

2,2-Dibromo-1-(3-bromo-5-ethyl-2,4-dihydroxyphenyl)ethanone

$C_{10}H_9Br_3O_3$ mol.wt. 416.89



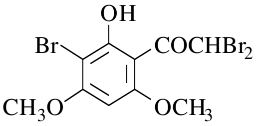
Synthesis

-Preparation by reaction of 5-ethyl-2,4-dihydroxyacetophenone with an excess of bromine in chloroform [1327].

m.p. 144-145° [1327].

2,2-Dibromo-1-(3-bromo-2-hydroxy-4,6-dimethoxyphenyl)ethanone

[88503-19-9] $C_{10}H_9Br_3O_4$ mol.wt. 432.89



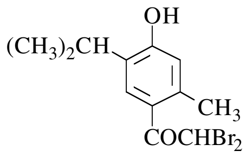
Synthesis

-Preparation by heating for 7 h on a steam bath a mixture of 2-hydroxy-3-iodo-4,6-dimethoxyacetophenone and bromine in acetic acid (67%) [415].

m.p. 167-168° [415].

2,2-Dibromo-1-[4-hydroxy-2-methyl-5-(1-methylethyl)phenyl]ethanone

[72235-94-0] $C_{12}H_{14}Br_2O_2$ mol.wt. 350.05



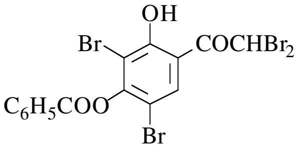
Synthesis

-Preparation by reaction of bromine on 4-hydroxy-2-methyl-5-isopropylacetophenone in acetic acid at 18° (45%) [105].

m.p. 111° [105].

1-[4-(Benzoyloxy)-3,5-dibromo-2-hydroxyphenyl]-2,2-dibromoethanone

$C_{15}H_8Br_4O_4$ mol.wt. 571.84



Synthesis

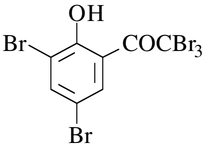
-Preparation by bromination of 4-(benzoyloxy)-2-hydroxy-acetophenone at r.t. [694].

m.p. 69-70° [694].

2.1.3. From tribromoacetic acid

2,2,2-Tribromo-1-(3,5-dibromo-2-hydroxyphenyl)ethanone

[98436-51-2] $C_8H_3Br_5O_2$ mol.wt. 530.63



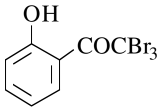
Synthesis

-Obtained by reaction of bromine on 4-hydroxycoumarin (benzotetronic acid) in methanol or acetic acid at r.t. [513].

m.p. 125-126° [513].

2,2,2-Tribromo-1-(2-hydroxyphenyl)ethanone

[101495-49-2] $C_8H_5Br_3O_2$ mol.wt. 372.84



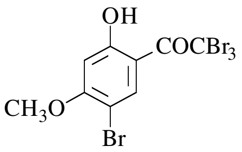
Synthesis

-Obtained by reaction of bromine on 4-hydroxycoumarin (benzotetronic acid) in acetic acid-dioxane mixture at r.t. [513].

m.p. 87° [513].

2,2,2-Tribromo-1-(5-bromo-2-hydroxy-4-methoxyphenyl)ethanone

$C_9H_6Br_4O_3$ mol.wt. 481.76



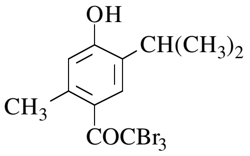
Synthesis

-Preparation by reaction of bromine on bromopaeonol (5-bromo-2-hydroxy-4-methoxyacetophenone) in the presence of a crystal of iodine at r.t. [6].

m.p. 123-124° [6].

2,2,2-Tribromo-1-[4-hydroxy-2-methyl-5-(1-methylethyl)phenyl]ethanone

$C_{12}H_{13}Br_3O_2$ mol.wt. 428.95



Synthesis

-Preparation by reaction of bromine on 4-hydroxy-2-methyl-5-isopropylacetophenone in acetic acid at 18° (90%) [105].

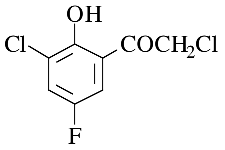
m.p. 69° [105].

2.2. *Compounds derived from chloroacetic acids*

2.2.1. From monochloroacetic acid

2-Chloro-1-(3-chloro-5-fluoro-2-hydroxyphenyl)ethanone

$C_8H_5Cl_2FO_2$ mol.wt. 223.03



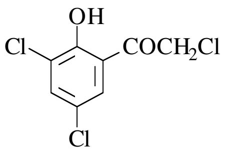
Synthesis

-Preparation by Fries rearrangement of 2-chloro-4-fluorophenyl chloroacetate with aluminium chloride without solvent at 130-140° (63%) [741].

b.p.$_2$ 116° [741].

2-Chloro-1-(3,5-dichloro-2-hydroxyphenyl)ethanone

[79214-30-5] $C_8H_5Cl_3O_2$ mol.wt. 239.48



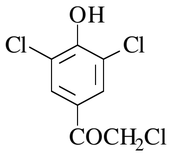
Syntheses

-Preparation by Fries rearrangement of 2,4-dichlorophenyl chloroacetate with aluminium chloride without solvent at 135-145° [1049] [1401], (56%) [1401].
-Preparation by reaction of chloroacetyl chloride on 2,4-dichloroanisole with aluminium chloride in refluxing carbon disulfide (45%) [1298].

m.p. 136-136°8 [1401], 133° [1298], 132-134° [1049].

2-Chloro-1-(3,5-dichloro-4-hydroxyphenyl)ethanone

[220291-97-4] $C_8H_5Cl_3O_2$ mol.wt. 239.48



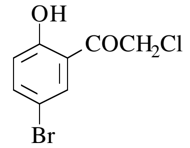
Syntheses

-Preparation by Fries rearrangement of 2,6-dichlorophenyl chloroacetate with aluminium chloride without solvent at 112-114° (77%) [1442].
-Also refer to: [770] (Japanese patent).

m.p. 120-121° [1442].

1-(5-Bromo-2-hydroxyphenyl)-2-chloroethanone

[100959-21-5] $C_8H_6BrClO_2$ mol.wt. 249.49



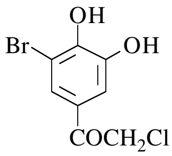
Synthesis

-Preparation by reaction of chloroacetyl chloride with 4-bromophenol in the presence of aluminium chloride at 40° (66%) [677].

m.p. 73-74° [677].

1-(3-Bromo-4,5-dihydroxyphenyl)-2-chloroethanone

$C_8H_6BrClO_3$ mol.wt. 265.50



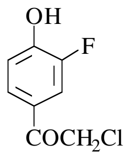
Synthesis

-Preparation by bromination of 3,4-dihydroxy-α-chloroacetophenone with bromine in the presence of quinoline sulfate while cooling (60%) [1250] according to the method [1244].

m.p. 137° [1250].

2-Chloro-1-(3-fluoro-4-hydroxyphenyl)ethanone

$C_8H_6ClFO_2$ mol.wt. 188.59



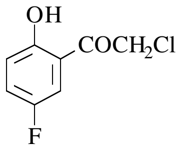
Synthesis

-Preparation by Fries rearrangement of 2-fluorophenyl chloroacetate with aluminium chloride without solvent at 135-140° (27-40%) [612].

m.p. 101-102° [612].

2-Chloro-1-(5-fluoro-2-hydroxyphenyl)ethanone

[2002-75-7] $C_8H_6ClFO_2$ mol.wt. 188.59



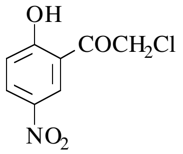
Synthesis

-Preparation by Fries rearrangement of 4-fluorophenyl chloroacetate with aluminium chloride without solvent at 130° (50%) [740].

b.p.$_{10}$ 177° [740].

2-Chloro-1-(2-hydroxy-5-nitrophenyl)ethanone

$C_8H_6ClNO_4$ mol.wt. 215.59



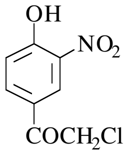
Synthesis

-Obtained by nitration of 2-hydroxy-α-chloroacetophenone in acetic acid [101].

m.p. 163-164° [101].

2-Chloro-1-(4-hydroxy-3-nitrophenyl)ethanone

$C_8H_6ClNO_4$ mol.wt. 215.59



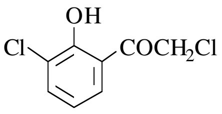
Syntheses

-Preparation by reaction of chlorine on 4-hydroxy-3-nitroacetophenone in acetic acid (45%) [275].
-Also obtained by reaction of chloroacetyl chloride on 2-nitrophenol with aluminium chloride in nitrobenzene at 50-60° (19%) [275].

m.p. 88° [275]; b.p.$_{0.1}$ 135-140° [275], b.p.$_{0.4}$ 140-145° [275].

2-Chloro-1-(3-chloro-2-hydroxyphenyl)ethanone

[75717-49-6] $C_8H_6Cl_2O_2$ mol.wt. 205.04



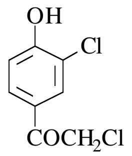
Synthesis

-Obtained by reaction of chloroacetonitrile on 2-chlorophenol with aluminium chloride and boron trichloride mixture in ethylene dichloride at r.t. (21%) [1409] [1466].

m.p. 72-73° [1409] [1466]; ^{1}H NMR [1466].

2-Chloro-1-(3-chloro-4-hydroxyphenyl)ethanone

[39066-18-7] $C_8H_6Cl_2O_2$ mol.wt. 205.04



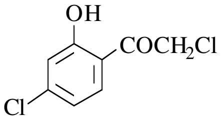
Synthesis

-Preparation by Fries rearrangement of 2-chlorophenyl chloroacetate with aluminium chloride without solvent at 135-140° (39 to 59%) [164] [507] [612].

m.p. 141-142° [612].

2-Chloro-1-(4-chloro-2-hydroxyphenyl)ethanone

[75717-50-9] $C_8H_6Cl_2O_2$ mol.wt. 205.04



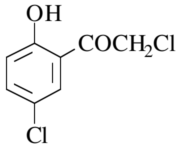
Synthesis

-Preparation by reaction of chloroacetonitrile on 3-chlorophenol with aluminium chloride and boron trichloride mixture in refluxing ethylene dichloride (51%) [1409] [1466].

m.p. 75-76° [1409] [1466]; ^{1}H NMR [1466].

2-Chloro-1-(5-chloro-2-hydroxyphenyl)ethanone

[24483-75-8] $C_8H_6Cl_2O_2$ mol.wt. 205.04



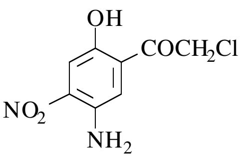
Syntheses

-Preparation by Fries rearrangement of 4-chlorophenyl chloroacetate with aluminium chloride without solvent at 140-150° [520] [1049] [1219], (30%) [1219].
-Also obtained by reaction of chloroacetonitrile on 4-chlorophenol with aluminium chloride and boron trichloride mixture in ethylene dichloride [1409] [1466], (18%) [1409].

m.p. 107-110° [1049], 65-66° [1409] [1466], 65° [520] [1219]. One of the reported melting points is obviously wrong. ^{1}H NMR [1466].

1-(5-Amino-2-hydroxy-4-nitrophenyl)-2-chloroethanone

$C_8H_7ClN_2O_4$ mol.wt. 230.61



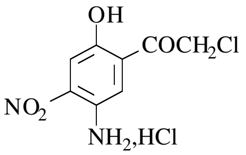
Synthesis

-Preparation by treatment of 5-acetamido-2-hydroxy-4-nitro-α-chloroacetophenone with boiling 25% aqueous hydrochloric acid solution [859].

m.p. 145° (d) [859].

1-(5-Amino-2-hydroxy-4-nitrophenyl)-2-chloroethanone *(Hydrochloride)*

$C_8H_7ClN_2O_4$, HCl mol.wt. 267.07



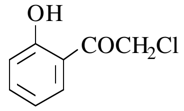
Synthesis

-Preparation from 5-amino-2-hydroxy-4-nitro-α-chloroacetophenone [859] (see above).

m.p. 210° (d) [859].

2-Chloro-1-(2-hydroxyphenyl)ethanone

[53074-73-0] $C_8H_7ClO_2$ mol.wt. 170.60



Syntheses

-Preparation by reaction of acetonitrile on phenol with aluminium chloride and boron trichloride in refluxing ethylene dichloride (78%) [1409] or in methylene chloride at r.t. (85%) [1466].

-Preparation by halogenation of o-hydroxyacetophenone,

*using EGDMA crosslinked polystyrene based benzyltriethylammonium dichloroiodate or tetrachloroiodate reagents in chloroform for 7-11 h at 30° (80%) [1013];

*using 5% N,N'-MBA crosslinked polyacrylamide-based dichloroiodate or tetrachloroiodate reagents in chloroform at 30° for 8 h (77-79%) [1012];

*with benzyltrimethylammonium dichloroiodate in refluxing methylene chloride/methanol mixture for 10 h (73%) [748].

-Preparation by reaction of hexachloro-2,4-cyclohexadienone on 2-hydroxyacetophenone in refluxing ethanol (66%) [603].

-Preparation by Fries rearrangement of phenyl monochloroacetate,

*with aluminium chloride(50%) [956], without solvent at 120° (50%) [519] or at 140° (by-product) [351];

*with beryllium chloride without solvent at 130-140° (30%) [225].

-Also obtained by reaction of chloroacetyl chloride on bromomagnesium phenolate in toluene at r.t. (17%) [1286].

-Also obtained by reaction of aluminium chloride on 2-chloroacetylanisole in refluxing carbon disulfide [100] [1482].

-Also obtained (by-product) by reaction of chloroacetyl chloride on phenol with aluminium chloride at 140° [351].

-Also obtained (by-product) by treatment of anisole with chloroacetyl chloride in the presence of aluminium chloride in tetrachloroethane in a boiling water bath for 2-3 h [254] [1538].

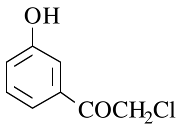
-Also refer to: [156] [161] [162] [401] [906] [1461] [1478] [1479] [1524].

m.p. 101° [1482], 74-75° [1286], 74° [351] [519] [956] [1012], 73-74° [100], 73° [225] [254] [603] [748] [1482] [1538], 72-73° [1466], 72° [1013], 71-71°5 [906]; One of the reported melting points is obviously wrong.

^{1}H NMR [603] [748] [1286], IR [603] [748].

2-Chloro-1-(3-hydroxyphenyl)ethanone

[62932-90-5] $C_8H_7ClO_2$ mol.wt. 170.60



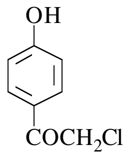
Synthesis

-Preparation by reaction of hexachloro-2,4-cyclohexadienone on 3-hydroxyacetophenone in refluxing ethanol (50%) [603].

m.p. 93° [603]; ^{1}H NMR [603], IR [603].

2-Chloro-1-(4-hydroxyphenyl)ethanone

[6305-04-0] $C_8H_7ClO_2$ mol.wt. 170.60



Syntheses

-Preparation by reaction of p-hydroxyacetophenone with benzyltrimethylammonium dichloroiodate in refluxing methylene chloride/methanol mixture for 10 h (95%) [748] or for 12 h (92%) [597].

-Preparation by reaction of chloroacetyl chloride,

*with anisole in the presence of aluminium chloride in ligroin (44%) [36], for 1 h in a water bath (50-55°) (32%) [1363], for 4 h (36%) [1263] or for 3 h (41-42%) [515];

*with anisole in the presence of aluminium chloride without solvent [857], in carbon disulfide [1483] or in tetrachloroethane in a boiling water bath for 2-3 h [254], (53%) [1538];

*with phenol in the presence of aluminium chloride without solvent at 140° (71%) [351] or in tetrachloroethane, first at 70° for 5 h, then at r.t. for 10 h [1537].

-Also obtained by Fries rearrangement of phenyl chloroacetate,

*with aluminium chloride without solvent at 120-140° [351] [519], (65%) [351];

*with beryllium chloride without solvent at 130-140° (23%) [225].

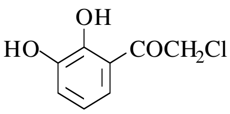
-Preparation by reaction of hexachloro-2,4-cyclohexadienone on 4-hydroxyacetophenone in refluxing ethanol (77%) [603].

-Also refer to: [147] [306] [908].

m.p. 151-152° [906], 150-151° [597], 150° [748], 148° [36] [351] [515] [857] [1483], 147-148° (d) [1363], 147°5 [1263], 147° [254] [1538], 145-146° [225], 142° [603];
^{1}H NMR [597] [603] [748], IR [603] [748].

2-Chloro-1-(2,3-dihydroxyphenyl)ethanone

[63704-55-2] $C_8H_7ClO_3$ mol.wt. 186.59

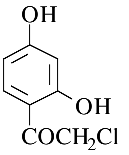


Synthesis

-Refer to: [1412] (Japanese patent).

2-Chloro-1-(2,4-dihydroxyphenyl)ethanone

[25015-92-3] $C_8H_7ClO_3$ mol.wt. 186.59



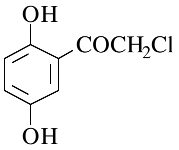
Syntheses

-Preparation by reaction of chloroacetonitrile on resorcinol with zinc chloride (Hoesch reaction) (90%) [1381], (82%) [1579] or with triflic acid (trifluoromethanesulfonic acid) (23%) [207].
-Also obtained by reaction of chloroacetic acid on resorcinol with boron trifluoride (30%) [248] or with zinc chloride or phosphorous oxychloride (poor yield) [436] [516].

m.p. 132° [248], 131° [1381], 130-132° [207], 130° [1579];
^{1}H NMR [207], IR [207], UV [666].

2-Chloro-1-(2,5-dihydroxyphenyl)ethanone

[60912-82-5] $C_8H_7ClO_3$ mol.wt. 186.59



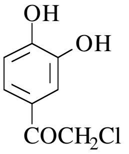
Syntheses

-Obtained by reaction of hydrochloric acid on 2,5-diacetoxy-α-chloroacetophenone in methanol at r.t. (85%) [819].
-Preparation by reaction of aluminium bromide on 2,5-dimethoxy-α-chloroacetophenone in carbon disulfide at r.t. (72%) [819].
-Also obtained by action of acetic acid saturated with hydrochloric acid (10 min, r.t.) on 2,5-diacetoxy-α-diazoacetophenone, reduced pressure elimination of acetic acid, then action (overnight, r.t.) of a methanolic solution of hydrochloric acid (53%) [819].
-Also obtained by reaction of sulfur dioxide on 2-chloroacetyl-1,4-benzoquinone in water [819].

m.p. 132-133° [819].

2-Chloro-1-(3,4-dihydroxyphenyl)ethanone

[99-40-1] $C_8H_7ClO_3$ mol.wt. 186.59



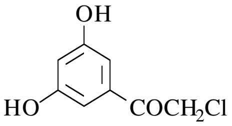
Syntheses

-Preparation by Fries rearrangement of pyrocatechol monochloroacetate with aluminium chloride in nitrobenzene at 100° (60%) [1245] or without solvent at 100° (25%) [836].
-Preparation by reaction of chloroacetic acid on pyrocatechol with boron trifluoride in tetrachloroethane or in carbon tetrachloride at 65-85° (95-98%) [248] or with phosphorous oxychloride [437] [738] [963] [1081] [1365], (80%) [437], (35-58%) [738] [963] [1365].
-Preparation by reaction of chloroacetyl chloride on pyrocatechol [437].
-Preparation by reaction of chloroacetyl chloride on veratrole with aluminium chloride in nitrobenzene at 40° (82%) [1402].

m.p. 173° [248] [437] [738] [963] [1245] [1402], 172° [435] [1365], 171° [836], 169-170° [1193]; b.p.$_{12}$ 190° [1402].

2-Chloro-1-(3,5-dihydroxyphenyl)ethanone

[39878-43-8] $C_8H_7ClO_3$ mol.wt. 186.59



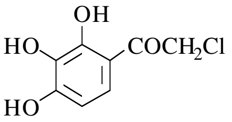
Synthesis

-Preparation by reaction of hydrochloric acid on 3,5-di-acetoxy-α-diazoacetophenone in aqueous methanol at reflux (97%) [1027].

m.p. 117° [1027].

2-Chloro-1-(2,3,4-trihydroxyphenyl)ethanone

[17345-68-5] $C_8H_7ClO_4$ mol.wt. 202.59



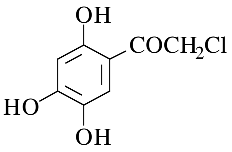
Syntheses

-Preparation by Fries rearrangement of 2,6-dimethoxyphenyl chloroacetate with aluminium chloride without solvent at 100° [980].
-Preparation by reaction of chloroacetyl chloride on pyrogallol [437].
-Preparation by reaction of chloroacetic acid on pyrogallol with phosphorous oxychloride [366] [436] [487] [516] [1081] [1083] [1365] [1381], (55%) [487], (40-41%) [366] [1365], with boron trifluoride [248] [880] or with zinc chloride (poor yield) [436] [516].
-Preparation by reaction of chloroacetic anhydride with pyrogallol in the presence of boron trifluoride in ethyl ether [554].

m.p. 169° [366], 167-168° [1083], 167° [248], 166° [1365], 163-165° [1193].

2-Chloro-1-(2,4,5-trihydroxyphenyl)ethanone

[14771-02-9] $C_8H_7ClO_4$ mol.wt. 202.59



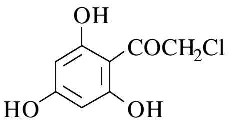
Synthesis

-Preparation by reaction of chloroacetonitrile on 1,2,4-benzenetriol (hydroxyhydroquinone) with zinc chloride in ethyl ether (Hoesch reaction) [553] [1294] [1295].

m.p. 182° [1294], 139-140° [1295]. One of the reported melting points is obviously wrong.
^{1}H NMR [1294], IR [1294] [1295], UV [1294] [1295].

2-Chloro-1-(2,4,6-trihydroxyphenyl)ethanone

[110865-03-7] $C_8H_7ClO_4$ mol.wt. 202.59



Syntheses

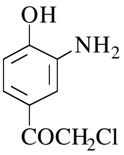
-Preparation by reaction of chloroacetyl chloride on phloroglucinol with aluminium chloride in nitromethane (86%) [880].
-Preparation by reaction of chloroacetonitrile on phloroglucinol (Hoesch reaction) (88%) [1352], (68%) [292].

-Also refer to: [294] (compound **1**).

m.p. 190° [880], 188-191° [292] [1352]; ^{1}H NMR [292], IR [292], MS [292].

1-(3-Amino-4-hydroxyphenyl)-2-chloroethanone

[108708-12-9] $C_8H_8ClNO_2$ mol.wt. 185.61



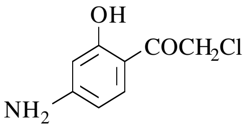
Synthesis

-Preparation by Friedel-Crafts chloroacetylation of N-acetyl-o-anisidine followed by hydrolysis with concentrated hydrochloric acid in ethanol [1153].

m.p. 113° [1153].

1-(4-Amino-2-hydroxyphenyl)-2-chloroethanone

[108708-13-0] $C_8H_8ClNO_2$ mol.wt. 185.61



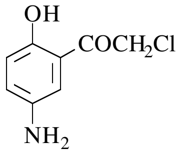
Synthesis

-Preparation by Friedel-Crafts chloroacetylation of N-acetyl-m-anisidine followed by hydrolysis with concentrated hydrochloric acid in ethanol [1153].

m.p. 214° (d) [1153].

1-(5-Amino-2-hydroxyphenyl)-2-chloroethanone

[108708-11-8] $C_8H_8ClNO_2$ mol.wt. 185.61



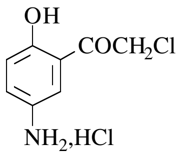
Synthesis

-Preparation by Friedel-Crafts chloroacetylation of N-acetyl-p-anisidine followed by hydrolysis with concentrated hydrochloric acid in ethanol [858] [859] [1153].

m.p. 135° [858] [859], 128° [1153].

1-(5-Amino-2-hydroxyphenyl)-2-chloroethanone *(Hydrochloride)*

$C_8H_8ClNO_2$, HCl mol.wt. 222.07



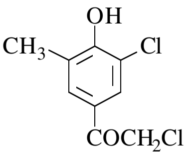
Synthesis

-Obtained by reaction of gaseous hydrochloric acid on 5-amino-2-hydroxy-α-chloroacetophenone in ethyl ether [859].

m.p. 210° (d) [859].

2-Chloro-1-(3-chloro-4-hydroxy-5-methylphenyl)ethanone

$C_9H_8Cl_2O_2$ mol.wt. 219.07



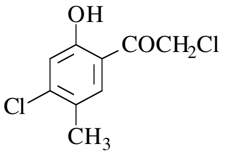
Synthesis

-Preparation by Fries rearrangement of 2-chloro-6-methylphenyl chloroacetate with aluminium chloride at 140° [94].

m.p. 98°5-99°5 [94]; b.p.$_{12}$ 172-180° [94].

2-Chloro-1-(4-chloro-2-hydroxy-5-methylphenyl)ethanone

[22307-95-5] $C_9H_8Cl_2O_2$ mol.wt. 219.07

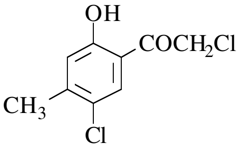


Synthesis not yet described

-See [1130]; this reference mentioned in the Chem. Abstr., **70**, 11442s (1969) is erroneous. Actually, the ketone described here as the 2,4'-dichloro-2'-hydroxy-5'-methylacetophenone should be the 2,5'-dichloro-2'-hydroxy-4'-methylacetophenone. In fact, on one hand, it is obtained by Fries rearrangement of 4-chloro-3-methylphenyl chloroacetate and on the other hand, it provides the 5-chloro-6-methyl-3-[2*H*]-benzofuranone by cyclisation (see below).

2-Chloro-1-(5-chloro-2-hydroxy-4-methylphenyl)ethanone

$C_9H_8Cl_2O_2$ mol.wt. 219.07



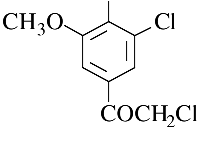
Synthesis

-Preparation by Fries rearrangement of 4-chloro-3-methylphenyl chloroacetate with aluminium chloride without solvent at 150° [1130].

m.p. 111° [1130]; ^{1}H NMR [1130], IR [1130].

2-Chloro-1-(3-chloro-4-hydroxy-5-methoxyphenyl)ethanone

[160925-81-5] $C_9H_8Cl_2O_3$ mol.wt. 235.07



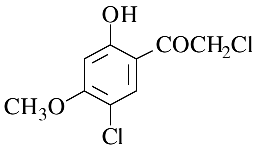
Syntheses

-Preparation by chlorination of acetoguaiacone (4-hydroxy-3-methoxyacetophenone) in dioxane with 2.5 mol. equiv chlorine in acetic acid (67%) [1374].
-Also refer to: [1519].

m.p. 149-150° [1374]; ^{1}H NMR [1374], ^{13}C NMR [1374], MS [1374].

2-Chloro-1-(5-chloro-2-hydroxy-4-methoxyphenyl)ethanone

$C_9H_8Cl_2O_3$ mol.wt. 235.07



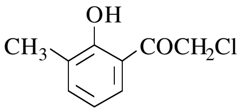
Syntheses

-Preparation by reaction of chloroacetyl chloride on 4-chlororesorcinol dimethyl ether with aluminium chloride in carbon disulfide (66%) [96].
-Preparation by reaction of chlorine on 2-hydroxy-4-methoxy-α-chloroacetophenone in chloroform (40-45%) [96].

m.p. 178°5-180° [96].

2-Chloro-1-(2-hydroxy-3-methylphenyl)ethanone

[75717-51-0] $C_9H_9ClO_2$ mol.wt. 184.62



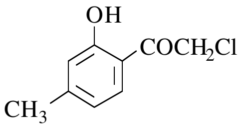
Syntheses

-Preparation by reaction of chloroacetonitrile on o-cresol with aluminium chloride and boron trichloride mixture in ethylene dichloride at r.t. (75%) [1409] [1466] or with only boron trichloride in methylene chloride at r.t. under nitrogen (18%) [183].
-Preparation by Fries rearrangement of 2-methylphenyl chloroacetate with aluminium chloride without solvent at 140° (50%) [679], (20%) [98].

m.p. 67° [98], 66-67° [679], 65-66° [1409] [1466], 63-64° [183];
^{1}H NMR [183] [1466], IR [183], UV [183], MS [183].

2-Chloro-1-(2-hydroxy-4-methylphenyl)ethanone

[20834-75-7] $C_9H_9ClO_2$ mol.wt. 184.62



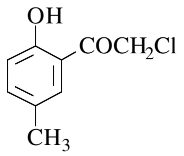
Syntheses

-Preparation by Fries rearrangement of 3-methylphenyl chloroacetate with aluminium chloride without solvent between 140 to 150° [274] [518] [679] [1130] [1370], (70%) [679], (50%) [518] [1370], (12%) [274].
-Preparation by reaction of chloroacetonitrile on m-cresol with boron trichloride and aluminium chloride in refluxing ethylene dichloride (quantitative yield) [1409].
-Also refer to: [109] [1478].

m.p. 102-102°5 [679], 102° [1130], 101° [518], 100° [274], 95-96° [1409];
^{1}H NMR [1130], IR [1130].

2-Chloro-1-(2-hydroxy-5-methylphenyl)ethanone

[22307-94-4] $C_9H_9ClO_2$ mol.wt. 184.62



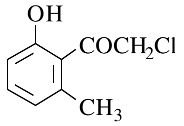
Syntheses

-Preparation by Fries rearrangement of p-tolyl chloroacetate with aluminium chloride without solvent at 140° [351] [518] [679] [1049], (90-93%) [518] [679], (37%) [351].
-Preparation by reaction of chloroacetic acid on p-cresol with boron trifluoride etherate (66%) or boron trifluoride (46%) in an autoclave at 70° [1111].
-Preparation by reaction of chloroacetyl chloride on 4-methylanisole with aluminium chloride in refluxing carbon disulfide (50-60%) [95].
-Preparation by reaction of chloroacetyl chloride on p-cresol with aluminium chloride without solvent at 140° (31%) [351].

m.p. 65° [351] [518], 63° [95], 62-63° [679] [1049], 62° [1111].

2-Chloro-1-(2-hydroxy-6-methylphenyl)ethanone

[73331-41-6] $C_9H_9ClO_2$ mol.wt. 184.62

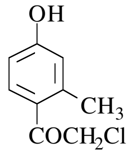


Synthesis

-Refer to: [1020].

2-Chloro-1-(4-hydroxy-2-methylphenyl)ethanone

[37904-71-5] $C_9H_9ClO_2$ mol.wt. 184.62



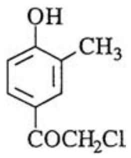
Synthesis

-Preparation by Fries rearrangement of 3-methylphenyl chloroacetate with aluminium chloride without solvent at 140° [274] [679], (30%) [679].

m.p. 148°5-149° [679], 147°5 [274].

2-Chloro-1-(4-hydroxy-3-methylphenyl)ethanone

[40943-24-6] $C_9H_9ClO_2$ mol.wt. 184.62



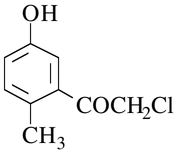
Synthesis

-Preparation by Fries rearrangement of 2-methylphenyl chloroacetate with aluminium chloride without solvent at 140° [98] [679], (50%) [679].

m.p. 144-145° [98], 144-144°5 [679].

2-Chloro-1-(5-hydroxy-2-methylphenyl)ethanone

$C_9H_9ClO_2$ mol.wt. 184.62



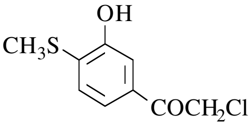
Synthesis

-Obtained (by-product) by Fries rearrangement of 4-methylphenyl chloroacetate with aluminium chloride without solvent at 140° (7%) [679].

m.p. 155°5-156° [679].

2-Chloro-1-[3-hydroxy-4-(methylthio)phenyl]ethanone

[151792-80-2] $C_9H_9ClO_2S$ mol.wt. 216.69



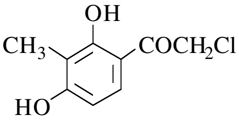
Synthesis

-Preparation by hydrolysis of 3-hydroxy-4-methylthio-α-chloroacetophenone chloroacetate with 1 N sodium hydroxide in methanol at r.t. (94%) [82].

m.p. 140° [82]; ^{1}H NMR [82], IR [82], MS [82].

2-Chloro-1-(2,4-dihydroxy-3-methylphenyl)ethanone

[21861-21-2] $C_9H_9ClO_3$ mol.wt. 200.62



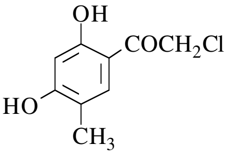
Synthesis

-Preparation by reaction of chloroacetonitrile with 2-methylresorcinol (72%) (Hoesch reaction) [264].

m.p. 155° [264].

2-Chloro-1-(2,4-dihydroxy-5-methylphenyl)ethanone

$C_9H_9ClO_3$ mol.wt. 200.62



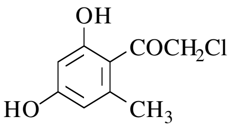
Syntheses

-Preparation by reaction of chloroacetonitrile with 4-methylresorcinol (Hoesch reaction) [1053].
-Also obtained by Friedel-Crafts acylation of 4-methylresorcinol with chloroacetyl chloride in the presence of aluminium chloride in nitrobenzene [653].

m.p. 157° [653], 156° [1053].

2-Chloro-1-(2,4-dihydroxy-6-methylphenyl)ethanone

[22670-61-7] $C_9H_9ClO_3$ mol.wt. 200.62



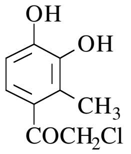
Synthesis

-Preparation by reaction of chloroacetonitrile with orcinol (68%) (Hoesch reaction) [264].

m.p. 151° [264].

2-Chloro-1-(3,4-dihydroxy-2-methylphenyl)ethanone

$C_9H_9ClO_3$ mol.wt. 200.62



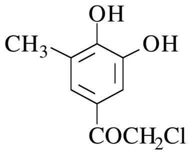
Synthesis

-Preparation by reaction of chloroacetyl chloride on 3-methylpyrocatechol with aluminium chloride in refluxing carbon disulfide (59%) [624].

m.p. 178° [624]; ^{1}H NMR [624], IR [624].

2-Chloro-1-(3,4-dihydroxy-5-methylphenyl)ethanone

$C_9H_9ClO_3$ mol.wt. 200.62



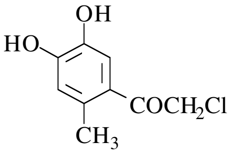
Synthesis

-Preparation by reaction of chloroacetic acid on 3-methylpyrocatechol with phosphorous oxychloride in refluxing benzene (28%) [624].

m.p. 180° [624]; ^{1}H NMR [624], IR [624].

2-Chloro-1-(4,5-dihydroxy-2-methylphenyl)ethanone

$C_9H_9ClO_3$ mol.wt. 200.62



Syntheses

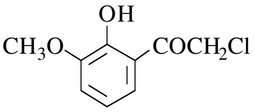
-Preparation by reaction of chloroacetyl chloride on homoveratrole (3,4-dimethoxytoluene) with aluminium chloride in carbon disulfide or nitrobenzene at 40° (82%) [1402].

-Also obtained (very low yield) by Fries rearrangement of creosol chloroacetate with aluminium chloride at 100° [836].

m.p. 130° [836], 128° [1402]; b.p.$_{14}$ 187° [1402].

2-Chloro-1-(2-hydroxy-3-methoxyphenyl)ethanone

[75717-52-1] $C_9H_9ClO_3$ mol.wt. 200.62



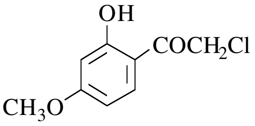
Synthesis

-Preparation by reaction of chloroacetonitrile on guaiacol with aluminium chloride and boron trichloride in refluxing ethylene dichloride (42%) [1409] [1466].

m.p. 113-114° [1409] [1466]; ^1H NMR [1466].

2-Chloro-1-(2-hydroxy-4-methoxyphenyl)ethanone

[60965-23-3] $C_9H_9ClO_3$ mol.wt. 200.62



Syntheses

-Preparation by reaction of diazomethane on 2,4-dihydroxy-α-chloroacetophenone in ethyl ether (60%) [1381].

-Preparation by reaction of chloroacetyl chloride on 2,4-dimethoxybenzene with aluminium chloride in refluxing carbon disulfide (86%) [96], (55%) [846] or in ethyl ether at r.t. (57%) [952].

-Preparation by reaction of chloroacetyl chloride on bromomagnesium 3-methoxyphenolate in toluene at r.t. (84%) [1286].

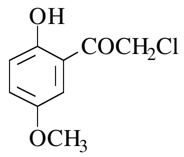
-Preparation by reaction of chloroacetonitrile on 3-methoxyphenol with aluminium chloride and boron trichloride in methylene chloride at r.t. (81%) [1409] [1466] or with zinc chloride and hydrochloric acid in ethyl ether (by-product) [1382].

-Also refer to: [1478].

m.p. 117-118° [1409] [1466], 116° [96] [952], 115-117° [1286], 115-116° [846], 114° [1381];
^1H NMR [952] [1286], MS [1286].

2-Chloro-1-(2-hydroxy-5-methoxyphenyl)ethanone

[75717-53-2] $C_9H_9ClO_3$ mol.wt. 200.62



Syntheses

-Preparation by reaction of chloroacetyl chloride on hydroquinone dimethyl ether with aluminium chloride in refluxing carbon disulfide (65%) [96].

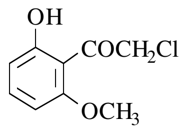
-Preparation by reaction of chloroacetonitrile on hydroquinone monomethyl ether with boron trichloride and aluminium chloride in ethylene dichloride (67%) [1409] [1466].

-Also refer to: [1478].

m.p. 83-84° [1409] [1466], 81-81°5 [96]; ^1H NMR [1466].

2-Chloro-1-(2-hydroxy-6-methoxyphenyl)ethanone

[75717-59-8] $C_9H_9ClO_3$ mol.wt. 200.62



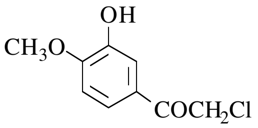
Syntheses

-Obtained (by-product) by reaction of chloroacetyl chloride on bromomagnesium 3-methoxyphenolate in toluene at r.t. (10%) [1286].
-Also obtained (by-product) by reaction of chloroacetonitrile on 3-methoxyphenol with aluminium chloride and boron trichloride mixture in ethylene dichloride at r.t. (5%) [1466].

m.p. 105-109° [1286]; ^{1}H NMR [1286], IR [1286].

2-Chloro-1-(3-hydroxy-4-methoxyphenyl)ethanone

[55761-46-1] $C_9H_9ClO_3$ mol.wt. 200.62



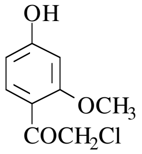
Syntheses

-Preparation by Fries rearrangement of guaiacol chloroacetate with aluminium chloride in refluxing carbon disulfide (63%) [1408], (49%) [84] [1094].
-Also obtained by reaction of 5 N sodium hydroxide with 5-chloroacetylguaiacol chloroacetate in dioxane, the mixture being gently warmed [564].

m.p. 122-123° [1094], 121-122° [564], 116-118° [1408].

2-Chloro-1-(4-hydroxy-2-methoxyphenyl)ethanone

[104691-67-0] $C_9H_9ClO_3$ mol.wt. 200.62



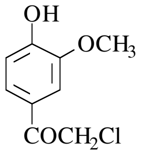
Synthesis

-Preparation by reaction of chloroacetonitrile on resorcinol monomethyl ether (Hoesch reaction) (major product, good yield) [1382].

m.p. 173-174° [1382].

2-Chloro-1-(4-hydroxy-3-methoxyphenyl)ethanone

[6344-28-1] $C_9H_9ClO_3$ mol.wt. 200.62



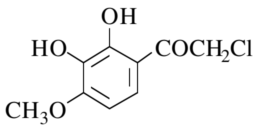
Syntheses

-Preparation by reaction of chloroacetyl chloride on veratrole with aluminium chloride in carbon disulfide (72%) [1198].
-Preparation by reaction of chloroacetyl chloride with guaiacol in the presence of aluminium chloride in boiling carbon disulfide (56%) [478]; the same yield was obtained using tetrachloroethane as solvent [478].
-Preparation by chlorination of the acetate of acetoguaiacone (4-acetoxy-3-methoxyacetophenone) with 1.1 mol. equiv chlorine in chloroform and subsequent hydrolysis (67%) [1374].

m.p. 102-104° [564], 102° [1198], 100-102° [478] [1374];
^{1}H NMR [1374], ^{13}C NMR [1374], MS [210].

2-Chloro-1-(2,3-dihydroxy-4-methoxyphenyl)ethanone

$C_9H_9ClO_4$ mol.wt. 216.62

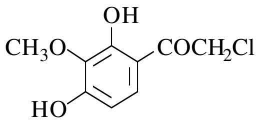


Synthesis

-Preparation from 2,3-dihydroxyanisole by Hoesch acylation by means of chloroacetonitrile (70%) [554].

2-Chloro-1-(2,4-dihydroxy-3-methoxyphenyl)ethanone

[69151-93-5] $C_9H_9ClO_4$ mol.wt. 216.62



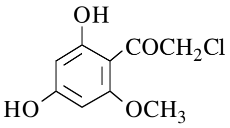
Synthesis

-Preparation by reaction of chloroacetonitrile with 2,6-dihydroxyanisole (Hoesch reaction) [916].

m.p. 71-72° [916].

2-Chloro-1-(2,4-dihydroxy-6-methoxyphenyl)ethanone

[70651-70-6] $C_9H_9ClO_4$ mol.wt. 216.62



Syntheses

-Obtained by treatment of 2-hydroxy-4,6-dimethoxy-α-chloroacetophenone with aluminium chloride in refluxing chlorobenzene for 1 h (85%) [592].

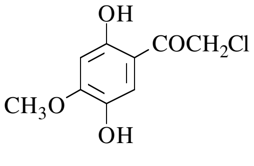
-Preparation by reaction of chloroacetonitrile with phloroglucinol monomethyl ether (Hoesch reaction) (41%) [596].

-Also refer to: [580] [581].

m.p. 184-186° (d) [596], 174-175° [592].
One of the reported melting points is obviously wrong.

2-Chloro-1-(2,5-dihydroxy-4-methoxyphenyl)ethanone

[163980-43-6] $C_9H_9ClO_4$ mol.wt. 216.62



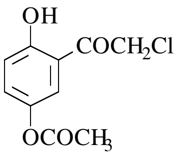
Synthesis

-Preparation by reaction of chloroacetonitrile with methoxyhydroquinone (Hoesch reaction) (84%) [480].

light brown crystals [480]; ^{1}H NMR [480], MS [480].

1-[5-(Acetyloxy)-2-hydroxyphenyl]-2-chloroethanone

$C_{10}H_9ClO_4$ mol.wt. 228.63



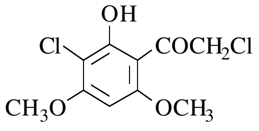
Syntheses

-Preparation by reaction of acetyl chloride on 2,5-dihydroxy-α-chloroacetophenone at reflux (73%) [819].
-Also obtained (by-product) by reaction of 2,5-diacetoxy-α-chloroacetophenone with sodium acetate (7%) [819].

m.p. 151-152° [819].

2-Chloro-1-(3-chloro-2-hydroxy-4,6-dimethoxyphenyl)ethanone

[72565-72-1] $C_{10}H_{10}Cl_2O_4$ mol.wt. 265.09



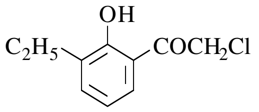
Synthesis

-Preparation by reaction of chloroacetyl chloride with 2-chloro-3,5-dimethoxyphenol in the presence of aluminium chloride in nitrobenzene at r.t. [362] [942] [1558], (88%) [1558], (70%) [942].

m.p. 211° (d) [942]; ^{1}H NMR [1558], IR [942].

2-Chloro-1-(3-ethyl-2-hydroxyphenyl)ethanone

$C_{10}H_{11}ClO_2$ mol.wt. 198.65



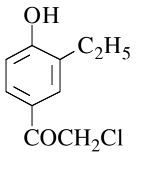
Synthesis

-Preparation by Fries rearrangement of 2-ethylphenyl chloroacetate with aluminium chloride without solvent at 140° (39%) [290].

oil [290].

2-Chloro-1-(3-ethyl-4-hydroxyphenyl)ethanone

[145736-97-6] $C_{10}H_{11}ClO_2$ mol.wt. 198.65

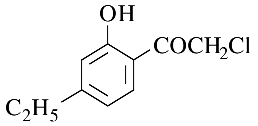


Synthesis

-Refer to: [301].

2-Chloro-1-(4-ethyl-2-hydroxyphenyl)ethanone

$C_{10}H_{11}ClO_2$ mol.wt. 198.65



Syntheses

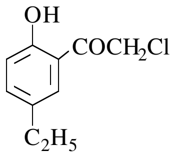
-Preparation by Fries rearrangement of 3-ethylphenyl chloroacetate with aluminium chloride without solvent at 140° (49%) [290].

-Also obtained also by Fries rearrangement of 4-ethylphenyl chloroacetate with aluminium chloride without solvent at 140°, on account of a migration of the ethyl group (46%) [290].

m.p. 69-70° [290].

2-Chloro-1-(5-ethyl-2-hydroxyphenyl)ethanone

$C_{10}H_{11}ClO_2$ mol.wt. 198.65



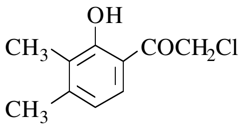
Synthesis

-Preparation by reaction of chloroacetyl chloride on 4-ethylanisole with aluminium chloride in carbon disulfide (32%) [290].

m.p. 50-52° [290].

2-Chloro-1-(2-hydroxy-3,4-dimethylphenyl)ethanone

$C_{10}H_{11}ClO_2$ mol.wt. 198.65



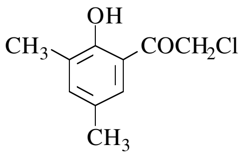
Synthesis

-Preparation by reaction of chloroacetonitrile on 2,3-dimethylphenol with aluminium chloride and boron trifluoride in refluxing ethylene dichloride (quantitative yield) [1466].

m.p. 95-96° [1466].

2-Chloro-1-(2-hydroxy-3,5-dimethylphenyl)ethanone

$C_{10}H_{11}ClO_2$ mol.wt. 198.65

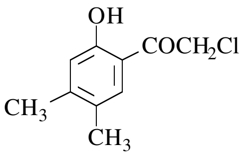


Synthesis

-Preparation by reaction of chloroacetyl chloride on 2,4-dimethylanisole with aluminium chloride in carbon disulfide (20%) [93].

2-Chloro-1-(2-hydroxy-4,5-dimethylphenyl)ethanone

[22307-96-6] $C_{10}H_{11}ClO_2$ mol.wt. 198.65



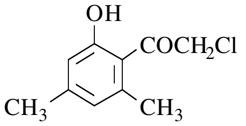
Synthesis

-Preparation by Fries rearrangement of 3,4-dimethylphenyl chloroacetate with aluminium chloride without solvent at 150° [1130].

m.p. 101° [1130]; ^{1}H NMR [1130], IR [1130].

2-Chloro-1-(2-hydroxy-4,6-dimethylphenyl)ethanone

$C_{10}H_{11}ClO_2$ mol.wt. 198.65



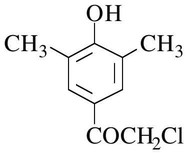
Synthesis

-Preparation by Fries rearrangement of 3,5-dimethylphenyl chloroacetate with aluminium chloride without solvent at 135-140° [98] [518], (good yield) [518].

m.p. 92° [518].

2-Chloro-1-(4-hydroxy-3,5-dimethylphenyl)ethanone

[40943-25-7] $C_{10}H_{11}ClO_2$ mol.wt. 198.65



Syntheses

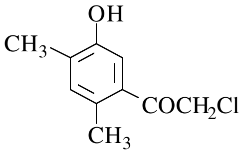
-Preparation by reaction of chloroacetyl chloride with 2,6-dimethylphenol in the presence of aluminium chloride in nitrobenzene at 60° (43%) [171].

-Also obtained (poor yield) by reaction of aluminium chloride on 2,6-dimethyl-4-ethylphenyl chloroacetate without solvent at 150° [94].

m.p. 107°7 [171]; ^{1}H NMR [171], IR [171], MS [171].

2-Chloro-1-(5-hydroxy-2,4-dimethylphenyl)ethanone

$C_{10}H_{11}ClO_2$ mol.wt. 198.65



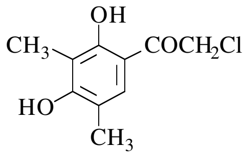
Synthesis

-Preparation (by-product) by reaction of chloroacetyl chloride on 2,4-dimethylanisole with aluminium chloride in carbon disulfide (10%) [93].

m.p. 107-107°5 [93].

2-Chloro-1-(2,4-dihydroxy-3,5-dimethylphenyl)ethanone

$C_{10}H_{11}ClO_3$ mol.wt. 214.65



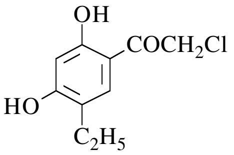
Synthesis

-Preparation by reaction of acetonitrile on 2,4-dimethylresorcinol (Hoesch reaction) (93%) [846].

m.p. 126-127° [846].

2-Chloro-1-(5-ethyl-2,4-dihydroxyphenyl)ethanone

$C_{10}H_{11}ClO_3$ mol.wt. 214.65



Syntheses

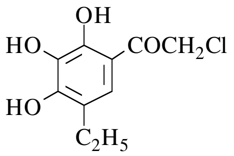
-Preparation by reaction of 4-ethylresorcinol with chloroacetonitrile (Hoesch reaction) [1053], (95%) [367], (88%) [1051].

-Preparation by Friedel-Crafts acylation of 4-ethylresorcinol with chloroacetyl chloride in nitrobenzene in the presence of aluminium chloride for 24 h at r.t. (70%) [653].

m.p. 163-165° [653], 161-161°5 [367], 161° [1051] [1053].

2-Chloro-1-(5-ethyl-2,3,4-trihydroxyphenyl)ethanone

$C_{10}H_{11}ClO_4$ mol.wt. 230.65



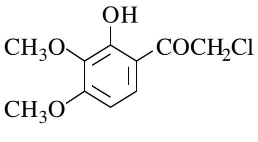
Synthesis

-Preparation by reaction of chloroacetonitrile with 4-ethylpyrogallol (m.p. 105-106°) (Hoesch reaction) (60%) [1051].

m.p. 131-132°5 [1051].

2-Chloro-1-(2-hydroxy-3,4-dimethoxyphenyl)ethanone

[7507-92-8] $C_{10}H_{11}ClO_4$ mol.wt. 230.65



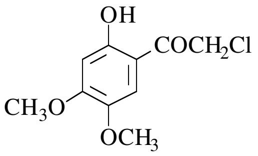
Synthesis

-Preparation by reaction of chloroacetyl chloride with 1,2,3-trimethoxybenzene in the presence of aluminium chloride in ethylene dichloride first at 0°, then at r.t. (70%) [1102] or without solvent at 100° (16%) [1199].

m.p. 161°5 [1199], 160-162° [1102]; ^{1}H NMR [1102], MS [1102].

2-Chloro-1-(2-hydroxy-4,5-dimethoxyphenyl)ethanone

$C_{10}H_{11}ClO_4$ mol.wt. 230.65



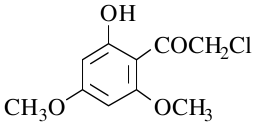
Synthesis

-Preparation by reaction of chloroacetonitrile on 3,4-dimethoxyphenol (Hoesch reaction) (47%) [739].

m.p. 154-155° [739].

2-Chloro-1-(2-hydroxy-4,6-dimethoxyphenyl)ethanone

[103040-51-3] $C_{10}H_{11}ClO_4$ mol.wt. 230.65



Syntheses

-Preparation by reaction of chloroacetonitrile on phloroglucinol dimethyl ether (Hoesch reaction) [292].

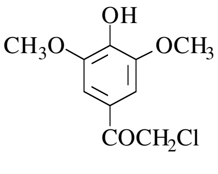
-Preparation by reaction of chloroacetyl chloride on phloroglucinol trimethyl ether with aluminium chloride in boiling ligroin [517].

-Preparation by partial demethylation of 2,4,6-trimethoxy-α-chloroacetophenone by heating with aluminium chloride without solvent at 120° (89%) [514].

m.p. 144-146° [514], 142-144° [517], 136-140° [292];
^{1}H NMR [292], IR [292], MS [292].

2-Chloro-1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone

[59719-58-3] $C_{10}H_{11}ClO_4$ mol.wt. 230.65

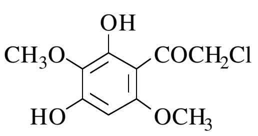


Synthesis

-Preparation by chlorination of 4-(benzyloxy)-3,5-dimethoxybenzoylacetic acid methyl ester with sulfuryl chloride in acetic acid at r.t., and subsequent hydrolysis of the keto ester so obtained by refluxing in hydrochloric acid (90%) [43].

2-Chloro-1-(2,4-dihydroxy-3,6-dimethoxyphenyl)ethanone

$C_{10}H_{11}ClO_5$ mol.wt. 246.65



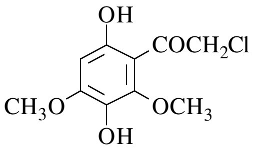
Synthesis

-Preparation by reaction of chloroacetonitrile on 2,5-dimethoxyresorcinol (Hoesch reaction) (52%) [548], (25%) [1357].

m.p. 150-151°5 [1357], 148-149° [548].

2-Chloro-1-(3,6-dihydroxy-2,4-dimethoxyphenyl)ethanone

$C_{10}H_{11}ClO_5$ mol.wt. 246.65



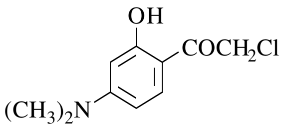
Synthesis

-Obtained by reaction of chloroacetyl chloride with 1,4-dihydroxy-2,6-dimethoxybenzene in ethyl ether in the presence of aluminium chloride, cooling in ice and standing overnight (45%) [124].

m.p. 154° [124].

2-Chloro-1-[4-(dimethylamino)-2-hydroxyphenyl]ethanone

[127354-36-3] $C_{10}H_{12}ClNO_2$ mol.wt. 213.66



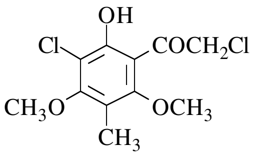
Synthesis

-Preparation by reaction of chloroacetyl chloride on bromomagnesium 3-(N,N-dimethylamino)phenolate in toluene at r.t. (92%) [1286].

m.p. 96-98° (d) [1286]; ^{1}H NMR [1286], IR [1286], MS [1286].

2-Chloro-1-(3-chloro-2-hydroxy-4,6-dimethoxy-5-methylphenyl)ethanone

[201288-73-5] $C_{11}H_{12}Cl_2O_4$ mol.wt. 279.12



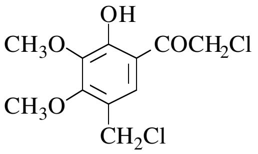
Synthesis

-Preparation by reaction of chloroacetyl chloride with 2-chloro-3,5-dimethoxy-4-methylphenol in ethyl ether in the presence of aluminium chloride, first at 0° under an argon atmosphere, then at r.t. for 0.5 h and at reflux for 3 h (90%) [1435].

m.p. 144-146° [1435]; ^{1}H NMR [1435], IR [1435], MS [1435].

2-Chloro-1-[5-(chloromethyl)-2-hydroxy-3,4-dimethoxyphenyl]ethanone

[76439-46-8] $C_{11}H_{12}Cl_2O_4$ mol.wt. 279.12



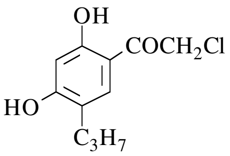
Synthesis

-Preparation by reaction of paraformaldehyde with 2-hydroxy-3,4-dimethoxy-α-chloroacetophenone in the presence of hydrochloric acid gas in acetic acid between 60-70° (77%) [1102].

m.p. 130-131° [1102]; ^{1}H NMR [1102], MS [1102].

2-Chloro-1-(2,4-dihydroxy-5-propylphenyl)ethanone

$C_{11}H_{13}ClO_3$ mol.wt. 228.68



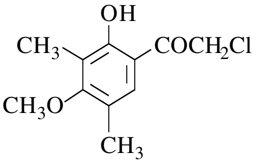
Synthesis

-Preparation by reaction of chloroacetonitrile with 4-propylresorcinol (Hoesch reaction) [1053].

m.p. 156-157° [1053].

2-Chloro-1-(2-hydroxy-4-methoxy-3,5-dimethylphenyl)ethanone

$C_{11}H_{13}ClO_3$ mol.wt. 228.68



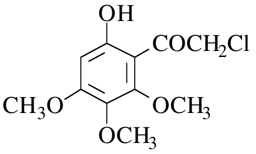
Synthesis

-Preparation by reaction of chloroacetyl chloride on 2,4-dimethylresorcinol dimethyl ether with aluminium chloride in refluxing carbon disulfide (42%) [846].

m.p. 158-160° [846].

2-Chloro-1-(6-hydroxy-2,3,4-trimethoxyphenyl)ethanone

$C_{11}H_{13}ClO_5$ mol.wt. 260.67



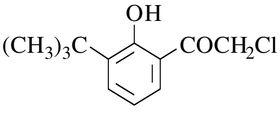
Synthesis

-Preparation by reaction of chloroacetonitrile on 3,4,5-trimethoxyphenol (antiarol) (Hoesch reaction) (42%) [1357].

m.p. 107-107°5 [1357].

2-Chloro-1-[3-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone

[127354-33-0] $C_{12}H_{15}ClO_2$ mol.wt. 226.70



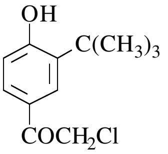
Synthesis

-Preparation by reaction of chloroacetyl chloride with aluminium or titanium 2-tert-butylphenolate in toluene at r.t. (98% and 70% yields, respectively) [1286].

m.p. 52-53° [1286]; ^{1}H NMR [1286], IR [1286], MS [1286].

2-Chloro-1-[3-(1,1-dimethylethyl)-4-hydroxyphenyl]ethanone

[127354-34-1] $C_{12}H_{15}ClO_2$ mol.wt. 226.70

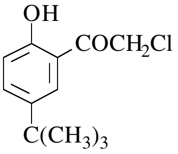


Synthesis

-Obtained by reaction of chloroacetyl chloride with dichloroaluminium 2-tert-butylphenolate or with trichloro (2-tert-butylphenoxy)titanium in toluene at r.t. (50 and 52% yields, respectively) [1286].

2-Chloro-1-[5-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone

[75060-43-4] $C_{12}H_{15}ClO_2$ mol.wt. 226.70



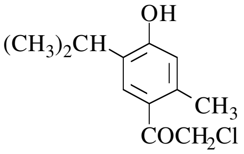
Synthesis

-Obtained by reaction of chloroacetyl chloride on 4-tert-butylanisole with aluminium chloride in methylene chloride at r.t. (10%) [685].

m.p. 51-52° [685]; ^{1}H NMR [685], IR [685].

2-Chloro-1-[4-hydroxy-2-methyl-5-(1-methylethyl)phenyl]ethanone

[72235-89-3] $C_{12}H_{15}ClO_2$ mol.wt. 226.70



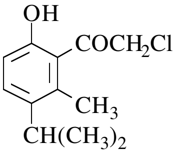
Syntheses

-Obtained by reaction of chloroacetyl chloride on thymol with aluminium chloride in nitrobenzene at 50° (21%) [737].
-Also obtained by Fries rearrangement of thymyl chloroacetate with aluminium chloride in nitrobenzene at r.t. (15%) [105].

m.p. 133° [737], 132° [105]; b.p.$_{0.0018}$ 175-178° [737].

2-Chloro-1-[6-hydroxy-2-methyl-3-(1-methylethyl)phenyl]ethanone

[23053-74-9] $C_{12}H_{15}ClO_2$ mol.wt. 226.70



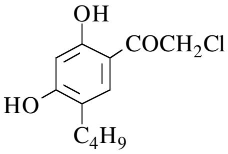
Synthesis

-Obtained by reaction of chloroacetyl chloride on 3-methyl-4-isopropylanisole (p-thymol methyl ether) with aluminium chloride in carbon disulfide [1261].

m.p. 68°5 [1261].

1-(5-Butyl-2,4-dihydroxyphenyl)-2-chloroethanone

$C_{12}H_{15}ClO_3$ mol.wt. 242.70



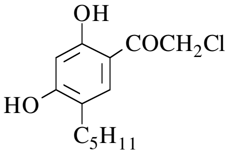
Synthesis

-Preparation by reaction of chloroacetonitrile with 4-butylresorcinol (Hoesch reaction) [1053].

m.p. 155-156° [1053].

2-Chloro-1-(2,4-dihydroxy-5-pentylphenyl)ethanone

$C_{13}H_{17}ClO_3$ mol.wt. 256.73



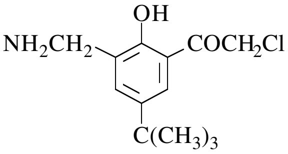
Synthesis

-Preparation by reaction of chloroacetonitrile with 4-pentylresorcinol (Hoesch reaction) [1053].

m.p. 148-149° [1053].

1-[3-(Aminomethyl)-5-(1,1-dimethylethyl)-2-hydroxyphenyl]-2-chloroethanone

[75060-96-7] $C_{13}H_{18}ClNO_2$ mol.wt. 255.74

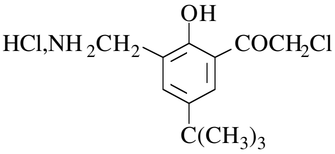


Synthesis

-From the corresponding hydrochloride (see below) [685].

1-[3-(Aminomethyl)-5-(1,1-dimethylethyl)-2-hydroxyphenyl]-2-chloroethanone *(Hydrochloride)*

[75060-68-3] $C_{13}H_{18}ClNO_2$, HCl mol.wt. 292.20



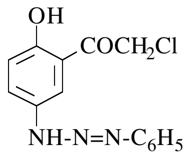
Synthesis

-Preparation by reaction of concentrated hydrochloric acid on 2-chloroacetyl-4-tert-butyl-6-(N-chloroacetylaminomethyl)phenol in refluxing ethanol (64%) [685].

m.p. 160° (d) [685]; ^{1}H NMR [685], IR [685].

2-Chloro-1-[2-hydroxy-5-(1-triazene-3-phenyl)phenyl]ethanone

$C_{14}H_{12}ClN_3O_2$ mol.wt. 289.72



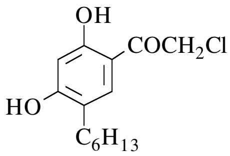
Synthesis

-Obtained by reaction of benzenediazonium chloride on 5-amino-2-hydroxy-α-chloroacetophenone in the presence of an aqueous sodium acetate solution [859].

m.p. 127° [859].

2-Chloro-1-(5-hexyl-2,4-dihydroxyphenyl)ethanone

$C_{14}H_{19}ClO_3$ mol.wt. 270.76



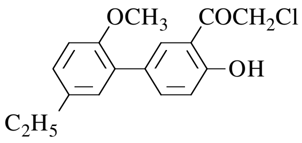
Synthesis

-Preparation by reaction of chloroacetonitrile with 4-hexylresorcinol (Hoesch reaction) [1053].

m.p. 145° [1053].

2-Chloro-1-(5'-ethyl-4-hydroxy-2'-methoxy[1,1'-biphenyl]-3-yl)ethanone

[131845-71-1] $C_{17}H_{17}ClO_3$ mol.wt. 304.77



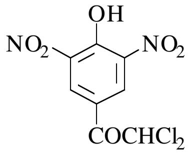
Synthesis

-Refer to: [1441].

2.2.2. From dichloroacetic acid

2,2-Dichloro-1-(4-hydroxy-3,5-dinitrophenyl)ethanone

[52129-63-2] $C_8H_4Cl_2N_2O_6$ mol.wt. 295.04

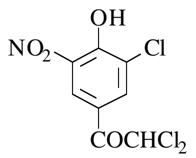


Synthesis

-Preparation by reaction of chlorine on 4-hydroxy-3,5-dinitroacetophenone in methylene chloride-ethanol mixture (93%) [241] [1171].

2,2-Dichloro-1-(3-chloro-4-hydroxy-5-nitrophenyl)ethanone

[52501-35-6] $C_8H_4Cl_3NO_4$ mol.wt. 284.48

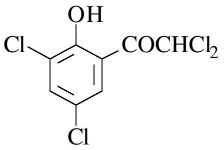


Synthesis

-Preparation by reaction of chlorine on 4-hydroxy-3-nitroacetophenone with ferric chloride in methylene chloride-ethanol mixture (94%) [241] [1171].

2,2-Dichloro-1-(3,5-dichloro-2-hydroxyphenyl)ethanone

$C_8H_4Cl_4O_2$ mol.wt. 273.93



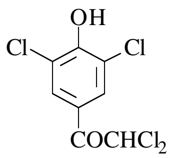
Syntheses

-Preparation by Fries rearrangement of 2,4-dichlorophenyl dichloroacetate with aluminium chloride without solvent at 120° (50%) [1311].
-Also obtained when 4-hydroxycoumarin in acetic acid was treated with an excess of gaseous chlorine at 10-15° and the polychlorinated product so formed hydrolyzed [994] [995].

m.p. 90° [1311], 70° [994] [995].

2,2-Dichloro-1-(3,5-dichloro-4-hydroxyphenyl)ethanone

$C_8H_4Cl_4O_2$ mol.wt. 273.93



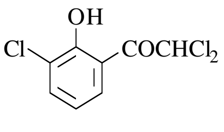
Synthesis

-Obtained (by-product) by Fries rearrangement of 2,6-dichlorophenyl dichloroacetate with aluminium chloride without solvent at 135° (9%) [1442].

m.p. 92°5-94°5 [1442].

2,2-Dichloro-1-(3-chloro-2-hydroxyphenyl)ethanone

$C_8H_5Cl_3O_2$ mol.wt. 239.48



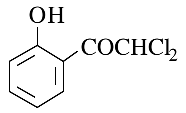
Synthesis

-Preparation by Fries rearrangement of 2-chlorophenyl dichloroacetate with aluminium chloride without solvent at 120° (76%) [1311].

b.p.$_8$ 173° [1311].

2,2-Dichloro-1-(2-hydroxyphenyl)ethanone

[29003-58-5] $C_8H_6Cl_2O_2$ mol.wt. 205.04



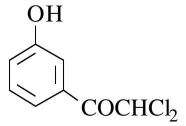
Synthesis

-Preparation by Fries rearrangement of phenyl dichloroacetate with aluminium chloride without solvent at 120° (50%) [508].

b.p.$_{0.1}$ 65-72° [508].

2,2-Dichloro-1-(3-hydroxyphenyl)ethanone

[85299-04-3] $C_8H_6Cl_2O_2$ mol.wt. 205.04



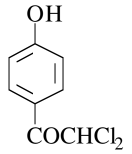
Synthesis

-Preparation by reaction of hexachloro-2,4-cyclohexadienone on 3-hydroxyacetophenone in refluxing ethanol (34%) [603].

pale yellow oil [603]; ^{1}H NMR [603], IR [603].

2,2-Dichloro-1-(4-hydroxyphenyl)ethanone

$C_8H_6Cl_2O_2$ mol.wt. 205.04



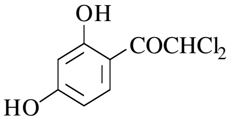
Synthesis

-Preparation by reaction of dichloroacetyl chloride on anisole with aluminium chloride in carbon disulfide at 25-30° (34%) [979].

m.p. 98° [979].

2,2-Dichloro-1-(2,4-dihydroxyphenyl)ethanone

[29003-59-6] $C_8H_6Cl_2O_3$ mol.wt. 221.04

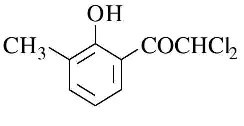


Synthesis

-Refer to: [756].

2,2-Dichloro-1-(2-hydroxy-3-methylphenyl)ethanone

[145818-23-1] $C_9H_8Cl_2O_2$ mol.wt. 219.07



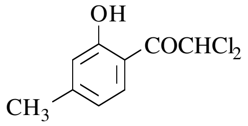
Synthesis

-Preparation by reaction of dichloroacetonitrile on o-cresol (Hoesch reaction) (25%) [183].

m.p. 33°5 [183]; ^{1}H NMR [183], IR [183], UV [183], MS [183].

2,2-Dichloro-1-(2-hydroxy-4-methylphenyl)ethanone

[116046-02-7] $C_9H_8Cl_2O_2$ mol.wt. 219.07



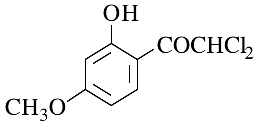
Synthesis

-Preparation by reaction of dichloroacetyl chloride with 3-methylanisole in the presence of aluminium chloride at 80° (30%) [945].

m.p. 125-126° [945]; ^{1}H NMR [945], IR [945], MS [945].

2,2-Dichloro-1-(2-hydroxy-4-methoxyphenyl)ethanone

[95235-25-9] $C_9H_8Cl_2O_3$ mol.wt. 235.07



Syntheses

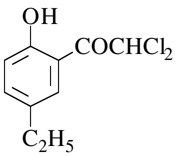
-Preparation by Fries rearrangement of 3-methoxyphenyl dichloroacetate with aluminium chloride without solvent at 120° (42%) [1311].

-Also obtained (by-product) by reaction of dichloroacetyl chloride with resorcinol dimethyl ether in the presence of aluminium chloride at 0-10° (9%) [945].

m.p. 86° [945], 84° [1311].

2,2-Dichloro-1-(5-ethyl-2-hydroxyphenyl)ethanone

$C_{10}H_{10}Cl_2O_2$ mol.wt. 233.09



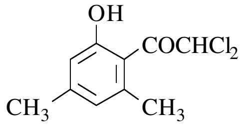
Synthesis

-Preparation by Fries rearrangement of 4-ethylphenyl dichloroacetate with aluminium chloride without solvent at 120° (53%) [1311].

b.p.$_8$ 110° [1311].

2,2-Dichloro-1-(2-hydroxy-4,6-dimethylphenyl)ethanone

$C_{10}H_{10}Cl_2O_2$ mol.wt. 233.09



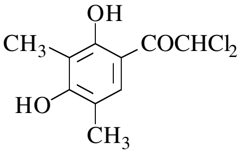
Synthesis

-Preparation by Fries rearrangement of 3,5-dimethylphenyl dichloroacetate with aluminium chloride without solvent at 120° (58%) [1311].

b.p.$_4$ 150° [1311].

2,2-Dichloro-1-(2,4-dihydroxy-3,5-dimethylphenyl)ethanone

$C_{10}H_{10}Cl_2O_3$ mol.wt. 249.09



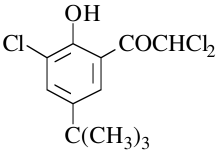
Synthesis

-Preparation by reaction of dichloroacetonitrile on 2,4-dimethylresorcinol (Hoesch reaction) [846].

m.p. 123° [846]; b.p.$_{0.001}$ 150° [846].

2,2-Dichloro-1-[3-chloro-5-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone

$C_{12}H_{13}Cl_3O_2$ mol.wt. 295.59



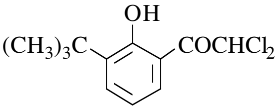
Synthesis

-Preparation by Fries rearrangement of 4-tert-butyl-2-chlorophenyl dichloroacetate with aluminium chloride at 120° (79%) [1311].

b.p.$_{20}$ 175° [1311].

2,2-Dichloro-1-[3-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone

[127354-38-5] $C_{12}H_{14}Cl_2O_2$ mol.wt. 261.15



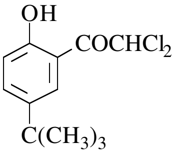
Synthesis

-Preparation by reaction of dichloroacetyl chloride on bromomagnesium 2-tert-butylphenolate in toluene at r.t. (58%) [1286].

yellow oil [1286]; ^{1}H NMR [1286], IR [1286], MS [1286].

2,2-Dichloro-1-[5-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone

$C_{12}H_{14}Cl_2O_2$ mol.wt. 261.15



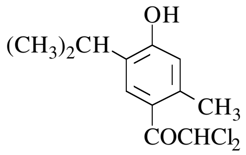
Synthesis

-Preparation by Fries rearrangement of 4-tert-butylphenyl dichloroacetate with aluminium chloride at 120° (86%) [1311].

b.p.$_{10}$ 120° [1311].

2,2-Dichloro-1-[4-hydroxy-2-methyl-5-(1-methylethyl)phenyl]ethanone

[72235-91-7] $C_{12}H_{14}Cl_2O_2$ mol.wt. 261.15



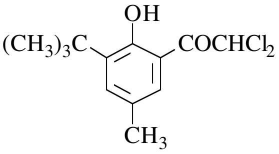
Synthesis

-Preparation by reaction of dichloroacetyl chloride on thymol with aluminium chloride in nitrobenzene at r.t., *via* a Fries rearrangement (20%) [105].

m.p. 110° [105].

2,2-Dichloro-1-[3-(1,1-dimethylethyl)-2-hydroxy-5-methylphenyl]ethanone

[127354-45-4] $C_{13}H_{16}Cl_2O_2$ mol.wt. 275.17



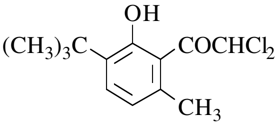
Syntheses

-Preparation by reaction of dichloroacetyl chloride,
*on aluminium tri 2-tert-butyl-4-methylphenolate in toluene at r.t. (98%) [1286];
*on bromomagnesium 2-tert-butyl-4-methylphenolate in toluene at r.t. (78%) [1286].

m.p. 55-59° [1286]; ^1H NMR [1286], IR [1286], MS [1286].

2,2-Dichloro-1-[3-(1,1-dimethylethyl)-2-hydroxy-6-methylphenyl]ethanone

$C_{13}H_{16}Cl_2O_2$ mol.wt. 275.17



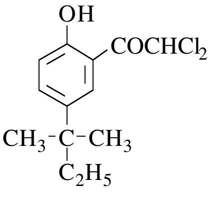
Synthesis

-Preparation by Fries rearrangement of 2-tert-butyl-5-methylphenyl dichloroacetate without solvent at 120° (60%) [1311].

b.p.$_6$ 88° [1311].

2,2-Dichloro-1-[5-(1,1-dimethylpropyl)-2-hydroxyphenyl]ethanone

$C_{13}H_{16}Cl_2O_2$ mol.wt. 275.17



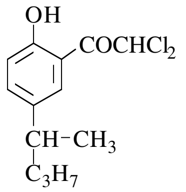
Synthesis

-Preparation by Fries rearrangement of 4-tert-pentylphenyl dichloroacetate with aluminium chloride without solvent at 120° (54%) [1311].

b.p.$_2$ 122° [1311].

2,2-Dichloro-1-[2-hydroxy-5-(1-methylbutyl)phenyl]ethanone

$C_{13}H_{16}Cl_2O_2$ mol.wt. 275.17



Synthesis

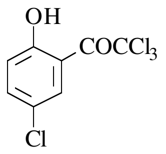
-Preparation by Fries rearrangement of 5-sec-pentylphenyl dichloroacetate with aluminium chloride without solvent at 120° (43%) [1311].

b.p.$_{10}$ 125° [1311].

2.2.3. From trichloroacetic acid

2,2,2-Trichloro-1-(5-chloro-2-hydroxyphenyl)ethanone

[145818-26-4] $C_8H_4Cl_4O_2$ mol.wt. 273.93



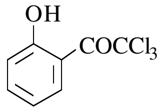
Syntheses

-Preparation by Fries rearrangement of 4-chlorophenyl trichloroacetate with aluminium chloride without solvent at 125-130° (25%) [177] [1310].
-Preparation by reaction of trichloroacetonitrile on 4-chlorophenol (Hoesch reaction) [183].

b.p.$_{44}$ 129-132° [177] [183] [1310]; ^{1}H NMR [183], IR [183], UV [183], MS [183].

2,2,2-Trichloro-1-(2-hydroxyphenyl)ethanone

[75717-55-4] $C_8H_5Cl_3O_2$ mol.wt. 239.48



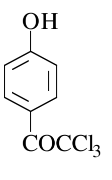
Syntheses

-Preparation by reaction of trichloroacetonitrile on phenol with aluminium chloride and boron trichloride mixture in refluxing methylene chloride (92%) [1409] [1466].
-Preparation by reaction of trichloroacetonitrile on phenol (Hoesch reaction) (64%) [183].

m.p. 53-54° [183]; ^{1}H NMR [183] [1466], IR [183], UV [183], MS [183].

2,2,2-Trichloro-1-(4-hydroxyphenyl)ethanone

[131170-16-6] $C_8H_5Cl_3O_2$ mol.wt. 239.48



Synthesis

-Preparation by reaction of trichloroacetonitrile on phenol (Hoesch reaction) (95%) [241] [655] [656] [1171], (30%) [183].

m.p. 99-99°5 [183] [655] [656]; b.p.$_{0.5}$ 170° [655] [656]; ^{1}H NMR [183], IR [183], UV [183], MS [183].

2,2,2-Trichloro-1-(2,4-dihydroxyphenyl)ethanone

[76569-42-1] $C_8H_5Cl_3O_3$ mol.wt. 255.48

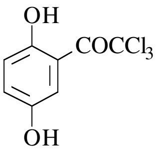
Synthesis

-Preparation by reaction of trichloroacetonitrile with resorcinol in the presence of triflic acid (52%) [207] or zinc chloride (55%) [439].

m.p. 142°5 [439], 138-141° [207];
^{1}H NMR [207], IR [207], UV [207], MS [207].

2,2,2-Trichloro-1-(2,5-dihydroxyphenyl)ethanone

[145818-27-5] $C_8H_5Cl_3O_3$ mol.wt. 255.48



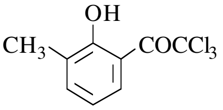
Synthesis

-Preparation by reaction of trichloroacetonitrile on hydroquinone (Hoesch reaction) (40%) [183].

m.p. 123-124° [183];
^{1}H NMR [183], IR [183], UV [183], MS [183].

2,2,2-Trichloro-1-(2-hydroxy-3-methylphenyl)ethanone

[145818-22-0] $C_9H_7Cl_3O_2$ mol.wt. 253.51



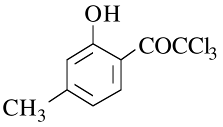
Synthesis

-Preparation by reaction of trichloroacetonitrile on o-cresol (Hoesch reaction) (70%) [183].

oil [183]; ^{1}H NMR [183], IR [183], UV [183], MS [183].

2,2,2-Trichloro-1-(2-hydroxy-4-methylphenyl)ethanone

$C_9H_7Cl_3O_2$ mol.wt. 253.51



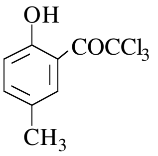
Synthesis

-Preparation by reaction of trichloroacetonitrile on m-cresol with aluminium chloride and gazeous hydrochloric acid in chlorobenzene at r.t. (37%) [656].

b.p.$_{17}$ 162-163° [656].

2,2,2-Trichloro-1-(2-hydroxy-5-methylphenyl)ethanone

$C_9H_7Cl_3O_2$ mol.wt. 253.51

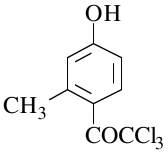


Synthesis

-Obtained by reaction of trichloroacetonitrile on p-cresol with aluminium chloride and gazeous hydrochloric acid in chlorobenzene at 50-60° (11%) [656].

2,2,2-Trichloro-1-(4-hydroxy-2-methylphenyl)ethanone

$C_9H_7Cl_3O_2$ mol.wt. 253.51



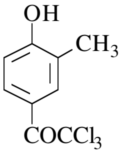
Synthesis

-Preparation by reaction of trichloroacetonitrile on m-cresol with aluminium chloride and gazeous hydrochloric acid in chlorobenzene at r.t. (36%) [656].

m.p. 84-87° [656].

2,2,2-Trichloro-1-(4-hydroxy-3-methylphenyl)ethanone

$C_9H_7Cl_3O_2$ mol.wt. 253.51



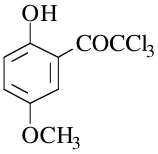
Synthesis

-Preparation by reaction of trichloroacetonitrile on o-cresol with aluminium chloride and gazeous hydrochloric acid in chlorobenzene at 60° (90%) [656].

m.p. 90-91° [656].

2,2,2-Trichloro-1-(2-hydroxy-5-methoxyphenyl)ethanone

[145818-25-3] $C_9H_7Cl_3O_3$ mol.wt. 269.51



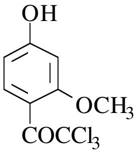
Synthesis

-Preparation by reaction of trichloroacetonitrile on 4-methoxyphenol (Hoesch reaction) (73%) [183].

m.p. 65-66° [183];
^1H NMR [183], IR [183], UV [183], MS [183].

2,2,2-Trichloro-1-(4-hydroxy-2-methoxyphenyl)ethanone

$C_9H_7Cl_3O_3$ mol.wt. 269.51



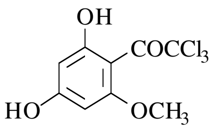
Synthesis

-Preparation by reaction of trichloroacetonitrile on 3-methoxyphenol with zinc chloride and gazeous hydrochloric acid in ethyl ether at 0° (Hoesch reaction) (34%) [1533].

m.p. 144° [1533].

2,2,2-Trichloro-1-(2,4-dihydroxy-6-methoxyphenyl)ethanone

$C_9H_7Cl_3O_4$ mol.wt. 285.51



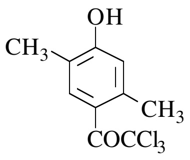
Synthesis

-Preparation by reaction of trichloroacetonitrile on phloroglucinol monomethyl ether with zinc chloride and gazeous hydrochloric acid in ethyl ether at 0° (Hoesch reaction) (39 to 49%) [1533].

m.p. 152° [1533].

2,2,2-Trichloro-1-(4-hydroxy-2,5-dimethylphenyl)ethanone

$C_{10}H_9Cl_3O_2$ mol.wt. 267.54



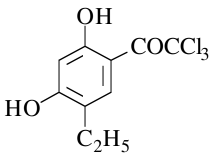
Synthesis

-Preparation by reaction of trichloroacetonitrile on 2,5-dimethylphenol with aluminium chloride and gazeous hydrochloric acid in chlorobenzene at r.t. (70%) [655].

m.p. 85-86° [655].

2,2,2-Trichloro-1-(5-ethyl-2,4-dihydroxyphenyl)ethanone

$C_{10}H_9Cl_3O_3$ mol.wt. 283.54



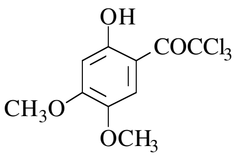
Synthesis

-Preparation by reaction of trichloroacetonitrile on 4-ethylresorcinol (Hoesch reaction) (52%) [439].

m.p. 138° [439].

2,2,2-Trichloro-1-(2-hydroxy-4,5-dimethoxyphenyl)ethanone

$C_{10}H_9Cl_3O_4$ mol.wt. 299.54



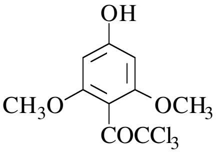
Synthesis

-Preparation by reaction of trichloroacetonitrile on 3,4-dimethoxylphenol (Hoesch reaction) (26%) [1533].

m.p. 107° [1533].

2,2,2-Trichloro-1-(4-hydroxy-2,6-dimethoxyphenyl)ethanone

$C_{10}H_9Cl_3O_4$ mol.wt. 299.54



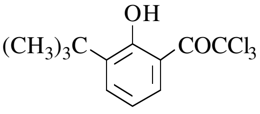
Synthesis

-Preparation by reaction of trichloroacetonitrile on phloroglucinol dimethyl ether (Hoesch reaction) (38%) [1535].

-m.p. 117° [1535].

2,2,2-Trichloro-1-[3-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone

[111422-36-7] $C_{12}H_{13}Cl_3O_2$ mol.wt. 295.59



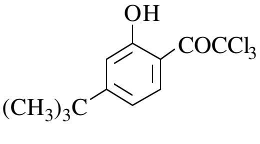
Synthesis

-Preparation by reaction of trichloroacetyl chloride on bromomagnesium 2-tert-butylphenolate in toluene at r.t. (65%) [1286].

m.p. 54-58° [1286]; ^{1}H NMR [1286], IR [1286], MS [1286].

2,2,2-Trichloro-1-[4-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone

[145818-24-2] $C_{12}H_{13}Cl_3O_2$ mol.wt. 295.59



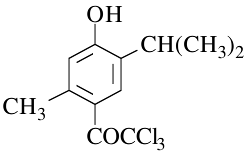
Synthesis

-Preparation by reaction of trichloroacetonitrile on 3-tert-butylphenol (Hoesch reaction) (74%) [183].

m.p. 46-47°5 [183]; ^{1}H NMR [183], IR [183], UV [183], MS [183].

2,2,2-Trichloro-1-[4-hydroxy-2-methyl-5-(1-methylethyl)phenyl]ethanone

$C_{12}H_{13}Cl_3O_2$ mol.wt. 295.59



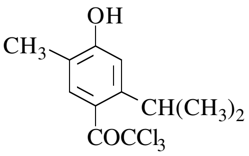
Synthesis

-Preparation by reaction of trichloroacetonitrile on thymol (Hoesch reaction) (73%) [657].

m.p. 99-100° [657].

2,2,2-Trichloro-1-[4-hydroxy-5-methyl-2-(1-methylethyl)phenyl]ethanone

$C_{12}H_{13}Cl_3O_2$ mol.wt. 295.59



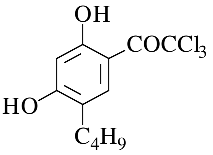
Synthesis

-Preparation by reaction of trichloroacetonitrile on carvacrol (Hoesch reaction) (75%) [657].

oil [657].

1-(5-Butyl-2,4-dihydroxyphenyl)-2,2,2-trichloroethanone

$C_{12}H_{13}Cl_3O_3$ mol.wt. 311.59



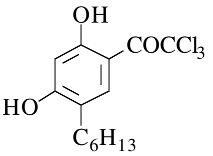
Synthesis

-Preparation by reaction of trichloroacetonitrile on 4-n-butylresorcinol (Hoesch reaction) (57%) [439].

m.p. 95-98° [439].

2,2,2-Trichloro-1-(5-hexyl-2,4-dihydroxyphenyl)ethanone

$C_{14}H_{17}Cl_3O_3$ mol.wt. 339.65



Synthesis

-Preparation by reaction of trichloroacetonitrile on 4-n-hexylresorcinol (Hoesch reaction) (56%) [439].

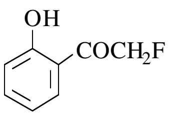
m.p. 71-73° [439].

2.3. *Compounds derived from fluoroacetic acids*

2.3.1. From monofluoroacetic acid

2-Fluoro-1-(2-hydroxyphenyl)ethanone

[83505-27-5] $C_8H_7FO_2$ mol.wt. 154.14



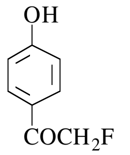
Synthesis

-When refluxed with water, 3-fluoro-4-hydroxycoumarin, undergoes hydrolytic ring opening and decarboxylation to give 2-fluoro-2'-hydroxyacetophenone (32%) [402].

m.p. 67-69° [402]; ^{1}H NMR [402], ^{19}F NMR [402], IR [402], MS [402].

2-Fluoro-1-(4-hydroxyphenyl)ethanone

[295779-85-0] $C_8H_7FO_2$ mol.wt. 154.14



Synthesis

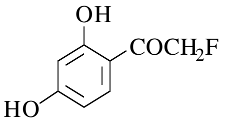
-Preparation by fluorination of p-hydroxyacetophenone (2 mmol) with 1-fluoro-4-hydroxy-1,4-diazoniabicyclo-[2.2.2]octane bis(tetrafluoroborate) (Accufluor ™ NFTh) (2.1 mmol of active compound) in refluxing methanol for 0.5 to 4 h until potassium iodide starch paper showed the consumption of the fluorinating reagent. Then, hydrolysis of the dimethylketal formed with 10% hydrochloric acid solution in acetonitrile (75-85%) [1399].

N.B.: Accufluor ™ NFTh is commercially available as 50% w/w on alumina.

m.p. 180-183°5 [1397];
^{1}H NMR [1397], ^{13}C NMR [1397], ^{19}F NMR [1397], IR [1397], MS [1397].

1-(2,4-Dihydroxyphenyl)-2-fluoroethanone

[147220-82-4] $C_8H_7FO_3$ mol.wt. 170.14

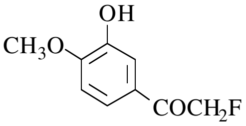


Synthesis

-Refer to: [1182] (compound Io).

2-Fluoro-1-(3-hydroxy-4-methoxyphenyl)ethanone

[85465-61-8] $C_9H_9FO_3$ mol.wt. 184.17



Synthesis

-Preparation by heating a mixture of 3-acetoxy-4-methoxy-α-bromoacetophenone and potassium hydrogen fluoride in diethylene glycol for 8 h at 100° (61%) [1128] [1129].

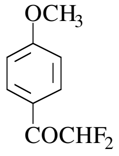
m.p. 70-71° [1128] [1129].

2.3.2. From difluoroacetic acid

There is no hydroxyketone derived from difluoroacetic acid such as described up to December 2003. Only, a methyl ether, the α,α-difluoro-4-methoxyacetophenone [825] (compound 1G), is mentioned in 1988.

2,2-Difluoro-1-(4-methoxyphenyl)ethanone

[114829-07-1] $C_9H_8F_2O_2$ mol.wt. 401.97



Synthesis

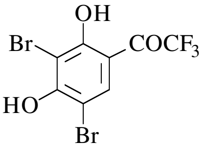
-Preparation by reaction of difluoroacetyl chloride with anisole in the presence of aluminium chloride in methylene chloride, first at 4°, then at 20° (56%) [825].

m.p. 39-40° [825]; b.p.$_{25}$ 134-135° [825];
^{1}H NMR [825].

2.3.3. From trifluoroacetic acid

1-(3,5-Dibromo-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65240-11-1] $C_8H_3Br_2F_3O_3$ mol.wt. 363.91



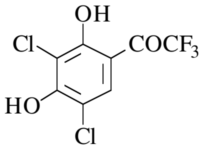
Synthesis

-Preparation by reaction of bromine on 2,4-dihydroxy-α,α,α-trifluoroacetophenone in acetic acid at r.t. (49%) [232].

m.p. 81° [232].

1-(3,5-Dichloro-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65240-09-7] $C_8H_3Cl_2F_3O_3$ mol.wt. 275.01



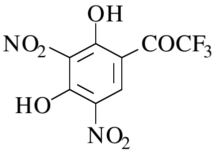
Synthesis

-Preparation by reaction of sulfuryl chloride on 2,4-dihydroxy-α,α,α-trifluoroacetophenone at r. t [232].

m.p. 101° [232].

1-(2,4-Dihydroxy-3,5-dinitrophenyl)-2,2,2-trifluoroethanone

[65240-17-7] $C_8H_3F_3N_2O_7$ mol.wt. 296.12



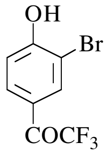
Synthesis

-Preparation by reaction of 65% nitric acid on 2,4-dihydroxy-α,α,α-trifluoroacetophenone in concentrated sulfuric acid [232].

m.p. 68° [232].

1-(3-Bromo-4-hydroxyphenyl)-2,2,2-trifluoroethanone

[303143-05-7] $C_8H_4BrF_3O_2$ mol.wt. 269.02

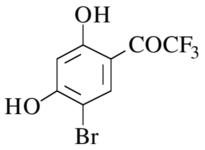


Synthesis

-Obtained by demethylation of 3-bromo-4-methoxy-α,α,α-trifluoroacetophenone with lithium chloride in refluxing DMF for 2 h (93%) [911].

1-(5-Bromo-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65239-86-3] $C_8H_4BrF_3O_3$ mol.wt. 285.02



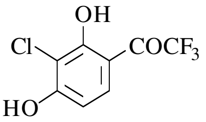
Synthesis

-Preparation by reaction of trifluoroacetic anhydride on 4-bromoresorcinol with aluminium chloride in ethylene dichloride at r.t. (88%) [232].

m.p. 81° [232].

1-(3-Chloro-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65239-93-2] $C_8H_4ClF_3O_3$ mol.wt. 240.57



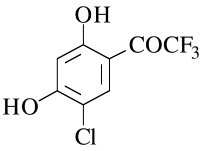
Synthesis

-Preparation by reaction of trifluoroacetic anhydride on 2-chlororesorcinol with aluminium chloride in ethylene dichloride at r.t. (83%) [232].

m.p. 113° [232].

1-(5-Chloro-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65233-63-8] $C_8H_4ClF_3O_3$ mol.wt. 240.57



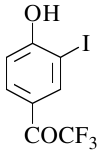
Synthesis

-Preparation by reaction of trifluoroacetic anhydride on 4-chlororesorcinol with aluminium chloride in ethylene dichloride at r.t. (90%) [232].

m.p. 110° [232].

2,2,2-Trifluoro-1-(4-hydroxy-3-iodophenyl)ethanone

[303143-06-8] $C_8H_4F_3IO_2$ mol.wt. 316.02

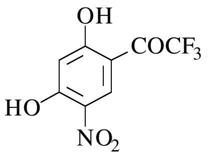


Synthesis

-Obtained by demethylation of 3-iodo-4-methoxy-α,α,α-trifluoroacetophenone with lithium chloride in refluxing DMF for 2 h (87%) [911].

1-(2,4-Dihydroxy-5-nitrophenyl)-2,2,2-trifluoroethanone

[65240-16-6] $C_8H_4F_3NO_5$ mol.wt. 251.12



Synthesis

-Preparation by reaction of 26% nitric acid on 2,4-dihydroxy-α,α,α-trifluoroacetophenone in acetic acid at 0° [232].

m.p. 81° [232].

2,2,2-Trifluoro-1-(2-hydroxyphenyl)ethanone

[25666-51-7] $C_8H_5F_3O_2$ mol.wt. 190.12

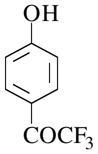
Synthesis

-Preparation by Fries rearrangement of phenyl trifluoroacetate with aluminium chloride without solvent at 90° (42%) [976].

b.p.$_{55}$ 92° [976]; ^{1}H NMR [976], IR [976].

2,2,2-Trifluoro-1-(4-hydroxyphenyl)ethanone

[1823-63-8] $C_8H_5F_3O_2$ mol.wt. 190.12



Syntheses

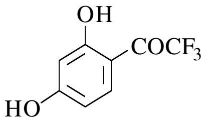
-Preparation by reaction of trifluoroacetic acid with phenol in hydrofluoric acid at 100° (75%) [1002].

-Obtained in small amount by Fries rearrangement of phenyl trifluoroacetate with aluminium chloride without solvent at 90° [976].

m.p. 105°5-106° [976]; ^{1}H NMR [1002], ^{19}F NMR [1002], IR [976] [1002].

1-(2,4-Dihydroxyphenyl)-2,2,2-trifluoroethanone

[315-44-6] $C_8H_5F_3O_3$ mol.wt. 206.12



Syntheses

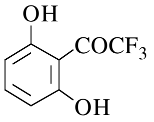
-Preparation by reaction of trifluoroacetonitrile on resorcinol (Hoesch reaction) (62%) [1511] [1512] [1533].

-Preparation by reaction of trifluoroacetic anhydride on resorcinol with aluminium chloride in ethylene dichloride at r.t. (73-83%) [993].

m.p. 106-108° [993], 103° [1511] [1533].

1-(2,6-Dihydroxyphenyl)-2,2,2-trifluoroethanone

[70211-42-6] $C_8H_5F_3O_3$ mol.wt. 206.12



Syntheses

-Obtained by total demethylation of 2,6-dimethoxy-α,α,α-trifluoroacetophenone with boron tribromide in methylene chloride, first at 0° for 15 min, then at r.t. overnight (22%) [755].

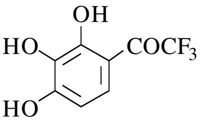
-Also refer to: [891].

N.B.: There is also an erroneous reference. It concerns the 2',6'-dihydroxytrifluoroacetanilide [1346].

^{1}H NMR [755], MS [755].

2,2,2-Trifluoro-1-(2,3,4-trihydroxyphenyl)ethanone

[65239-87-4] $C_8H_5F_3O_4$ mol.wt. 222.12



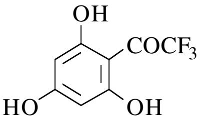
Synthesis

-Preparation by reaction of trifluoroacetic anhydride on pyrogallol with aluminium chloride in ethylene dichloride at r.t. (75%) [232].

m.p. 134° [232].

2,2,2-Trifluoro-1-(2,4,6-trihydroxyphenyl)ethanone

[13340-79-9] $C_8H_5F_3O_4$ mol.wt. 222.12



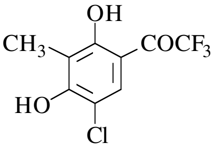
Synthesis

-Preparation by reaction of trifluoroacetic anhydride on phloroglucinol with aluminium chloride in ethylene dichloride at r.t. (40%) [993].

m.p. 174-177° [993]; ^{1}H NMR [993], ^{19}F NMR [993], IR [993].

1-(5-Chloro-2,4-dihydroxy-3-methylphenyl)-2,2,2-trifluoroethanone

[65240-08-6] $C_9H_6ClF_3O_3$ mol.wt. 254.59



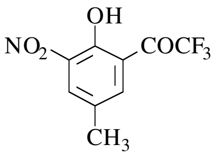
Synthesis

-Preparation by reaction of sulfuryl chloride on 2,4-dihydroxy-3-methyl-α,α,α-trifluoroacetophenone in ethylene dichloride at r.t. (76%) [232].

m.p. 96° [232].

2,2,2-Trifluoro-1-(2-hydroxy-5-methyl-3-nitrophenyl)ethanone

[70978-48-2] $C_9H_6F_3NO_4$ mol.wt. 249.15



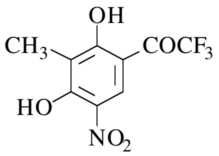
Synthesis

-Preparation by reaction of fuming nitric acid (d = 1.5) on 2-hydroxy-5-methyl-α,α,α-trifluoroacetophenone in acetic acid-methylene chloride mixture at r.t. [506] [1215], (44%) [506].

m.p. 94-96° [506], 49-50° [1215]. One of the reported melting points is obviously wrong.

1-(2,4-Dihydroxy-3-methyl-5-nitrophenyl)-2,2,2-trifluoroethanone

[65240-15-5] $C_9H_6F_3NO_5$ mol.wt. 265.15



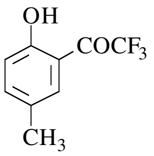
Synthesis

-Obtained by reaction of 26% nitric acid on 2,4-dihydroxy-3-methyl-α,α,α-trifluoroacetophenone in acetic acid at 0° (21%) [232].

m.p. 104° [232].

2,2,2-Trifluoro-1-(2-hydroxy-5-methylphenyl)ethanone

[70978-57-3] $C_9H_7F_3O_2$ mol.wt. 204.15



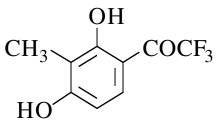
Synthesis

-Preparation by Fries rearrangement of 4-methylphenyl trifluoroacetate with aluminium chloride without solvent at 115° (25%) [1215].

m.p. 40°5-42° [1215].

1-(2,4-Dihydroxy-3-methylphenyl)-2,2,2-trifluoroethanone

[65233-60-5] $C_9H_7F_3O_3$ mol.wt. 220.15



Syntheses

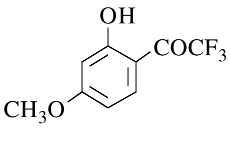
-Preparation by reaction of trifluoroacetic anhydride on 2-methylresorcinol with aluminium chloride in ethylene dichloride at r.t. (90%) [232].

-Preparation by Fries rearrangement of 2-methylresorcinol monotrifluoroacetate with aluminium chloride in nitrobenzene or without solvent at 120° [232].

m.p. 101° [232].

2,2,2-Trifluoro-1-(2-hydroxy-4-methoxyphenyl)ethanone

[123716-19-8] $C_9H_7F_3O_3$ mol.wt. 220.15



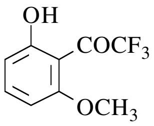
Synthesis

-Obtained by refluxing α-(difluoronitromethyl)-2-hydroxy-4-methoxy-α-(trifluoromethyl)benzenemethanol (SM) in hexane for 6 h in the presence of activated charcoal (91%). SM was prepared by reaction of NPFA with resorcinol monomethyl ether in carbon tetrachloride or nitromethane for 12 h at 20° (99%, m.p. 67-69°) [433].

m.p. 62-64° [433];
^{1}H NMR [433], ^{13}C NMR [433], ^{19}F NMR [433]; TLC [433].

2,2,2-Trifluoro-1-(2-hydroxy-6-methoxyphenyl)ethanone

[193738-66-8] $C_9H_7F_3O_3$ mol.wt. 220.15



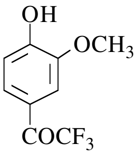
Synthesis

-Obtained by partial demethylation of 2,6-dimethoxy-α,α,α-trifluoroacetophenone with boron tribromide in methylene chloride, first at 0° for 15 min, then at r.t. overnight (17%) [755].

yellow oil [755]; ^{1}H NMR [755], MS [755].

2,2,2-Trifluoro-1-(4-hydroxy-3-methoxyphenyl)ethanone

[188194-66-3] $C_9H_7F_3O_3$ mol.wt. 220.15

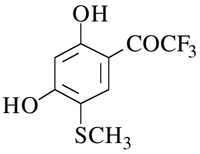


Synthesis

-This compound (**6**) [893] was synthesized according to Dudley [421].

1-[2,4-Dihydroxy-5-(methylthio)phenyl]-2,2,2-trifluoroethanone

[65239-90-9] $C_9H_7F_3O_3S$ mol.wt. 252.21



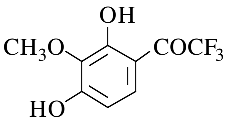
Synthesis

-Preparation by reaction of trifluoroacetic anhydride on 4-methylthioresorcinol with aluminium chloride in ethylene dichloride at r.t. (68%) [232].

m.p. 57° [232].

1-(2,4-Dihydroxy-3-methoxyphenyl)-2,2,2-trifluoroethanone

[65239-88-5] $C_9H_7F_3O_4$ mol.wt. 236.15



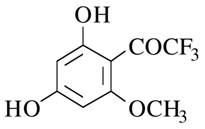
Synthesis

-Preparation by reaction of trifluoroacetic anhydride on 2-methoxyresorcinol with aluminium chloride in ethylene dichloride at r.t. (78%) [232].

m.p. 79° [232].

1-(2,4-Dihydroxy-6-methoxyphenyl)-2,2,2-trifluoroethanone

$C_9H_7F_3O_4$ mol.wt. 236.15



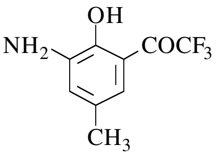
Synthesis

-Preparation by reaction of trifluoroacetonitrile on phloroglucinol monomethyl ether with zinc chloride and gazeous hydrochloric acid in ethyl ether at 0° (Hoesch reaction) (33%) [1533].

m.p. 154° [1533].

1-(3-Amino-2-hydroxy-5-methylphenyl)-2,2,2-trifluoroethanone

[70977-83-2] $C_9H_8F_3NO_2$ mol.wt. 219.16



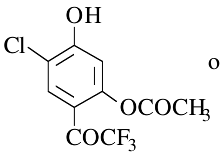
Synthesis

-Preparation by catalytic hydrogenation of 2-hydroxy-5-methyl-3-nitro-α,α,α-trifluoroacetophenone in the presence of 5% Pt/C in ethanol at 25° [506] [1215], (57%) [506].

m.p. 87-88° [506] [1215].

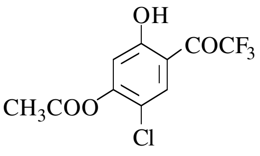
1-[2-(Acetyloxy)-5-chloro-4-hydroxyphenyl]-2,2,2-trifluoroethanone
or
1-[4-(Acetyloxy)-5-chloro-2-hydroxyphenyl]-2,2,2-trifluoroethanone

[65233-64-9] $C_{10}H_6ClF_3O_4$ mol.wt. 282.60



(**I**)

or



(**II**)

Synthesis

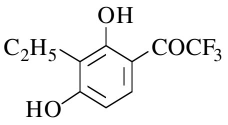
-Preparation by reaction of acetyl chloride on 5-chloro-2,4-dihydroxy-α,α,α-trifluoroacetophenone with pyridine in benzene at r.t. (72%) [232].

m.p. 80-83° [232].

N.B.: The 4-(Acetyloxy)-5-chloro-2-hydroxy-α,α,α-trifluoroacetophenone (**II**) is the most likely formula, for two reasons: On the one hand, there is a strong chelation between hydroxyl and keto groups in the raw material and, on the other hand, the esterification was carried out at r.t.

1-(3-Ethyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[577-54-8] $C_{10}H_9F_3O_3$ mol.wt. 234.17



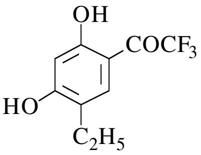
Synthesis

-Preparation by reaction of trifluoroacetonitrile on 2-ethylresorcinol (Hoesch reaction) (74%) [1533].

m.p. 139° [1533].

1-(5-Ethyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[584-41-8] $C_{10}H_9F_3O_3$ mol.wt. 234.17



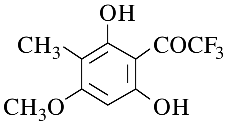
Synthesis

-Preparation by reaction of trifluoroacetonitrile on 4-ethylresorcinol (Hoesch reaction) (71%) [1533].

m.p. 99° [1533].

1-(2,6-Dihydroxy-4-methoxy-3-methylphenyl)-2,2,2-trifluoroethanone

$C_{10}H_9F_3O_4$ mol.wt. 250.17



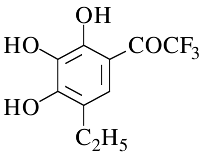
Synthesis

-Preparation by reaction of trifluoroacetonitrile on 1,3-dihydroxy-5-methoxy-4-methylbenzene (Hoesch reaction) (22%) [1535].

m.p. 145° [1535].

1-(5-Ethyl-2,3,4-trihydroxyphenyl)-2,2,2-trifluoroethanone

[65239-92-1] $C_{10}H_9F_3O_4$ mol.wt. 250.17



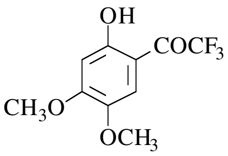
Synthesis

-Preparation by reaction of trifluoroacetic anhydride on 4-ethylpyrogallol with aluminium chloride in ethylene dichloride at r.t. (80%) [232].

m.p. 82° [232].

2,2,2-Trifluoro-1-(2-hydroxy-4,5-dimethoxyphenyl)ethanone

$C_{10}H_9F_3O_4$ mol.wt. 250.17



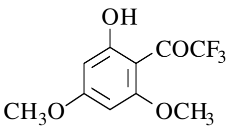
Synthesis

-Preparation by reaction of trifluoroacetonitrile on 3,4-dimethoxyphenol (Hoesch reaction) (62%) [1533].

m.p. 82° [1533].

2,2,2-Trifluoro-1-(2-hydroxy-4,6-dimethoxyphenyl)ethanone

$C_{10}H_9F_3O_4$ mol.wt. 250.17



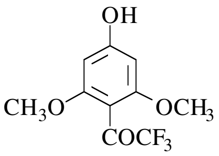
Synthesis

-Obtained (by-product) by reaction of trifluoroacetonitrile on phloroglucinol dimethyl ether (Hoesch reaction) (5%) [1535].

m.p. 87° [1535].

2,2,2-Trifluoro-1-(4-hydroxy-2,6-dimethoxyphenyl)ethanone

$C_{10}H_9F_3O_4$ mol.wt. 250.17



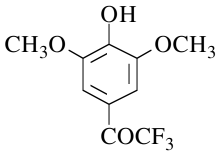
Synthesis

-Preparation by reaction of trifluoroacetonitrile on phloroglucinol dimethyl ether (Hoesch reaction) (25%) [1535].

m.p. 155° [1535].

2,2,2-Trifluoro-1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone

[188194-67-4] $C_{10}H_9F_3O_4$ mol.wt. 250.17

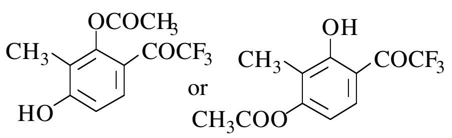


Synthesis

-This compound (**7**) [893] was synthesized according to Dudley [421].

1-[2-(Acetyloxy)-4-hydroxy-3-methylphenyl]-2,2,2-trifluoroethanone
or
1-[4-(Acetyloxy)-2-hydroxy-3-methylphenyl]-2,2,2-trifluoroethanone

[65233-62-7] $C_{11}H_9F_3O_4$ mol.wt. 262.19



(**I**) (**II**)

Synthesis

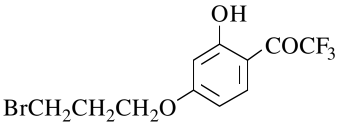
-Preparation by reaction of acetyl chloride on 2,4-dihydroxy-3-methyl-α,α,α-trifluoroacetophenone with pyridine in benzene at r.t. (87%) [232].

m.p. 49-50° [232].

N.B.: The 1-[4-(Acetyloxy)-2-hydroxy-3-methylphenyl]-2,2,2-trifluoroethanone (**II**) is the most likely formula. This hypothesis is supported by the fact that, considering the precursor (2,4-dihydroxy-3-methyl-α,α,α-trifluoroacetophenone), the hydroxy group in the 4-position is less hindered than the hydroxyl substituent in the 2-position which is furthermore chelated with the vicinal carbonyl group. In addition, the reported melting point (49-50°) is in good agreement with those generally measured for o-hydroxyketones (below 80°) compared to those of p-hydroxyketones which are considerably higher (usually 120-200°).

1-[4-(3-Bromopropoxy)-2-hydroxyphenyl]-2,2,2-trifluoroethanone

[125617-37-0] $C_{11}H_{10}BrF_3O_3$ mol.wt. 327.10



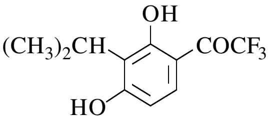
Synthesis

-Preparation by reaction of 1,3-dibromopropane with 2,4-dihydroxy-α,α,α-trifluoroacetophenone in the presence of potassium carbonate and potassium iodide in refluxing methyl ethyl ketone [1388].

pale yellow oil [1388]; IR [1388].

1-[2,4-Dihydroxy-3-(1-methylethyl)phenyl]-2,2,2-trifluoroethanone

[65239-70-5] $C_{11}H_{11}F_3O_3$ mol.wt. 248.20



Syntheses

-Preparation by reaction of trifluoroacetic anhydride on 2-isopropylresorcinol with aluminium chloride in ethylene dichloride at r.t. (85%) [232].

-Preparation by reaction of isopropanol on 2,4-dihydroxy-α,α,α-trifluoroacetophenone with polyphosphoric acid at 80° (30%) [232].

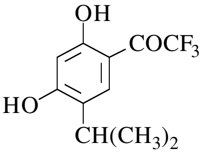
-Preparation by reaction of propylene on 2,4-dihydroxy-α,α,α-trifluoroacetophenone with phosphorous oxychloride and phosphoric anhydride at 50° [232].

-Preparation by Fries rearrangement of 2-isopropylresorcinol trifluoroacetate with aluminium chloride without solvent or in nitrobenzene at 120° [232].

m.p. 145° [232].

1-[2,4-Dihydroxy-5-(1-methylethyl)phenyl]-2,2,2-trifluoroethanone

[65239-68-1] $C_{11}H_{11}F_3O_3$ mol.wt. 248.20



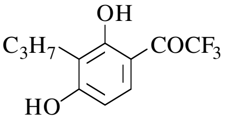
Synthesis

-Preparation by reaction of trifluoroacetic anhydride on 4-isopropylresorcinol with aluminium chloride in chloroform at r.t. (70%) [232].

m.p. 97° [232].

1-(2,4-Dihydroxy-3-propylphenyl)-2,2,2-trifluoroethanone

[65239-69-2] $C_{11}H_{11}F_3O_3$ mol.wt. 248.20



Syntheses

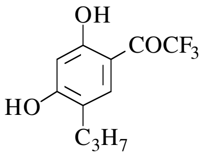
-Preparation by reaction of trifluoroacetic anhydride on 2-propylresorcinol with aluminium chloride in ethylene dichloride at r.t. (88%) [232].

-Preparation by reaction of trifluoroacetonitrile on 2-propylresorcinol (Hoesch reaction) (66%) [237].

m.p. 114° [232], 110-112° [237]; ^1H NMR [237].

1-(2,4-Dihydroxy-5-propylphenyl)-2,2,2-trifluoroethanone

[65239-67-0] $C_{11}H_{11}F_3O_3$ mol.wt. 248.20



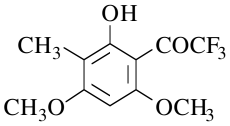
Synthesis

-Preparation by reaction of trifluoroacetic anhydride on 4-propylresorcinol with aluminium chloride in ethylene dichloride at r.t. (87%) [232].

m.p. 95° [232].

2,2,2-Trifluoro-1-(2-hydroxy-4,6-dimethoxy-3-methylphenyl)ethanone

$C_{11}H_{11}F_3O_4$ mol.wt. 264.20



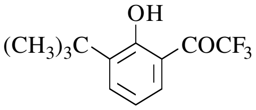
Synthesis

-Preparation by reaction of trifluoroacetonitrile on 3,5-dimethoxy-2-methylphenol (Hoesch reaction) (43%) [1535].

m.p. 100° [1535].

1-[3-(1,1-Dimethylethyl)-2-hydroxyphenyl]-2,2,2-trifluoroethanone

[111422-37-8] $C_{12}H_{13}F_3O_2$ mol.wt. 246.23



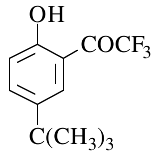
Synthesis

-Preparation by reaction of trifluoroacetyl chloride on bromomagnesium 2-tert-butylphenolate in toluene at r.t. (74%) [1286].

yellow oil [1286]; ^1H NMR [1286], IR [1286], MS [1286].

1-[5-(1,1-Dimethylethyl)-2-hydroxyphenyl]-2,2,2-trifluoroethanone

[75060-56-9] $C_{12}H_{13}F_3O_2$ mol.wt. 246.23



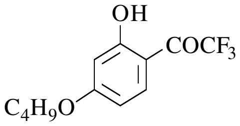
Synthesis

-Preparation by demethylation of 5-tert-butyl-2-methoxy-α,α,α-trifluoroacetophenone with 47% hydrobromic acid and 57% hydriodic acid in refluxing acetic acid (70%) [685].

^1H NMR [685], IR [685], MS [685].

1-(4-Butoxy-2-hydroxyphenyl)-2,2,2-trifluoroethanone

[65240-27-9] $C_{12}H_{13}F_3O_3$ mol.wt. 262.23



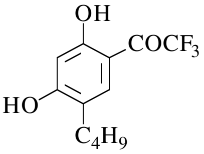
Synthesis

-Obtained by reaction of butyl iodide on 2,4-dihydroxy-α,α,α-trifluoroacetophenone with potassium carbonate in refluxing acetone (29%) [232].

m.p. 66° [232].

1-(5-Butyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65239-71-6] $C_{12}H_{13}F_3O_3$ mol.wt. 262.23



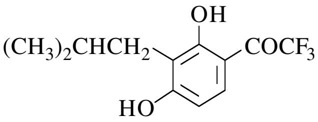
Synthesis

-Preparation by reaction of trifluoroacetic anhydride on 4-butylresorcinol with aluminium chloride in ethylene dichloride at r.t. (82%) [232].

m.p. 96° [232].

1-[2,4-Dihydroxy-3-(2-methylpropyl)phenyl]-2,2,2-trifluoroethanone

[65239-73-8] $C_{12}H_{13}F_3O_3$ mol.wt. 262.23



Syntheses

-Preparation by reaction of trifluoroacetic anhydride on 2-isobutylresorcinol with aluminium chloride in ethylene dichloride at r.t. (78%) [232].

-Preparation by Fries rearrangement of 2-isobutylresorcinol monotrifluoroacetate with aluminium chloride in nitrobenzene at 120° [232].

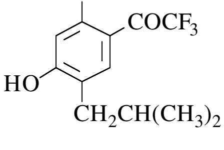
-Preparation by reaction of isobutyl alcohol on 2,4-dihydroxy-α,α,α-trifluoroacetophenone with polyphosphoric acid at 80° [232].

-Preparation by reaction of isobutylene on 2,4-dihydroxy-α,α,α-trifluoroacetophenone with phosphorous pentoxide and phosphorous oxychloride at 50° [232].

m.p. 114° [232].

1-[2,4-Dihydroxy-5-(2-methylpropyl)phenyl]-2,2,2-trifluoroethanone

[65239-72-7] $C_{12}H_{13}F_3O_3$ mol.wt. 262.23



Syntheses

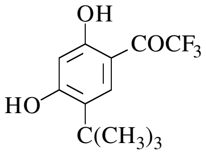
-Preparation by reaction of trifluoroacetic anhydride on 4-isobutylresorcinol with aluminium chloride in ethylene dichloride at r.t. (78-84%) [232].

-Preparation by reaction of isobutyl alcohol on 2,4-dihydroxy-α,α,α-trifluoroacetophenone with polyphosphoric acid at 80° [232].

m.p. 90° [232]; b.p.$_{0.1}$ 90° [232].

1-[5-(1,1-Dimethylethyl)-2,4-dihydroxyphenyl]-2,2,2-trifluoroethanone

[65239-74-9] $C_{12}H_{13}F_3O_3$ mol.wt. 262.23



Syntheses

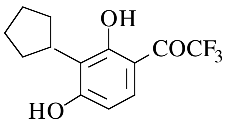
-Preparation by reaction of trifluoroacetic anhydride on 4-tert-butylresorcinol with aluminium chloride in ethylene dichloride at r.t. (80%) [232].

-Preparation by reaction of tert-butyl alcohol on 2,4-dihydroxy-α,α,α-trifluoroacetophenone with polyphosphoric acid at 80° [232].

m.p. 159° [232].

1-(3-Cyclopentyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65240-20-2] $C_{13}H_{13}F_3O_3$ mol.wt. 274.24



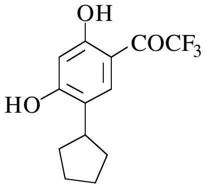
Synthesis

-Preparation by reaction of cyclopentene on 2,4-dihydroxy-α,α,α-trifluoroacetophenone with phosphorous oxychloride-phosphorous pentoxide mixture at 50° [232].

m.p. 166° [232].

1-(5-Cyclopentyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65239-76-1] $C_{13}H_{13}F_3O_3$ mol.wt. 274.24



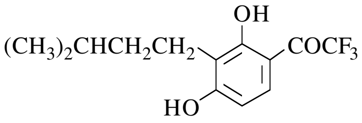
Synthesis

-Preparation by reaction of trifluoroacetic anhydride on 4-cyclopentylresorcinol with aluminium chloride in ethylene dichloride at r.t. (75%) [232].

m.p. 94° [232].

1-[2,4-Dihydroxy-3-(3-methylbutyl)phenyl]-2,2,2-trifluoroethanone

[65239-77-2] $C_{13}H_{15}F_3O_3$ mol.wt. 276.26



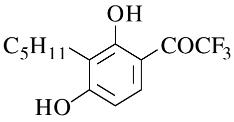
Synthesis

-Preparation by reaction of trifluoroacetic anhydride on 2-isopentylresorcinol with aluminium chloride in ethylene dichloride at r.t. (84%) [232].

m.p. 101° [232].

1-(2,4-Dihydroxy-3-pentylphenyl)-2,2,2-trifluoroethanone

[65239-78-3] $C_{13}H_{15}F_3O_3$ mol.wt. 276.26



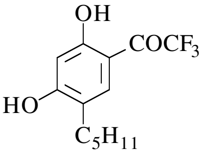
Synthesis

-Preparation by reaction of trifluoroacetic anhydride on 2-pentylresorcinol with aluminium chloride in ethylene dichloride at r.t. (87%) [232].

m.p. 105° [232].

1-(2,4-Dihydroxy-5-pentylphenyl)-2,2,2-trifluoroethanone

[65239-75-0] $C_{13}H_{15}F_3O_3$ mol.wt. 276.26



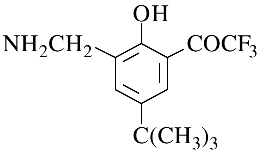
Synthesis

-Preparation by reaction of trifluoroacetic anhydride on 4-pentylresorcinol with aluminium chloride in ethylene dichloride at r.t. (86%) [232].

m.p. 97° [232].

1-[3-(Aminomethyl)-5-(1,1-dimethylethyl)-2-hydroxyphenyl]-2,2,2-trifluoroethanone

[75060-97-8] $C_{13}H_{16}F_3NO_2$ mol.wt. 275.27

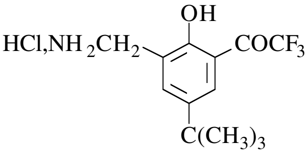


Synthesis

-Preparation from the corresponding hydrochloride (see below) [685].

1-[3-(Aminomethyl)-5-(1,1-dimethylethyl)-2-hydroxyphenyl]-2,2,2-trifluoroethanone *(Hydrochloride)*

[75060-74-1] $C_{13}H_{16}F_3NO_2$, HCl mol.wt. 311.73



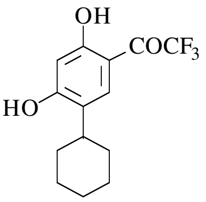
Synthesis

-Preparation by reaction of concentrated hydrochloric acid on 4-tert-butyl-6-(N-chloroacetylaminomethyl)-2-(trifluoroacetyl)phenol in refluxing ethanol (83%) [685].

m.p. 180-186° [685]; ^{1}H NMR [685], IR [685].

1-(5-Cyclohexyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65239-79-4] $C_{14}H_{15}F_3O_3$ mol.wt. 288.27



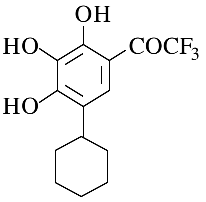
Synthesis

-Preparation by reaction of trifluoroacetic anhydride with 4-cyclohexylresorcinol in the presence of aluminium chloride in ethylene dichloride at r.t. (78%) [232].

m.p. 80° [232].

1-(5-Cyclohexyl-2,3,4-trihydroxyphenyl)-2,2,2-trifluoroethanone

[65239-91-0] $C_{14}H_{15}F_3O_4$ mol.wt. 304.27



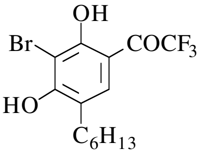
Synthesis

-Preparation by reaction of trifluoroacetic anhydride with 4-cyclohexylpyrogallol in the presence of aluminium chloride in ethylene dichloride at r.t. (78%) [232].

m.p. 128° [232].

1-(3-Bromo-5-hexyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65240-12-2] $C_{14}H_{16}BrF_3O_3$ mol.wt. 369.18



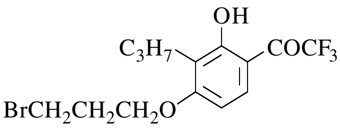
Synthesis

-Preparation by reaction of bromine on 5-n-hexyl-2,4-dihydroxy-α,α,α-trifluoroacetophenone in acetic acid at r.t. (43%) [232].

m.p. 39° [232].

1-[4-(3-Bromopropoxy)-2-hydroxy-3-propylphenyl]-2,2,2-trifluoroethanone

[125617-40-5] $C_{14}H_{16}BrF_3O_3$ mol.wt. 369.18



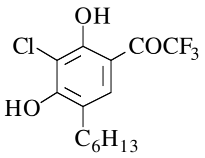
Synthesis

-Preparation by reaction of 1,3-dibromopropane with 2,4-dihydroxy-3-propyl-α,α,α-trifluoroacetophenone in the presence of potassium carbonate and potassium iodide in refluxing methyl ethyl ketone [1388].

yellow oil [1388]; IR [1388].

1-(3-Chloro-5-hexyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65240-10-0] $C_{14}H_{16}ClF_3O_3$ mol.wt. 324.73



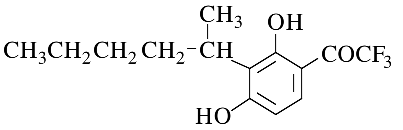
Synthesis

-Preparation by reaction of sulfuryl chloride on 5-n-hexyl-2,4-dihydroxy-α,α,α-trifluoroacetophenone at r.t. [232].

m.p. 40° [232].

1-[2,4-Dihydroxy-3-(1-methylpentyl)phenyl]-2,2,2-trifluoroethanone

[65240-18-8] $C_{14}H_{17}F_3O_3$ mol.wt. 290.28



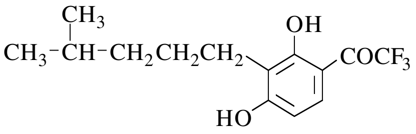
Synthesis

-Preparation by reaction of 1-hexene on 2,4-dihydroxy-α,α,α-trifluoroacetophenone with phosphorous oxychloride and phosphorous pentoxide at 50° (30%) [232].

m.p. 97° [232].

1-[2,4-Dihydroxy-3-(4-methylpentyl)phenyl]-2,2,2-trifluoroethanone

[65240-07-5] $C_{14}H_{17}F_3O_3$ mol.wt. 290.28



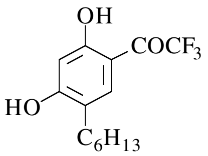
Synthesis

-Preparation by Fries rearrangement of 2-iso-hexyl-3-hydroxyphenyl trifluoroacetate with aluminium chloride in nitrobenzene or without solvent at 120° [232].

m.p. 97° [232].

2,2,2-Trifluoro-1-(5-hexyl-2,4-dihydroxyphenyl)ethanone

[65233-68-3] $C_{14}H_{17}F_3O_3$ mol.wt. 290.28



Syntheses

-Preparation by Fries rearrangement of 4-hexyl-3-hydroxyphenyl trifluoroacetate with aluminium chloride at 120°, in nitrobenzene (47%) or without solvent (38%) [232].
-Preparation by reaction of trifluoroacetamide on 4-hexylresorcinol at reflux, with boron trifluoride etherate (55%) or with p-toluenesulfonic acid (20%) [232].
-Preparation by reaction of trifluoroacetonitrile on 4-hexylresorcinol, in the presence of hydrochloric acid,
*with zinc chloride in ethyl ether at 0° (Hoesch reaction) (69%) [232];
*with aluminium chloride (Houben reaction), in ethylene dichloride (60%), in phosphorous oxychloride (55%), in toluene (20%) or in nitrobenzene (15%) [232].

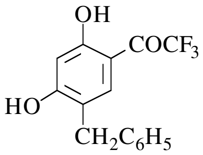
-Preparation by reaction of trifluoroacetyl chloride on 4-hexylresorcinol at r.t. [232],
*with aluminium chloride in ethylene dichloride (92%) or in phosphorous oxychloride (20%);
*with boron trifluoride etherate in ethylene dichloride (40%);
*with zinc chloride in ethylene dichloride (30%).
-Preparation by reaction of trifluoroacetic acid on 4-hexylresorcinol in ethylene dichloride [232],
*with phosphorous pentachloride (54%) or p-toluenesulfonic acid (30%) at r.t.;
*with boron trifluoride etherate at reflux (40%).
-Also obtained by reaction of ethyl trifluoroacetate on 4-hexylresorcinol with p-toluenesulfonic acid at reflux (25%) [232].
-Preparation by reaction of trifluoroacetic anhydride on 4-hexylresorcinol at r.t. (see table below) [232].

Catalyst	**Solvent**	**Yield (%)**
$AlCl_3$	$POCl_3$	80
"	$C_6H_5CH_3$	10
"	$C_6H_5NO_2$	75
"	$CH_2Cl\text{-}CH_2Cl$	85
$ZnCl_2$	$POCl_3$	60
"	$C_6H_5CH_3$	65
"	$C_6H_5NO_2$	83
"	$CH_2Cl\text{-}CH_2Cl$	87
"	$(C_2H_5)_2O$	15
$FeCl_3$	$POCl_3$	30
"	$C_6H_5CH_3$	30
"	$C_6H_5NO_2$	45
"	$CH_2Cl\text{-}CH_2Cl$	68
PCl_5	$POCl_3$	60 (at 100°)
"	$C_6H_5CH_3$	20
"	$C_6H_5NO_2$	20
$4\text{-}CH_3C_6H_4SO_3H$	$C_6H_5CH_3$	25
"	$C_6H_5NO_2$	25
"	$CH_2Cl\text{-}CH_2Cl$	22
$BF_3\text{-}Et_2O$	$C_6H_5CH_3$	35
"	$CH_2Cl\text{-}CH_2Cl$	60
"	$(C_2H_5)_2O$	70

m.p. 90° [232].

1-[2,4-Dihydroxy-5-(phenylmethyl)phenyl]-2,2,2-trifluoroethanone

[65239-81-8] $C_{15}H_{11}F_3O_3$ mol.wt. 296.25



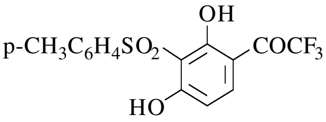
Synthesis

-Preparation by reaction of trifluoroacetic anhydride on 4-benzylresorcinol with aluminium chloride in ethylene dichloride at r.t. (80%) [232].

m.p. 114° [232].

1-[2,4-Dihydroxy-3-[(4-methylphenyl)sulfonyl]phenyl]-2,2,2-trifluoroethanone

[65240-14-4] $C_{15}H_{11}F_3O_5S$ mol.wt. 360.31



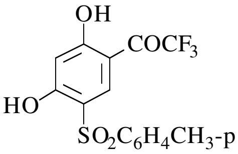
Synthesis

-Obtained by reaction of p-toluenesulfonyl chloride on 2,4-dihydroxy-α,α,α-trifluoroacetophenone with aluminium chloride in phosphorous oxychloride (22%) [232].

m.p. 127° [232].

1-[2,4-Dihydroxy-5-[(4-methylphenyl)sulfonyl]phenyl]-2,2,2-trifluoroethanone

[65240-13-3] $C_{15}H_{11}F_3O_5S$ mol.wt. 360.31



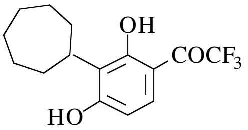
Synthesis

-Preparation by reaction of p-toluenesulfonyl chloride on 2,4-dihydroxy-α,α,α-trifluoroacetophenone with ferric chloride in phosphorous oxychloride at 120° (40%) [232].

m.p. 145° [232].

1-(3-Cycloheptyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65240-21-3] $C_{15}H_{17}F_3O_3$ mol.wt. 302.29



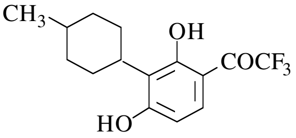
Synthesis

-Preparation by reaction of cycloheptene on 2,4-dihydroxy-α,α,α-trifluoroacetophenone with phosphorous trichloride and phosphorous pentoxide at 50° [232].

m.p. 174° [232].

1-[2,4-Dihydroxy-3-(4-methylcyclohexyl)phenyl]-2,2,2-trifluoroethanone

[65239-82-9] $C_{15}H_{17}F_3O_3$ mol.wt. 302.29



Syntheses

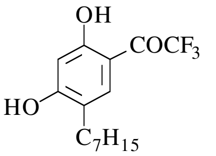
-Preparation by reaction of trifluoroacetic anhydride on 2-(4-methylcyclohexyl)resorcinol with aluminium chloride in ethylene dichloride at r.t. (76%) [232].

-Preparation by Fries rearrangement of 3-hydroxy-2-(4-methylcyclohexyl)phenyl trifluoroacetate with aluminium chloride in nitrobenzene or without solvent at 120° [232].

m.p. 143° [232].

2,2,2-Trifluoro-1-(5-heptyl-2,4-dihydroxyphenyl)ethanone

[65239-80-7] $C_{15}H_{19}F_3O_3$ mol.wt. 304.31



Syntheses

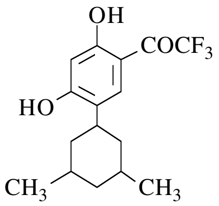
-Preparation by reaction of trifluoroacetic anhydride on 4-heptylresorcinol with aluminium chloride in ethylene dichloride at r.t. (79%) [232].

-Preparation by Fries rearrangement of 4-heptyl-3-hydroxyphenyl-α,α,α-trifluoroacetate with aluminium chloride in nitrobenzene or without solvent at 120° [232].

m.p. 85° [232].

1-[5-(3,5-Dimethylcyclohexyl)-2,4-dihydroxyphenyl]-2,2,2-trifluoroethanone

[65239-83-0] $C_{16}H_{19}F_3O_3$ mol.wt. 304.31



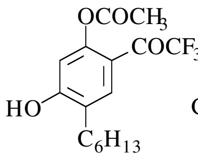
Synthesis

-Preparation by acylation of 4-(3,5-dimethylcyclohexyl)-resorcinol (1 mol) with trifluoroacetic anhydride (1.2 mol) in the presence of aluminium chloride (2 mol) in ethylene dichloride at r.t. (79%) [232].

m.p. 126° [232].

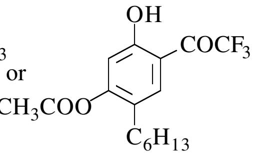
1-[2 (or 4)-(Acetyloxy)-5-hexyl-4 (or 2)-hydroxyphenyl]-2,2,2-trifluoroethanone

[65233-69-4] $C_{16}H_{19}F_3O_4$ mol.wt. 332.32



(**I**)

or



(**II**)

Synthesis

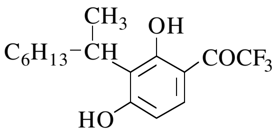
-Preparation by reaction of acetyl chloride on 5-hexyl-2,4-dihydroxy-α,α,α-trifluoroacetophenone with pyridine in benzene at r.t. (83%) [232].

m.p. 30° [232].

N.B.: The 1-[4-(acetyloxy)-5-hexyl-2-hydroxyphenyl]-2,2,2-trifluoroethanone (**II**) is the most likely formula. This hypothesis is supported by the fact that, considering the precursor (5-hexyl-2,4-dihydroxy-α,α,α-trifluoroacetophenone), the hydroxy group in the 2-position is chelated with the carbonyl group. In addition, the reported melting point (30°) is in good agreement with those generally measured for o-hydroxyketones (below 80°) compared to those of p-hydroxyketones which are considerably higher (usually 120-200°).

1-[2,4-Dihydroxy-3-(1-methylheptyl)phenyl]-2,2,2-trifluoroethanone

[65240-22-4] $C_{16}H_{21}F_3O_3$ mol.wt. 318.34

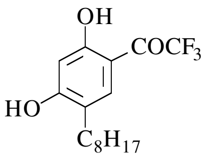


Synthesis

-Refer to: [232].

1-(2,4-Dihydroxy-5-octylphenyl)-2,2,2-trifluoroethanone

[65239-94-3] $C_{16}H_{21}F_3O_3$ mol.wt. 318.34



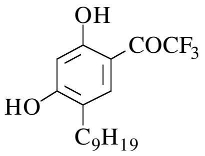
Synthesis

-Preparation by reaction of trifluoroacetic anhydride on 4-octylresorcinol with aluminium chloride in ethylene dichloride at r.t. (74%) [232].

m.p. 87° [232].

1-(2,4-Dihydroxy-5-nonylphenyl)-2,2,2-trifluoroethanone

[65239-84-1] $C_{17}H_{23}F_3O_3$ mol.wt. 332.36



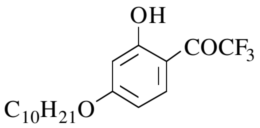
Synthesis

-Preparation by reaction of trifluoroacetic anhydride with 4-nonylresorcinol in the presence of aluminium chloride in ethylene dichloride at r.t. (85%) [232].

m.p. 87° [232].

1-[4-(Decyloxy)-2-hydroxyphenyl]-2,2,2-trifluoroethanone

[65240-25-7] $C_{18}H_{25}F_3O_3$ mol.wt. 346.39



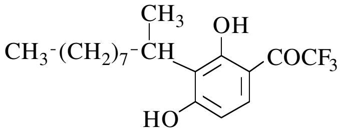
Synthesis

-Preparation by reaction of decyl iodide on 2,4-dihydroxy-α,α,α-trifluoroacetophenone with potassium carbonate in refluxing acetone (53%) [232].

m.p. 27-28° [232]; b.p.$_{0.1}$ 150° [232].

1-[2,4-Dihydroxy-3-(1-methylnonyl)phenyl]-2,2,2-trifluoroethanone

[65134-36-3] $C_{18}H_{25}F_3O_3$ mol.wt. 346.39



Synthesis

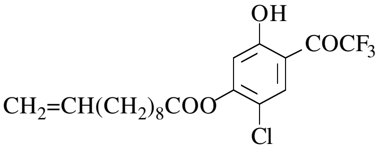
-Preparation by reaction of 1-decene on 2,4-dihydroxy-α,α,α-trifluoroacetophenone with phosphorous oxychloride and phosphorous pentoxide at 50° [232].

m.p. 98° [232].

1-[5-Chloro-2-hydroxy-4-(10-undecenoyloxy)phenyl]-2,2,2-trifluoroethanone

10-Undecenoic acid, 2 (or 4)-Chloro-5-hydroxy-4 (or 2)-(trifluoroacetyl)phenyl ester

[65233-67-2] $C_{19}H_{22}ClF_3O_4$ mol.wt. 406.83



Synthesis

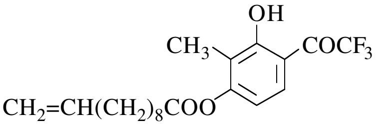
-Preparation by reaction of 10-undecenoyl chloride on 5-chloro-2,4-dihydroxy-α,α,α-trifluoroacetophenone with pyridine in benzene at r.t. (65%) [232].

b.p.$_{0.07}$ 168° [232].

1-[2-Hydroxy-3-methyl-4-(10-undecenoyloxy)phenyl]-2,2,2-trifluoroethanone

10-Undecenoic acid, 3-Hydroxy-2-methyl-4 (or 6)-(trifluoroacetyl)phenyl ester

[65233-66-1] $C_{20}H_{25}F_3O_4$ mol.wt. 386.41



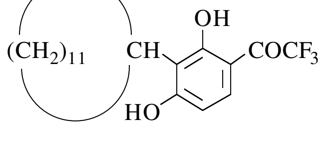
b.p.$_{0.07}$ 165° [232].

Synthesis

-Preparation by reaction of 10-undecenoyl chloride on 2,4-dihydroxy-3-methyl-α,α,α-trifluoroacetophenone with pyridine in benzene at r.t. (64%) [232].

1-(3-Cyclododecyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65240-19-9] $C_{20}H_{27}F_3O_3$ mol.wt. 372.43



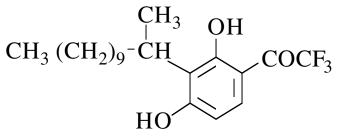
Synthesis

-Preparation by reaction of cyclododecene on 2,4-dihydroxy-α,α,α-trifluoroacetophenone with phosphorous oxychloride and phosphorous pentoxide at 50° [232].

m.p. 166° [232].

1-[2,4-Dihydroxy-3-(1-methylundecyl)phenyl]-2,2,2-trifluoroethanone

[65134-37-4] $C_{20}H_{29}F_3O_3$ mol.wt. 374.44



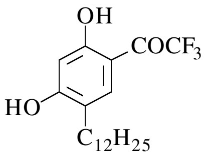
Synthesis

-Preparation by reaction of 1-dodecene on 2,4-dihydroxy-α,α,α-trifluoroacetophenone with phosphorous oxychloride and phosphorous pentoxide at 50° [232].

m.p. 96° [232].

1-(5-Dodecyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65239-85-2] $C_{20}H_{29}F_3O_3$ mol.wt. 374.44



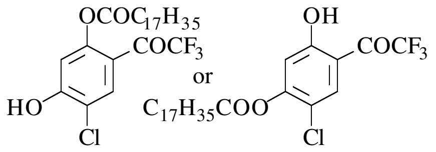
Synthesis

-Preparation by reaction of trifluoroacetic anhydride on 4-dodecylresorcinol with aluminium chloride in ethylene dichloride at r.t. (84%) [232].

m.p. 92° [232].

1-[5-Chloro-2 (or 4)-hydroxy-4 (or 2)-(octadecanoyloxy)phenyl]-2,2,2-trifluoroethanone

[65233-65-0] $C_{26}H_{38}ClF_3O_4$ mol.wt. 507.03



(**I**) (**II**)

Synthesis

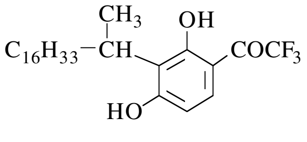
-Preparation by reaction of stearoyl chloride on 5-chloro-2,4-dihydroxy-α,α,α-trifluoroacetophenone with pyridine in benzene at r.t. (40%) [232].

m.p. 51° [232].

N.B.: The 1-[5-Chloro-2-hydroxy-4-(octadecanoyloxy)phenyl]-2,2,2-trifluoroethanone (**II**) is the most likely formula.

1-[2,4-Dihydroxy-3-(1-methylheptadecyl)phenyl]-2,2,2-trifluoroethanone

$C_{26}H_{41}F_3O_3$ mol.wt. 458.60



Synthesis

-Preparation by reaction of 1-octadecene on 2,4-dihydroxy-α,α,α-trifluoroacetophenone with phosphorous oxychloride and phosphorous pentoxide at 50° [232].

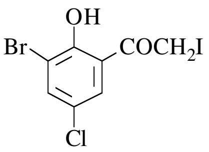
m.p. 98° [232].

2.4. *Compounds derived from iodoacetic acids*

2.4.1. From monoiodoacetic acid

1-(3-Bromo-5-chloro-2-hydroxyphenyl)-2-iodoethanone

$C_8H_5BrClIO_2$ mol.wt. 375.39

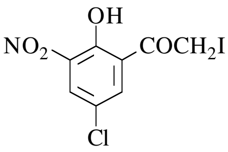


Synthesis

-Obtained by reaction of iodine monochloride with 3-bromo-5-chloro-2-hydroxyacetophenone in boiling acetic acid [172].

1-(5-Chloro-2-hydroxy-3-nitrophenyl)-2-iodoethanone

$C_8H_5ClINO_4$ mol.wt. 309.49

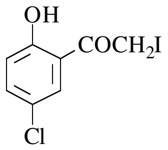


Synthesis

-Obtained by reaction of iodine monochloride with 5-chloro-2-hydroxy-3-nitroacetophenone in boiling acetic acid [172].

1-(5-Chloro-2-hydroxyphenyl)-2-iodoethanone

[438625-16-2] $C_8H_6ClIO_2$ mol.wt. 296.49

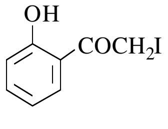


Synthesis

-Obtained by reaction of iodine monochloride with 5-chloro-2-hydroxyacetophenone in boiling acetic acid [172].

1-(2-Hydroxyphenyl)-2-iodoethanone

[99233-30-4] $C_8H_7IO_2$ mol.wt. 262.05



Syntheses

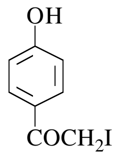
-Refer to: [254] [255] [1398] [1538] [1539].

N.B.: The iodination kinetics of o-hydroxy-acetophenone have been investigated at 25° in aqueous buffer solutions. The foregoing analysis assumes that only one mol of iodine reacts with each mol of o-hydroxyacetophenone, which may be incorrect. The title substance does not appear to have been isolated [156].

m.p. 65° [254] [1538].

1-(4-Hydroxyphenyl)-2-iodoethanone

[99233-31-5] $C_8H_7IO_2$ mol.wt. 262.05



Syntheses

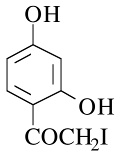
-Obtained by reaction of iodine with p-hydroxyacetophenone in the presence of 1-fluoro-4-chloromethyl-1,4-diazonia-bicyclo[2.2.2]octane bis(tetrafluoroborate)* in methanol for 19 h at r.t. (64%) [1398].
*This reagent is known under the commercial name of Selectfluor™ F-TEDA-BF_4.

-Also refer to: [254] [255] [1468] [1538].

m.p. 130° [254] [1538]; 126-128°8 [1398]; TLC [1398]; Crystal data [254] [1538]; ^{1}H NMR [1398], IR [1398], MS [1398].

1-(2,4-Dihydroxyphenyl)-2-iodoethanone

$C_8H_7IO_3$ mol.wt. 278.05



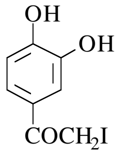
Synthesis

-Preparation by reaction of sodium iodide on 2,4-dihydroxy-α-chloroacetophenone in acetone at r.t. (70%) [1380].

m.p. 141° [1380].

1-(3,4-Dihydroxyphenyl)-2-iodoethanone

[105174-59-2] $C_8H_7IO_3$ mol.wt. 278.05



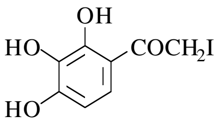
Syntheses

-Preparation by reaction of sodium iodide on 3,4-dihydroxy-α-chloroacetophenone in acetone at r.t. (34%) [827].
-Also refer to: [1350].

no m.p.: This compound progressively decomposed from 140° and gave a black residue at 162-163° [827]; ^{1}H NMR [827], IR [827], UV [827], MS [827].

2-Iodo-1-(2,3,4-trihydroxyphenyl)ethanone

[105174-62-7] $C_8H_7IO_4$ mol.wt. 294.05



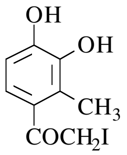
Synthesis

-Preparation by reaction of sodium iodide on 2,3,4-tri-hydroxy-α-chloroacetophenone in acetone at r.t. (63%) [827].

m.p. 144-145° [827]; ^{1}H NMR [827], IR [827], UV [827], MS [827].

1-(3,4-Dihydroxy-2-methylphenyl)-2-iodoethanone

C9H9IO3 mol.wt. 292.07



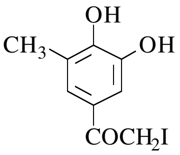
Synthesis

-Preparation by reaction of sodium iodide on 3,4-dihydroxy-2-methyl-α-chloroacetophenone in acetone at r.t. (62%) [624].

m.p. 171-172° [624].

1-(3,4-Dihydroxy-5-methylphenyl)-2-iodoethanone

C9H9IO3 mol.wt. 292.07



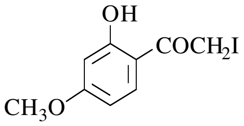
Synthesis

-Preparation by reaction of sodium iodide on 2,4-dihydroxy-5-methyl-α-chloroacetophenone in acetone [624].

m.p. 177° [624].

1-(2-Hydroxy-4-methoxyphenyl)-2-iodoethanone

C9H9IO3 mol.wt. 292.07



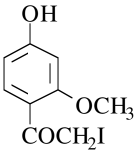
Synthesis

-Preparation by heating 2-hydroxy-4-methoxy-α-bromoacetophenone with concentrated aqueous potassium iodide solution [1438].

m.p. 102° [1438].

1-(4-Hydroxy-2-methoxyphenyl)-2-iodoethanone

C9H9IO3 mol.wt. 292.07



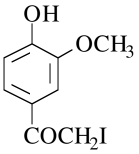
Synthesis

-Preparation by reaction of sodium iodide on 4-hydroxy-2-methoxy-α-chloroacetophenone in acetone at r.t. [1380].

m.p. 128° [1380].

1-(4-Hydroxy-3-methoxyphenyl)-2-iodoethanone

[105174-52-5] C9H9IO3 mol.wt. 292.07



Synthesis

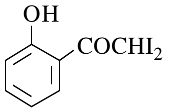
-Preparation by reaction of sodium iodide on 4-hydroxy-3-methoxy-α-bromoacetophenone in acetone at r.t. (52%) [827].

m.p. 103° [827]; ^{1}H NMR [827], IR [827], UV [827], MS [827].

2.4.2. From diiodoacetic acid

2,2-Diiodo-1-(2-hydroxyphenyl)ethanone

$C_8H_6I_2O_2$ mol.wt. 387.94



Synthesis not yet described

N.B.: Not obtained.
-The iodination kinetics of o-hydroxyacetophenone have been investigated at 25° in aqueous buffer solutions. The foregoing analysis assumes that only one mol of iodine reacts with each mol of o-hydroxyacetophenone, which may be incorrect. Cyclisation probably predominates over the introduction of a second iodine atom into o-hydroxyacetophenone, at least in the early stages of the reaction. There is formation of 3-coumaranone [156].

2.4.3. From triiodoacetic acid

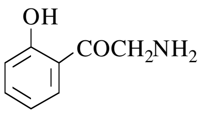
There is no hydroxyketone derived from triiodoacetic acid such as described up to December 2003.

Chapter 3. Compounds derived from aminoacetic acids

3.1. *Compounds derived from aminoacetic acid*

2-Amino-1-(2-hydroxyphenyl)ethanone

[72481-17-5] $C_8H_9NO_2$ mol.wt. 151.17

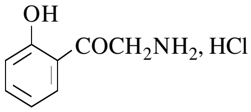


Syntheses

-Obtained by treatment of 3-nitro-4-hydroxycoumarin — m.p. 177° (d) — with refluxing in a mixture of 58% hydriodic acid solution and acetic acid for 15 min. The iodine produced during the reaction was reduced with hypophosphorous acid [664].
-Also refer to: [572] [1426].

2-Amino-1-(2-hydroxyphenyl)ethanone *(Hydrochloride)*

$C_8H_9NO_2$, HCl mol.wt. 187.63



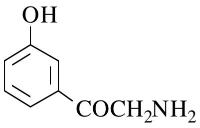
Synthesis

-Preparation by treatment of 3-nitro-4-hydroxycoumarin — m.p. 177° (d) — with refluxing in a mixture of 58% hydriodic acid solution and acetic acid for 15 min. The iodine produced during the reaction was reduced with hypophosphorous acid. Then, recrystallisation of the obtained base from concentrated hydrochloric acid (66%) [664].

m.p. 229-230° [664].

2-Amino-1-(3-hydroxyphenyl)ethanone

[90005-54-2] $C_8H_9NO_2$ mol.wt. 151.17



Syntheses

-Obtained by adding ammonia to an aqueous solution of its hydrochloride (63%) [226].
-Also refer to: [219] [220] [355] [572] [850].

m.p. 217-220° [220], 215-235° [226].

2-Amino-1-(3-hydroxyphenyl)ethanone *(Hydrochloride)*

[14665-75-9] $C_8H_9NO_2$, HCl mol.wt. 187.63

Syntheses

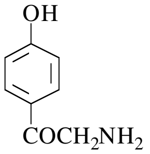
-Preparation by hydrolysis of m-(benzoyloxy)-α-aminoacetophenone hydrochloride (SM) (m.p. 202-205°) [220], (m.p. 206°) [226],
*with refluxing 10% hydrochloric acid (quantitative yield) [226], for 2 h (80%) [220];

*with 37% hydrochloric acid in chlorobenzene at 90° for 3 h (90%) [355]. SM was obtained by reaction of hexamethylenetetramine with m-(benzoyloxy)-α-bromoacetophenone (m.p. 162°) in ethanol in the presence of 37% hydrochloric acid for 6 h at r.t. (75%) [355].
-Also obtained by hydrolysis of 3,6-bis(3-hydroxyphenyl)-2,5-dihydropyrazine in aqueous suspension with hydrochloric acid at r.t. [1047].
-Also obtained by reaction of 3-acetoxy-α-bromoacetophenone (m.p. 71-72°) with hexamethylenetetramine in chloroform, followed by acetoxy group elimination in the obtained compound with hydrochloric acid [1270].
-Also obtained by reaction of 3-hydroxy-α-iodoacetophenone with hexamethylenetetramine, followed by transformation of the obtained iodo derivative (m.p. 138-139°) into hydrochloride salt [1269].
-Also refer to: [219].

m.p. 221-222° [1047] [1269] [1270], 219-220° [226],
218-220° (d) [355], 217-220° [220].

2-Amino-1-(4-hydroxyphenyl)ethanone

[77369-38-1]	$C_8H_9NO_2$	mol.wt. 151.17



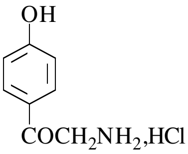
Syntheses

-Obtained by oxidation of the biogenic amine 1-(4-hydroxyphenyl)-2-aminoethanol at high pH [929].
-Also obtained by hydrogenation of p-hydroxyisonitrosoacetophenone — so called p-hydroxy-α-(hydroximino)-acetophenone — over Pd/C in acetic acid at a temperature < 60° (91%) [1426].
-Also obtained from the corresponding hydrochloride aqueous solution with ammonia [963].
-Also refer to: [327] [572] [689] [865] [1035] [1505].

N.B.: For the acetate [172417-70-8], refer to: [1504] [1505]; pK_B [555].

2-Amino-1-(4-hydroxyphenyl)ethanone *(Hydrochloride)*

[19745-72-3]	$C_8H_9NO_2$, HCl	mol.wt. 187.63



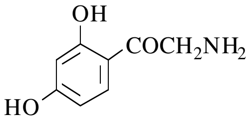
Syntheses

-Preparation by treatment of α-amino-p-hydroxyacetophenone with hydrogen chloride in DMF (70%) [1426].
-Preparation by hydrogenation of p-hydroxy-α-(hydroximino)acetophenone (SM) over Pd/C in DMF (70%). SM was obtained by adding tert-butyl nitrite to a mixture of p-hydroxyacetophenone, hydrogen chloride and DMF at 40-45° [1425].
-Preparation from α-amino-p-benzoyloxyacetophenone hydrochloride with refluxing 20% hydrochloric acid solution for 7 h (80%) [327].
-Preparation by condensation of phenol with aminoacetonitrile hydrochloride (Houben-Hoesch reaction) (51%) [89].
-Also obtained by demethylation of α-amino-p-methoxyacetophenone (m.p. 197°) with 38% hydrochloric acid at 160-170° for 2 h [963].
-Also refer to: [236].

m.p. 249-251° [89], 242° [963], 241-245° (d) [327].

2-Amino-1-(2,4-dihydroxyphenyl)ethanone

$C_8H_9NO_3$ mol.wt. 167.16



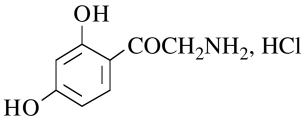
Syntheses

-Obtained from its hydriodide (m.p. 258°) or its hydrochloride (m.p. 280°) by addition of a hot concentrated solution of sodium carbonate [1482].
-Also refer to: [1121] [1555].

m.p. 310° (d) [1482].

2-Amino-1-(2,4-dihydroxyphenyl)ethanone *(Hydrochloride)*

$C_8H_9NO_3$, HCl mol.wt. 203.61



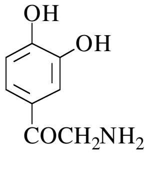
Syntheses

-Obtained by refluxing a mixture of 2,4-dihydroxy-α-[(ethoxycarbonyl)amino]acetophenone (m.p. 156-157°) and hydrochloric acid (1:1) for 2 h [1380].
-Also obtained by addition of concentrated hydrochloric acid to an alcoholic solution of the corresponding hydriodide (SM). SM — m.p. 128° (d) — was prepared from 2,4-dimethoxy-α-phthaliminoacetophenone (m.p. 188°) with boiling concentrated hydriodic acid containing some acetic acid [1482].
-Also obtained by treatment of 3-acetamido-4,7-dihydroxycoumarin (m.p. 268°) with 10% hydrochloric acid for 1 h [1121].
-Also refer to: [1555].

m.p. 280° (d) [1482], 271° [1121], 257° [1380].
One of the reported melting points is obviously wrong.

2-Amino-1-(3,4-dihydroxyphenyl)ethanone *(Arterenone; Noradrenalone; ART)*

[499-61-6] $C_8H_9NO_3$ mol.wt. 167.16



Syntheses

-Preparation by reaction of 35% aqueous ammonia with 3,4-dihydroxy-α-chloroacetophenone in methanol or in ethanol [874], (71-73%) [1233], (67%) [1404].
-Also obtained by adding ammonia to an aqueous solution of the corresponding hydrochloride [555] [797], (60-75%) [963].
-Also obtained by adding sodium carbonate to an aqueous solution of its hydriodide (m.p. 247-248°) (SM). SM was prepared from m,m',p,p'-tetramethoxy-2,5-diphenylpyrazine by boiling for 2 h with a mixture of acetic acid and concentrated hydriodic acid [1482].
-Preparation by hydrogenolysis of α-dibenzylamino-3,4-dihydroxyacetophenone hydrochloride in water in the presence of Pd/C under hydrogen atmosphere for 5 h. Then, treatment of the concentrated solution with 28% ammonia (85%) [1363].
-Also refer to: [357] [572] [1047] [1092].

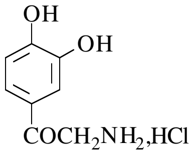
Isolation from natural sources

-From insect cuticle [47] [50].
-Also obtained by mild acid hydrolysis of sclerotized cuticles from locusts *(Schistocerca gregaria)* and beetles *(Pachynoda sinuata)* [45].
-From acid hydrolysates of insect sclerotized cuticle in refluxing 1 N formic acid for 1 h or in boiling methanolic hydrochloric acid. The cuticle used was obtained from the desert locust *Schistocerca gregaria* [46].
-Also obtained by hydrolysis of 2-(3',4'-dihydroxyphenyl)-3-acetylamino-6 (or 7)-(N-acetyl-2''-aminoethyl)-2,3-dihydro-1,4-benzodioxin (SM) with 6 N hydrochloric acid at 110° for 3 h. SM was formed by incubation of N-acetyldopamine with locust cuticle [48].
-ART was the major identified catechol recovered from strong acid hydrolysates of tanning pharate pupae cuticle from *Manduca sexta* [1120].

m.p. 300° (d) [1404], 235° (d) [1363] [1482], >200° (d) (not melted) [797] [963];
One note a very large dispersion of the various melting points.
^{1}H NMR [48], UV [45] [46], MS [45] [1242];
HPLC [1120]; pK_B [555]; column chromatography [45]; TLC [45].

2-Amino-1-(3,4-dihydroxyphenyl)ethanone *(Hydrochloride)*

[5090-29-9] $C_8H_9NO_3$, HCl mol.wt. 203.61



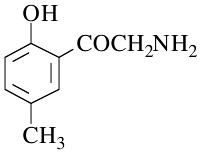
Syntheses

-Preparation by demethylation of α-amino-3,4-dimethoxy-acetophenone on heating with 37% hydrochloric acid for 2.5 h at 160-165° under carbon dioxide (85%) [797].
-Preparation by dissolving the corresponding base in a mixture of concentrated hydrochloric acid/methanol and allowing to stand several hours at -10° (82%) [874].
-Also obtained by hydrogenation of 3,4-dihydroxy-α-azidoacetophenone (m.p. 132°) in an ethanol and concentrated hydrochloric acid solution under hydrogen in the presence of 4% Pd/C for 7 h (65%) [226].
-Also obtained from the addition compound (SM) of 3,4-diacetoxy-α-chloroacetophenone and hexamethylene tetramine in chloroform at r.t. for 24 h (40%). SM in ethanolic solution was treated with 38% hydrochloric acid at r.t. for 3 days [963].
-Also obtained from hydrolysis of 3,6-bis(3,4-dihydroxyphenyl)-2,5-dihydropyrazine — m.p. 250° (d) — in aqueous suspension with hydrochloric acid at r.t. [1047].
-Also refer to: [1233].

m.p. 270° [1047], 260° [1404], 259° [555], 256° (d) [226] [797], 255° [874], 252° [963].
One note a very large dispersion of the various melting points.

2-Amino-1-(2-hydroxy-5-methylphenyl)ethanone

$C_9H_{11}NO_2$ mol.wt. 165.19

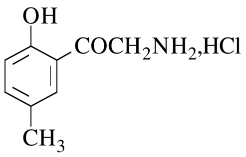


Synthesis

-Obtained by hydrogenation of the complex formed by addition of 2-(benzyloxy)-5-methyl-α-bromoacetophenone and hexamethylenetetramine in ethanol in the presence of Pd/C [67].

2-Amino-1-(2-hydroxy-5-methylphenyl)ethanone *(Hydrochloride)*

$C_9H_{11}NO_2$, HCl mol.wt. 201.66



Synthesis

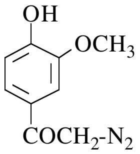
-Obtained by hydrogenolysis of 2-(benzyloxy)-5-methyl-α-aminoacetophenone hydrochloride (m.p. 191-192°) (SM) with hydrogen in the presence of Pd/C in 95% ethanol. SM was prepared by reaction of 2-(benzyloxy)-5-methyl-α-bromoacetophenone with hexamethylene-tetramine, followed by treatment with ethanolic hydrogen chloride [67].

m.p. 222-225° (d) [67].

3.2. *Compounds derived from substituted aminoacetic acids*

2-Diazo-1-(4-hydroxy-3-methoxyphenyl)ethanone

$C_9H_9N_2O_3$ mol.wt. 193.28



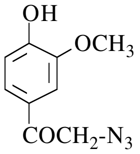
Synthesis

-Preparation by reaction of potassium hydroxide with 4-acetoxy-3-methoxy-α-diazoacetophenone (m.p. 92-93°) in methanol at 20° for 15 h (quantitative yield) [454].

amorphous solid [454].

2-Azido-1-(4-hydroxy-3-methoxyphenyl)ethanone

$C_9H_9N_3O_3$ mol.wt. 207.19

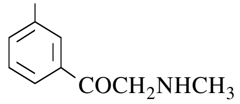


Synthesis

-Obtained by reaction of 4-hydroxy-3-methoxy-α-chloroacetophenone with an alkali metal azide in dilute alcohols (C_1-C_5) [1305].

1-(3-Hydroxyphenyl)-2-(methylamino)ethanone *(Phenylephrone)*

[52093-42-2] $C_9H_{11}NO_2$ mol.wt. 165.19



Syntheses

-Preparation by reductive condensation of m-hydroxyphenylglyoxal with methylamine in ethanol under saturated hydrogen atmosphere in the presence of Raney nickel at 45° (55%) [503].

-Also obtained by action of potassium N-methyl-p-toluene

sulfonamide with m-acetoxy-α-bromoacetophenone in acetone during some hours. Then, the resulting intermediate compound (m.p. 120-121°) was treated with boiling 55% aqueous hydriodic acid for 1 h [898] [901] [1400].
-Also obtained by reaction of methylamine with α-bromo-m-benzoyloxyacetophenone in isopropanol, and subsequent treatment with aqueous hydrochloric acid [1030].
-Also obtained by reaction of methylamine with α-bromo-m-hydroxyacetophenone in dilute ethanol [900] [897].
-Also refer to: [37] [572] [577] [850].

m.p. 135° [898] [901] [1400], 128° [503].

1-(3-Hydroxyphenyl)-2-(methylamino)ethanone *(Hydrochloride)*

[94240-17-2] $C_9H_{11}NO_2$, HCl mol.wt. 201.65

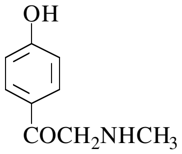
Syntheses

-Preparation by conversion of the base with 35% ethanolic hydrogen chloride [503].
-Also obtained by hydrogenolysis of 2-(benzyl-methyl-amino)-1-(3-hydroxyphenyl)ethanone hydrochloride with hydrogen in the presence of Pd-black in ethanol [37].
-Also refer to: [228] [898].

m.p. 238° [897] [900], 234° [503] [898] [901] [1400];
IR [37].

1-(4-Hydroxyphenyl)-2-(methylamino)ethanone

[21213-89-8] $C_9H_{11}NO_2$ mol.wt. 165.19



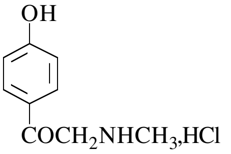
Syntheses

-Preparation by reductive condensation of p-hydroxyphenylglyoxal with methylamine in ethanol under saturated hydrogen atmosphere in the presence of Raney nickel at 45° [503].
-Also obtained by reductive condensation of p-hydroxyphenylglyoxal potassium bisulfite ($C_8H_7O_6SK$, preparation given) with methylamine in dilute ethanol under saturated hydrogen atmosphere and cooling with ice (71%) [503].
-Also obtained by reduction of potassium 2-(4-hydroxyphenyl)-2-oxo-1-methylaminoethane sulfonate ($C_9H_{10}NO_5SK$, preparation given) in dilute ethanol with hydrogen in the presence of Raney nickel (65%) [503].
-Also obtained by reaction of potassium N-methyl-p-toluenesulfonamide with p-acetoxy-α-bromoacetophenone in acetone during some hours. Then, the resulting intermediate compound was treated with boiling 55% aqueous hydriodic acid for 1 h [898].
-Also obtained by degradation of p-toluenesulfonamide (prepared from α-methylamino-p-methoxyacetophenone) on heating with 37% hydrochloric acid for 2 h at 150° under carbon dioxide [797].
-Also obtained by treatment of p-hydroxy-α-bromoacetophenone in ethanol with a 40% methylamine solution, first in an ice bath, then at r.t. overnight [899].
-Also obtained by reaction of methylaminoacetonitrile with phenol (Houben-Hoesch reaction) (75%) [89].
-Also refer to: [228] [327] [572].

m.p. 148° [898], 147-148° [899], 147° [503] [797], 142-144° (d) [89];
pK_B [555].

1-(4-Hydroxyphenyl)-2-(methylamino)ethanone *(Hydrochloride)*

[67828-68-6] $C_9H_{11}NO_2$, HCl mol.wt. 201.65



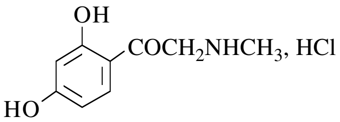
Syntheses

-Obtained by reaction of hydrochloric acid with the corresponding base [797], (83%) [89], (50%) [327].
-Also obtained by treatment of its oxalate (m.p. 166°) with ethanolic hydrogen chloride (72%) [503].
-Also obtained by reaction of methylaminoacetonitrile hydrochloride with phenol (Hoesch reaction) (88%) [1017].
-Also refer to: [30] [31] [32] [898].

m.p. 261-263° (d) (pure) [327], 244-246° [1017], 242-244° (d) [89],
242° (d) [797], 241-243° (d) [327], 239-240° [899], 238-240° [898],
238-239° [503].

1-(2,4-Dihydroxyphenyl)-2-(methylamino)ethanone *(Hydrochloride)*

$C_9H_{11}NO_3$, HCl mol.wt. 217.65



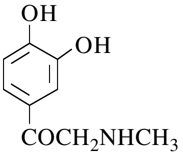
Synthesis

-Preparation by successively adding methylaminoacetonitrile hydrochloride and resorcinol to a solution of aluminium chloride in nitrobenzene, then bubbling hydrogen chloride for 6-8 h through the reaction mixture at 20-30° (73%) [1017].

m.p. 265-267° [1017].

1-(3,4-Dihydroxyphenyl)-2-(methylamino)ethanone *(Adrenalone)*

[99-45-6] $C_9H_{11}NO_3$ mol.wt. 181.19



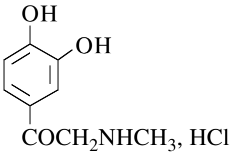
Syntheses

-Preparation by reaction of excess 33% aqueous methylamine with 3,4-dihydroxy-α-chloroacetophenone [356].
-Preparation by adding an aqueous solution of 40% methylamine to an ethanolic solution of 3,4-dihydroxy-α-chloroacetophenone. Then, adding of ammonia to a solution of recrystallized hydrochloride so formed, (71-73%) [1233], (62%) [1404].
-Preparation by reductive condensation of 3,4-dihydroxyphenylglyoxal with methylamine in ethanol under hydrogen atmosphere in the presence of 14% Pd/C [503].
-Also obtained by degradation of p-toluenesulfonamide, prepared from 3,4-dimethoxy-α-methylaminoacetophenone, with refluxing 37% hydrochloric acid (150-160°) for 2 h under carbon dioxide [797].
-Also obtained by treatment of 3,4-diacetoxy-α-chloroacetophenone (m.p. 110°) with 30% methylamine solution (good yield, not specified) [1510].
-Also refer to: [222] [357] [572] [586] [588] [850] [932] [1018] [1207].

m.p. 232° [356], 230° [1404], 229° (d) [797], 215° (d) [139];
UV [1262] [1454]; pK_B [555] [1226];
micellar liquid chromatography [1462] [1506] [1508]; electrophoresis [663].

1-(3,4-Dihydroxyphenyl)-2-(methylamino)ethanone *(Hydrochloride) (Stryphnon)*

[62-13-5] $C_9H_{11}NO_3$, HCl mol.wt. 217.65



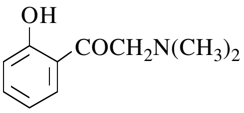
Syntheses

-Obtained by action of hydrochloric acid on 3,4-dihydroxy-α-methylaminoacetophenone (65%) [1233], in methanol [797] [1404].
-Also obtained (poor yield) from the base by saturation of its aqueous solution with hydrogen chloride (7%) [503].
-Also refer to: [31] [32] [228] [356].

m.p. 248° [555], 241° (d) [503] [797], 240° (d) [1404], 237-243° (d) [139];
UV [1018].

2-(Dimethylamino)-1-(2-hydroxyphenyl)ethanone

$C_{10}H_{13}NO_2$ mol.wt. 179.22

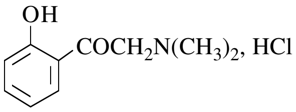


Synthesis

-Obtained by adding a solution of dimethylamine (2 mol) in ethyl ether to a cold solution of o-hydroxy-α-chloro-acetophenone (m.p. 71-71°5) (1 mol) and sodium iodide (1 mol) in acetone. The mixture was then allowed to stand for 14 h at 0° [906].

2-(Dimethylamino)-1-(2-hydroxyphenyl)ethanone *(Hydrochloride)*

$C_{10}H_{13}NO_2$, HCl mol.wt. 215.69



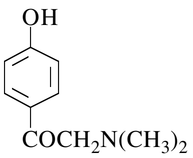
Synthesis

-Obtained by adding of ethanolic hydrochloric acid to a solution of the corresponding base in acetone (61%) [906].

m.p. 105-107° [906].

2-(Dimethylamino)-1-(4-hydroxyphenyl)ethanone

$C_{10}H_{13}NO_2$ mol.wt. 179.22



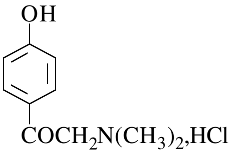
Syntheses

-Obtained by adding a solution of dimethylamine (2 mol) in ethyl ether to a cold solution of p-hydroxy-α-chloro-acetophenone (m.p. 151-152°) (1 mol) and sodium iodide (1 mol) in acetone. The mixture was then allowed to stand for 14 h at 0° [906].
-Also obtained by hydrolysis of 1-[4-(benzoyloxy)phenyl]-2-dimethylaminoethanone with aqueous hydrochloric acid [227].
-Also obtained by reaction of dimethylamine with p-(benzoyloxy)-α-bromoacetophenone in isopropanol [327].
-Also refer to: [1482].

m.p. 142° [1482].

2-(Dimethylamino)-1-(4-hydroxyphenyl)ethanone *(Hydrochloride)*

[2970-79-8] $C_{10}H_{13}NO_2$, HCl mol.wt. 215.69



Syntheses

-Obtained by reaction of dimethylamine with p-acetoxy-α-bromoacetophenone in benzene, followed by treatment with dilute hydrochloric acid [512].

-Also obtained by reaction of dimethylamine with p-benzoyloxy-α-bromoacetophenone in isopropanol [327] or in benzene [227] and subsequent treatment with hydrochloric acid (88%) [227], (47%) [327].

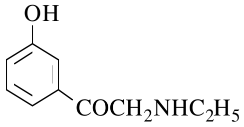
-Also obtained by adding ethanolic hydrochloric acid to a solution of the corresponding base in acetone (43%) [906].

-Also refer to: [511].

m.p. 242-243° [906], 235° [512], 234-237° [227], 233-235° [327].

2-(Ethylamino)-1-(3-hydroxyphenyl)ethanone

[22510-12-9] $C_{10}H_{13}NO_2$ mol.wt. 179.22



Syntheses

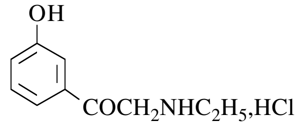
-Preparation by reductive condensation of 3-hydroxyphenylglyoxal with ethylamine in ethanol under saturated hydrogen atmosphere in the presence of Raney nickel at 45° (49%) [503].

-Also obtained by reaction of ethylamine with 1-(3-acetoxyphenyl)-2-bromoethanone in aqueous isopropanol [578].

m.p. 203-205° [503].

2-(Ethylamino)-1-(3-hydroxyphenyl)ethanone *(Hydrochloride)*

[22510-04-9] $C_{10}H_{13}NO_2$, HCl mol.wt. 215.69



Syntheses

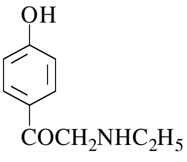
-Preparation by crystallization of the base in 2 N hydrochloric acid [503].

-Also obtained by reaction of 40% ethylamine solution with m-acetoxy-α-bromoacetophenone in isopropanol, first at 0°, then at 40° for 10 min, followed by treatment with hydrochloric acid [578].

m.p. 221-222° [503], 212-215° (d) [578].

2-(Ethylamino)-1-(4-hydroxyphenyl)ethanone

[99075-26-0] $C_{10}H_{13}NO_2$ mol.wt. 179.22



Syntheses

-Preparation by reductive condensation of 4-hydroxyphenylglyoxal with ethylamine in ethanol under saturated hydrogen atmosphere in the presence of Raney nickel at 45° [503].

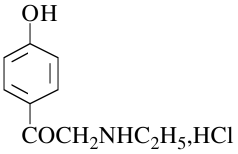
-Also obtained by reductive condensation of 4-hydroxyphenylglyoxal potassium bisulfite ($C_8H_7O_6SK$, preparation given) with ethylamine [503].

-Also obtained by reaction of ethylamine with 1-[4-(benzoyloxy)phenyl]-2-bromoethanone in isopropanol [327].

$pK_B = 6.23$ [555].

2-(Ethylamino)-1-(4-hydroxyphenyl)ethanone *(Hydrochloride)*

[74730-79-3] $C_{10}H_{13}NO_2$, HCl mol.wt. 215.69



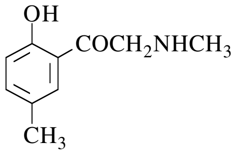
Syntheses

-Preparation by treatment of the oxalate with 28% ethanolic hydrogen chloride (65%) [503].
-Also obtained by reaction of α-bromo-p-benzoyloxy-acetophenone with ethylamine in isopropanol and subsequent treatment with hydrochloric acid (51%) [327].

m.p. 228-231° (d) [327], 221° [503].

1-(2-Hydroxy-5-methylphenyl)-2-(methylamino)ethanone

$C_{10}H_{13}NO_2$ mol.wt. 179.22

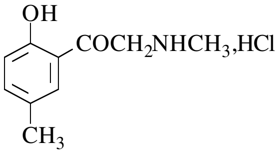


Synthesis

-Preparation by hydrogenolysis of 2-(benzylmethylamino)-1-(2-hydroxy-5-methylphenyl)ethanone with hydrogen in the presence of Pd/C as catalyst [67].

1-(2-Hydroxy-5-methylphenyl)-2-(methylamino)ethanone *(Hydrochloride)*

$C_{10}H_{13}NO_2$, HCl mol.wt. 215.69



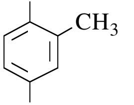
Synthesis

-Obtained by hydrogenolysis of 2-(benzyloxy)-5-methyl-N-benzylmethylaminoacetophenone hydrochloride or of 2-hydroxy-5-methyl-N-benzylmethylaminoacetophenone hydrochloride with hydrogen in the presence of Pd/C in 95% ethanol [67].

m.p. 204-206° [67].

1-(4-Hydroxy-3-methylphenyl)-2-(methylamino)ethanone *(Hydrochloride)*

$C_{10}H_{13}NO_2$, HCl mol.wt. 215.69



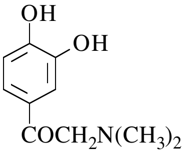
Synthesis

-Preparation by successively adding methylaminoacetonitrile hydrochloride and o-cresol to a solution of aluminium chloride in nitrobenzene, then bubbling hydrogen chloride for 6-8 h through the reaction mixture at 20-30° (90%) [1017].

m.p. 237-238° [1017].

1-(3,4-Dihydroxyphenyl)-2-(dimethylamino)ethanone

[150-10-7] $C_{10}H_{13}NO_3$ mol.wt. 195.22



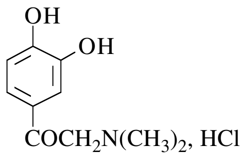
Syntheses

-Preparation by reaction of 3,4-dihydroxy-α-chloroacetophenone with dimethylamine [1151] [1152], in ethanol at 40° for 75 min [229] [230] or at 60° for 5 h [869].
-Also obtained by action of sodium ethoxide with N-methyladrenalone hydrochloride in boiling ethanol (72-74%) [1233].
-Also obtained by demethylation of 2-dimethylamino-1-(3-hydroxy-4-methoxyphenyl)ethanone with concentrated aqueous hydrochloric acid at 130° [1275].
-Also obtained by reaction of dimethylamine with α-chloro-3-acetoxy-4-hydroxyacetophenone in aqueous ethanol [1361].

m.p. >130° (d) [1233].

1-(3,4-Dihydroxyphenyl)-2-(dimethylamino)ethanone *(Hydrochloride)*

[16899-83-5] $C_{10}H_{13}NO_3$, HCl mol.wt. 231.69



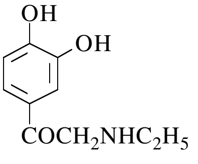
Syntheses

-Preparation by reaction of the corresponding base (SM) with hydrogen chloride in ethanol, [1151], (66%) [869], (62%) [588], (54%) [1275], (50%) [229] [230]. SM was obtained by reaction of 3,4-dihydroxy-α-chloroacetophenone with concentrated aqueous dimethylamine.
-Direct preparation by reaction of 3,4-dihydroxy-α-chloroacetophenone with dimethylamine in methanol for 20-30 min at < 5° (73-76%) [1233] or in absolute ethanol for 2 h at 60° (45%) [1152].
-Also obtained by treatment of 3,4-dimethoxy-α-dimethylaminoacetophenone (SM) with concentrated hydrochloric acid for 2.5 h at 150-160° in a sealed tube (41%) [1274] or for 2 h at 130° (25%) [1275]. SM was prepared by reaction of 3,4-dimethoxy-α-chloroacetophenone with dimethylamine in benzene at r.t. overnight (91%, b.p.$_6$ 155-157°) [1274].
-Also obtained by treatment of 3-hydroxy-4-methoxy-α-dimethylaminoacetophenone with concentrated hydrochloric acid for 2 h at 130°, (65%) [1275].
-Also refer to: [228].

m.p. 236-237° (d) [229] [230], 234-236° (d) [588] [1233], 232° (d) [1274], 231-232° (d) [1275], 225-227° (d) [1151] [1152], 213-214° [869].
One note a very large dispersion of the various melting points. ^{1}H NMR [1152], IR [1152].

1-(3,4-Dihydroxyphenyl)-2-(ethylamino)ethanone

$C_{10}H_{13}NO_3$ mol.wt. 195.22



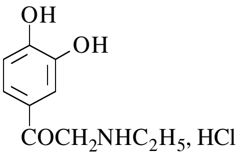
Syntheses

-Obtained by adding an aqueous solution of 40% ethylamine to an ethanolic solution of α-chloro-3,4-dihydroxyacetophenone, then adding ammonia in a solution of the recrytallized hydrochloride so formed (50%) [1404].
-Also refer to: [357].

m.p. 185° [1404]; pK_B [555].

1-(3,4-Dihydroxyphenyl)-2-(ethylamino)ethanone *(Hydrochloride)*

$C_{10}H_{13}NO_3$, HCl mol.wt. 231.69



Syntheses

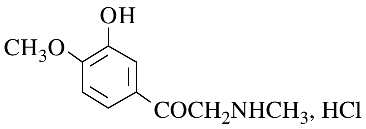
-Obtained by condensation of 3,4-dihydroxy-α-chloro-acetophenone with ethylamine in ethanol or isopropanol at 60-80°. The amino ketone base which separated was treated with concentrated hydrochloric acid [328].

-Also obtained by total demethylation of 1-(3,4-dimethoxyphenyl)-2-(ethylamino)ethanone hydrochloride (m.p. 190-192°), (71%) [1018] according to [1017].

m.p. 260° (d) [1404], 255-257° (d) [1018], 240-242° (d) [328].
One of the reported melting points is obviously wrong.

1-(3-Hydroxy-4-methoxyphenyl)-2-(methylamino)ethanone *(Hydrochloride)*

$C_{10}H_{13}NO_3$, HCl mol.wt. 231.69



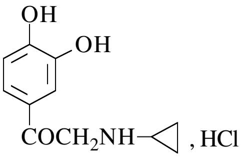
Synthesis

-Preparation by successively adding methylamino-acetonitrile hydrochloride and guaiacol to a solution of aluminium chloride in nitrobenzene, then bubbling hydrogen chloride for 6-8 h through the reaction mixture at 20-30° (25%) [1017].

m.p. 230-230°5 [1017].

2-(Cyclopropylamino)-1-(3,4-dihydroxyphenyl)ethanone *(Hydrochloride)*

$C_{11}H_{13}NO_3$, HCl mol.wt. 243.69



Synthesis

-Obtained (poor yield) by treatment of cyclopropylamine salt of 4-chloroacetylcatechol (m.p. 95-97°) in refluxing isopropanol under nitrogen for 3 h. The formed free base in methanol was treated with ethanolic hydrochloric acid [1446].

m.p. 200-204° [1446].

1-(3-Hydroxyphenyl)-2-[(1-methylethyl)amino]ethanone

$C_{11}H_{15}NO_2$ mol.wt. 193.25

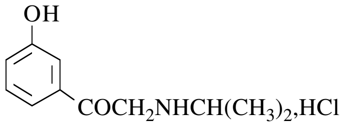
Syntheses

-Preparation by reductive condensation of 3-hydroxyphenylglyoxal with isopropylamine in ethanol under saturated hydrogen atmosphere in the presence of Raney nickel at 45° [503].

-Also obtained by reaction of isopropylamine with α-bromo-m-hydroxyacetophenone in ethanol [329].

1-(3-Hydroxyphenyl)-2-[(1-methylethyl)amino]ethanone *(Hydrochloride)*

[101241-90-1] $C_{11}H_{15}NO_2$, HCl mol.wt. 229.71



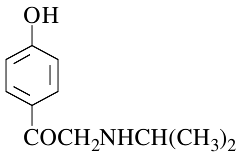
Syntheses

-Preparation by conversion of the oxalate in 28% ethanolic hydrogen chloride (35%) [503].
-Also obtained by [329] according to [327] [328].

m.p. 226-227° [503], 213-216° [329].
One of the reported melting points is obviously wrong.

1-(4-Hydroxyphenyl)-2-[(1-methylethyl)amino]ethanone

[99985-57-6] $C_{11}H_{15}NO_2$ mol.wt. 193.25



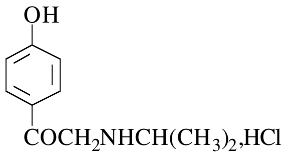
Syntheses

-Preparation by reductive condensation of 4-hydroxyphenylglyoxal with isopropylamine in ethanol under saturated hydrogen atmosphere in the presence of Raney nickel at 45° (86%) [503].
-Also obtained by reductive condensation of 4-hydroxyphenylglyoxal potassium bisulfite ($C_8H_7O_6SK$, preparation given) with isopropylamine [503].
-Also obtained by reaction of isopropylaminoacetonitrile with benzyl phenyl ether (m.p. 39-41°) [1017] or with phenol [89] in the presence of aluminium chloride and hydrogen chloride in nitrobenzene.
-Also obtained by reaction of isopropylamine with α-bromo-4-benzoyloxyacetophenone in isopropanol [327].
-Also refer to: [1375].

m.p. 120-121° [503]; pK_B [555] [910].

1-(4-Hydroxyphenyl)-2-[(1-methylethyl)amino]ethanone *(Hydrochloride)*

[69716-74-1] $C_{11}H_{15}NO_2$, HCl mol.wt. 229.71



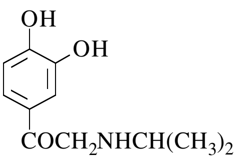
Syntheses

-Preparation from the base with aqueous hydrochloric acid (84%) [503].
-Also obtained by reaction of α-bromo-p-benzoyloxyacetophenone with isopropylamine in isopropanol between 20 to 30° for 2 h, then treatment of the formed base with refluxing 15% hydrochloric acid solution (64%) [327].
-Also obtained by reaction of isopropylaminoacetonitrile hydrochloride (m.p. 166-167°),
*with phenol (Houben-Hoesch reaction) (61%) [89], (42%) [1375];
*with phenyl benzyl ether in the presence of aluminium chloride in nitrobenzene at 20 to 30°, then bubbling hydrogen chloride for 6 h (39%) [1017].

m.p. 272-273° (d) [1017], 263° (d) [1375], 258-260° (d) [89], 250-252° [327], 248-249° [503]. One note a very large dispersion of the various melting points.

1-(3,4-Dihydroxyphenyl)-2-[(1-methylethyl)amino]ethanone *(Isoproterenone)*

[121-28-8] $C_{11}H_{15}NO_3$ mol.wt. 209.25



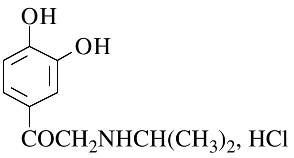
Syntheses

-Obtained by reductive condensation of 3,4-dihydroxyphenylglyoxal with isopropylamine in ethanol under hydrogen atmosphere in the presence of 14% Pd/C [503].
N.B.: In the same manner, the substance can also be obtained from 3,4-bis(benzyloxy)phenylglyoxal [502].
-Also obtained by reaction of 3,4-dihydroxy-α-chloroacetophenone with excess isopropylamine in refluxing ethanol for 2.5 h (76%) [1197].
-Also obtained from the corresponding sulfate by action of a hot sodium bicarbonate aqueous solution (60°) (80%) [228].
-Also obtained by treatment of the corresponding hydrochloride in concentrated aqueous solution at 0° with ammonia [153].

m.p. 173° [228], 168-169° [1197], 96° [153]. One of the reported melting points is obviously wrong. pK_B [555];
^{1}H NMR [1197], IR [1197], UV [1197].

1-(3,4-Dihydroxyphenyl)-2-[(1-methylethyl)amino]ethanone *(Hydrochloride)*

[16899-81-3] $C_{11}H_{15}NO_3$, HCl mol.wt. 245.71



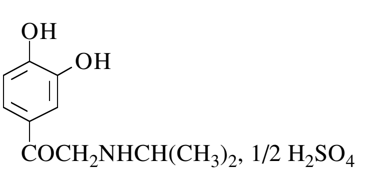
Syntheses

-Obtained by condensation of α-chloro-3,4-dihydroxyacetophenone with isopropylamine [667] in isopropanol at 65-70°. The amino ketone which separated was treated with concentrated hydrochloric acid (54%) [328], (46%) [727].
-Also obtained by demethylation of 3-methoxy-4-hydroxy-α-isopropylaminoacetophenone hydrochloride with concentrated hydrochloric acid at 140° for 6 h in a sealed tube (73%) [153].
-Also refer to: [224] [1008] [1009] [1017].

m.p. 257-259° [1017], 255-257° [153], 239-242° (d) [328] [727].
One of the reported melting points is obviously wrong.
^{1}H NMR [727], ^{13}C NMR [727], UV [1018].

1-(3,4-Dihydroxyphenyl)-2-[(1-methylethyl)amino]ethanone *(Sulfate)*

[27693-62-5] $C_{11}H_{15}NO_3$, 1/2 H_2SO_4 mol.wt. 258.28



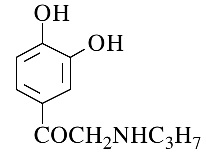
Synthesis

-Preparation by reaction of 5 N ethanolic sulfuric acid with the crude base (58%) [503].

m.p. 243° [503].

1-(3,4-Dihydroxyphenyl)-2-(propylamino)ethanone

$C_{11}H_{15}NO_3$ mol.wt. 209.25



Syntheses

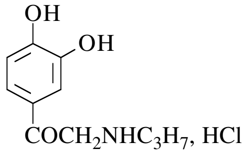
-Obtained by condensation of α-chloro-3,4-dihydroxyacetophenone with propylamine in ethanol or isopropanol at 60-80° [328].

-Also obtained by treatment of 1-(3,4-dimethoxyphenyl)-2-(propylamino)ethanone with aqueous hydrobromic acid [1018].

pK = 6.2 [555].

1-(3,4-Dihydroxyphenyl)-2-(propylamino)ethanone *(Hydrochloride)*

$C_{11}H_{15}NO_3$, HCl mol.wt. 245.71



Syntheses

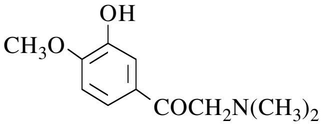
-Obtained by condensation of α-chloro-3,4-dihydroxyacetophenone with propylamine in ethanol or isopropanol at 60-80°. The amino base which separated was treated with concentrated hydrochloric acid [328].

-Also obtained by total demethylation of 1-(3,4-dimethoxyphenyl)-2-(propylamino)ethanone hydrochloride (m.p. 193-194°), (82%) [1018] according to [1017].

m.p. 240-241° (d) [1018], 234-236° (d) [328].

2-(Dimethylamino)-1-(3-hydroxy-4-methoxyphenyl)ethanone

[55761-48-3] $C_{11}H_{15}NO_3$ mol.wt. 209.25

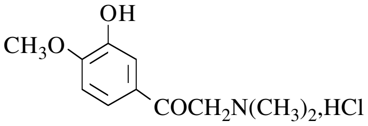


Synthesis

-Obtained by reaction of dimethylamine with α-chloro-3-hydroxy-4-methoxyacetophenone in benzene [1275].

2-(Dimethylamino)-1-(3-hydroxy-4-methoxyphenyl)ethanone *(Hydrochloride)*

$C_{11}H_{15}NO_3$, HCl mol.wt. 245.71



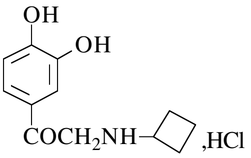
Synthesis

-Obtained by reaction of α-chloro-3-hydroxy-4-methoxyacetophenone with dimethylamine in benzene, first at r.t. overnight, then at 50-60° for 1 h, followed by treatment of the isolated base with hydrochloric acid in ethyl ether (41%) [1275].

m.p. 220-221° (d) [1275].

2-(Cyclobutylamino)-1-(3,4-dihydroxyphenyl)ethanone *(Hydrochloride)*

$C_{12}H_{15}NO_3$, HCl mol.wt. 257.72



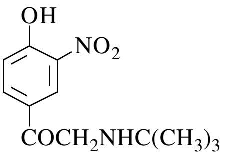
Synthesis

-Obtained by treatment of 4-chloroacetylcatechol cyclobutylamine salt (m.p. 100-104°) in refluxing isopropanol for 3 h (21%) or in a sealed tube at 100° for 1.5 h (28%) [1446].

m.p. 225-228° [1446]; IR [1446], UV [1446].

2-[(1,1-Dimethylethyl)amino]-1-(4-hydroxy-3-nitrophenyl)ethanone

$C_{12}H_{16}N_2O_4$ mol.wt. 252.27

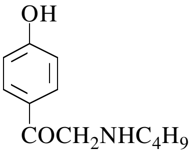


Synthesis

-Obtained by reaction of aqueous nitric acid with α-tert-butylamino-p-hydroxyacetophennone [1176].

2-(Butylamino)-1-(4-hydroxyphenyl)ethanone

[18986-11-3] $C_{12}H_{17}NO_2$ mol.wt. 207.27



Syntheses

-Preparation by reductive condensation of 4-hydroxyphenylglyoxal with n-butylamine in ethanol under saturated hydrogen chloride atmosphere in the presence of Raney nickel at 45° (75%) [503].

-Also obtained by reductive condensation of 4-hydroxyphenylglyoxal potassium bisulfite ($C_8H_7O_6SK$, preparation given) with n-butylamine (85%) [503].

-Also obtained by reaction of n-butylamine with α-bromo-p-benzoyloxyacetophenone in isopropanol [327].

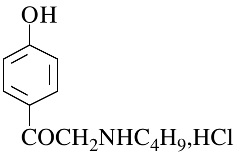
-Also obtained by reaction of n-butylaminoacetonitrile with phenol in the presence of aluminium chloride and hydrogen chloride in nitrobenzene [834] [1017].

-Also obtained from the corresponding hydrochloride with ammonia [834].

m.p. 119-120° [503] [834]; $pK_B = 5.45$ [555].

2-(Butylamino)-1-(4-hydroxyphenyl)ethanone *(Hydrochloride)*

[28836-20-6] $C_{12}H_{17}NO_2$, HCl mol.wt. 243.73



Syntheses

-Preparation from the base with hydrochloric acid (92%) [503].

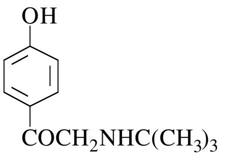
-Preparation by reaction of n-butylaminoacetonitrile hydrochloride (m.p. 101-102°5) [1017], (m.p. 95-96°) [834] with phenol in nitrobenzene in the presence of hydrogen chloride and aluminium chloride as catalyst

(Houben-Hoesch reaction), (78%) [1017], (66%) [834].
-Also obtained by reaction of α-bromo-p-benzoyloxyacetophenone with n-butylamine in isopropanol and subsequent treatment with hydrochloric acid (44%) [327].

m.p. 231° [503] [834], 228-230° [1017], 228-229° [327].

2-[(1,1-Dimethylethyl)amino]-1-(4-hydroxyphenyl)ethanone

[60853-18-1] $C_{12}H_{17}NO_2$ mol.wt. 207.27



Syntheses

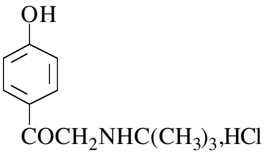
-Obtained by reaction of tert-butylamine with α-bromo-p-benzoyloxyacetophenone in isopropanol [327].
-Also obtained by reaction of tert-butylaminoacetonitrile hydrochloride with phenol in the presence of aluminium chloride and hydrogen chloride in nitrobenzene (modified Hoesch reaction) [1017] [1375].

-Also refer to: [835].

$pK_B = 6.1$ [555].

2-[(1,1-Dimethylethyl)amino]-1-(4-hydroxyphenyl)ethanone *(Hydrochloride)*

[41489-87-6] $C_{12}H_{17}NO_2$, HCl mol.wt. 243.73



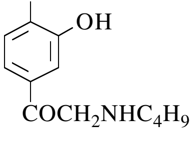
Syntheses

-Preparation by successively adding tert-butylamino-acetonitrile hydrochloride and phenol to a solution of aluminium chloride in nitrobenzene, then bubbling hydrogen chloride for 6-8 h through the reaction mixture at 20-30° (75%) [1017], (63%) [1375].
-Also obtained by reaction of α-bromo-p-benzoyloxyacetophenone with tert-butylamine in isopropanol and subsequent treatment with hydrochloric acid to complete hydrolysis (25%) [327].
-Also refer to: [835].

m.p. 268-270° (d) [835] [1017], 254-257° (d) [327], 253-255° [1375].
One of the reported melting points is obviously wrong.

2-(Butylamino)-1-(3,4-dihydroxyphenyl)ethanone

[33406-44-9] $C_{12}H_{17}NO_3$ mol.wt. 223.27



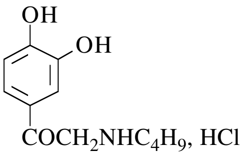
Synthesis

-Obtained by condensation of α-chloro-3,4-dihydroxy-acetophenone with butylamine in ethanol or isopropanol at 60-80° [328].

pK_B [555].

2-(Butylamino)-1-(3,4-dihydroxyphenyl)ethanone *(Hydrochloride)*

$C_{12}H_{17}NO_3$, HCl mol.wt. 259.73



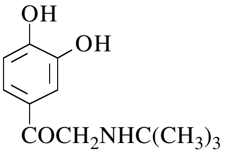
Synthesis

-Obtained by condensation of α-chloro-3,4-dihydroxyacetophenone with butylamine in ethanol or isopropanol at 60-80°. The amino base which separated was treated with concentrated hydrochloric acid [328].

m.p. 206-208° (d) [328].

1-(3,4-Dihydroxyphenyl)-2-[(1,1-dimethylethyl)amino]ethanone

[105644-17-5] $C_{12}H_{17}NO_3$ mol.wt. 223.27



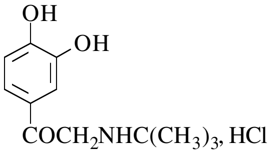
Syntheses

-Preparation by demethylation of 2-tert-butylamino-1-(3,4-dimethoxyphenyl)ethanone hydrochloride with aqueous hydrobromic acid [1017].
-Also obtained by reaction of tert-butylamine with 2-chloro-1-(3,4-dihydroxyphenyl)ethanone in dioxane [328].
-Also refer to: [643] [1006].

m.p. 199-201° [643]; pK_B [555].

1-(3,4-Dihydroxyphenyl)-2-[(1,1-dimethylethyl)amino]ethanone *(Hydrochloride)*

[34715-64-5] $C_{12}H_{17}NO_3$, HCl mol.wt. 259.73



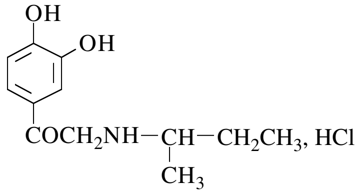
Syntheses

-Obtained by condensation of α-chloro-3,4-dihydroxyacetophenone with tert-butylamine in dioxane at 60-80°. The amino ketone base which separated was treated with concentrated hydrochloric acid [328].
-Also refer to: [1007] [1008] [1009].

m.p. 233-235° (d) [328].

1-(3,4-Dihydroxyphenyl)-2-[(1-methylpropyl)amino]ethanone *(Hydrochloride)*

$C_{12}H_{17}NO_3$, HCl mol.wt. 259.73



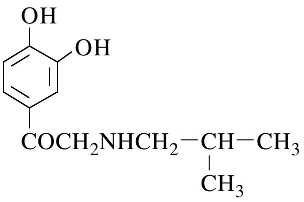
Synthesis

-Obtained by condensation of α-chloro-3,4-dihydroxyacetophenone with sec-butylamine in ethanol or isopropanol at 60-80°. The amino base which separated was treated with concentrated hydrochloric acid [328].

m.p. 226-227° [328].

1-(3,4-Dihydroxyphenyl)-2-[(2-methylpropyl)amino]ethanone

$C_{12}H_{17}NO_3$ mol.wt. 223.27



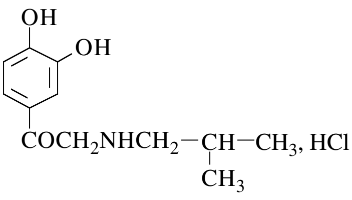
Synthesis

-Obtained by condensation of α-chloro-3,4-dihydroxyacetophenone with isobutylamine in ethanol or isopropanol at 60-80° [328].

$pK_B = 6.52$ [555].

1-(3,4-Dihydroxyphenyl)-2-[(2-methylpropyl)amino]ethanone *(Hydrochloride)*

$C_{12}H_{17}NO_3$, HCl mol.wt. 259.73



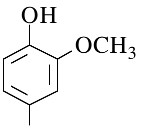
Synthesis

-Obtained by condensation of α-chloro-3,4-dihydroxyacetophenone with isobutylamine in ethanol or isopropanol at 60-80°. The amino ketone base which separated was treated with concentrated hydrochloric acid [328].

m.p. 214-216° [328].

1-(4-Hydroxy-3-methoxyphenyl)-2-[(1-methylethyl)amino]ethanone *(Hydrochloride)*

$C_{12}H_{17}NO_3$, HCl mol.wt. 259.73



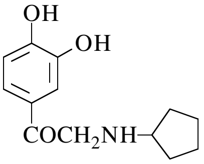
Synthesis

-Preparation by treatment of the corresponding oxalate (SM) with 26% ethanolic hydrogen chloride (61% yield). SM was obtained in two steps. First, gradual addition of a 3-methoxy-4-hydroxyphenylglyoxal potassium bisulfite and isopropylamine solution in dilute ethanol to a suspension of Raney nickel in 84% ethanol maintained at 45° under excess hydrogen. Then, after catalyst elimination, addition of oxalic acid to the obtained solution [153].

m.p. 236° (d) [153].

2-(Cyclopentylamino)-1-(3,4-dihydroxyphenyl)ethanone

[16149-16-9] $C_{13}H_{17}NO_3$ mol.wt. 235.28



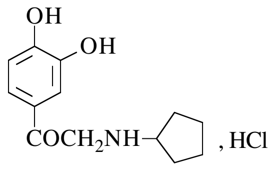
Synthesis

-Obtained by condensation of α-chloro-3,4-dihydroxyacetophenone with cyclopentylamine in ethanol or isopropanol at 60-80° [328] or in boiling isopropanol for 30 min (98%) [1446].

hemihydrate: m.p. 182° [1446]; UV [1446].

2-(Cyclopentylamino)-1-(3,4-dihydroxyphenyl)ethanone *(Hydrochloride)*

[16149-17-0] $C_{13}H_{17}NO_3$, HCl mol.wt. 271.74



Syntheses

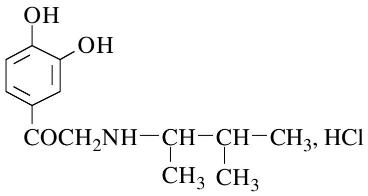
-Obtained by condensation of α-chloro-3,4-dihydroxyacetophenone with cyclopentylamine in ethanol or isopropanol at 60-80°. The amino ketone base which separated was treated with concentrated hydrochloric acid [328].

-Obtained by reaction of N-cyclopentylnoradrenalone with hydrochloric acid (44%) [1446].

m.p. 213-214° (d) [328], 205-207° [1446].

1-(3,4-Dihydroxyphenyl)-2-(1,2-dimethylpropylamino)ethanone *(Hydrochloride)*

$C_{13}H_{19}NO_3$, HCl mol.wt. 273.76


$COCH_2NH-CH(CH_3)-CH(CH_3)-CH_3$, HCl

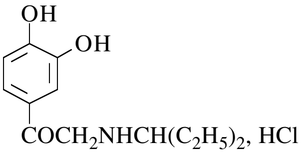
Synthesis

-Obtained by condensation of α-chloro-3,4-dihydroxyacetophenone with 1,2-dimethylpropylamine in ethanol or isopropanol at 60-80°. The amino ketone base which separated was treated with concentrated hydrochloric acid [328].

m.p. 231-233° [328].

1-(3,4-Dihydroxyphenyl)-2-(1-ethylpropylamino)ethanone *(Hydrochloride)*

$C_{13}H_{19}NO_3$, HCl mol.wt. 273.76



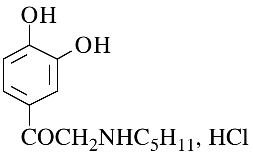
Synthesis

-Obtained by condensation of α-chloro-3,4-dihydroxyacetophenone with 1-ethylpropylamine in methanol or isopropanol at 60-80°. The amino ketone base which separated was treated with concentrated hydrochloric acid [328].

m.p. 198-201° [328].

1-(3,4-Dihydroxyphenyl)-2-(pentylamino)ethanone *(Hydrochloride)*

$C_{13}H_{19}NO_3$, HCl mol.wt. 273.76



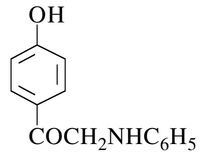
Synthesis

-Obtained by condensation of α-chloro-3,4-dihydroxyacetophenone with pentylamine in ethanol or isopropanol at 60-80°. The amino ketone base which separated was treated with concentrated hydrochloric acid [328].

m.p. 201-202° (d) [328].

1-(4-Hydroxyphenyl)-2-(phenylamino)ethanone

[100866-41-9] $C_{14}H_{13}NO_2$ mol.wt. 227.26



Syntheses

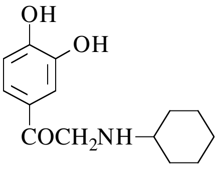
-Preparation by adding aniline (0.1 ml) and rhodium (II) acetate dimer (2 mg) to a suspension of resin **6** (52 mg) in benzene and the mixture stirred at 85° for 2 h. The compound was isolated and purified by preparative TLC (51%) [682].

N.B.: Resin **6** (resin-bound α-TMS diazoketone **6**) (preparation given).
-Also refer to: [1349].

^{1}H NMR [682], ^{13}C NMR [682], IR [682], MS [682].

2-(Cyclohexylamino)-1-(3,4-dihydroxyphenyl)ethanone

[16149-18-1] $C_{14}H_{19}NO_3$ mol.wt. 249.31



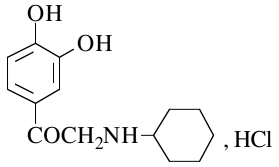
Syntheses

-Obtained by condensation of α-chloro-3,4-dihydroxyacetophenone with cyclohexylamine in ethanol or isopropanol at 60-80° [328] or in boiling isopropanol for 30 min [1446].
-Also obtained by reaction of 3,4-diacetoxy-α-iodoacetophenone with cyclohexylamine in the presence of potassium carbonate in boiling acetone for 4 h (24%) [1446].

hemihydrate [1446]; m.p. 187-188° [1446]; IR [1446], UV [1446].

2-(Cyclohexylamino)-1-(3,4-dihydroxyphenyl)ethanone *(Hydrochloride)*

[16149-19-2] $C_{14}H_{19}NO_3$, HCl mol.wt. 285.77



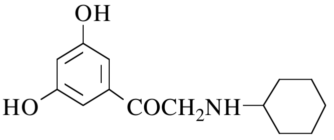
Synthesis

-Obtained by condensation of α-chloro-3,4-dihydroxyacetophenone with cyclohexylamine in ethanol or isopropanol at 60-80°. The amino ketone base which separated was treated with concentrated hydrochloric acid [328] [1446].

m.p. 256-258° (d) [328], 242-245° [1446].

2-(Cyclohexylamino)-1-(3,5-dihydroxyphenyl)ethanone

[161040-30-8] $C_{14}H_{19}NO_3$ mol.wt. 249.31

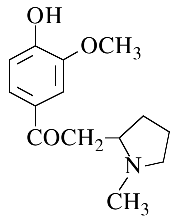


Synthesis

-Obtained by treatment of 3,5-diacetoxy-α-bromoacetophenone with cyclohexylamine in ethyl acetate and then refluxing with hydrochloric acid [240].

1-(4-Hydroxy-3-methoxyphenyl)-2-(1-methyl-2-pyrrolidinyl)ethanone (-) *(Phyllostone)*

[126262-24-6] $C_{14}H_{19}NO_3$ mol.wt. 249.31



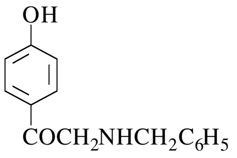
Isolation from natural sources

-From the New Caledonian lauraceous plant *Cryptocarya phyllostemon* [276].

Gum [276]; $(\alpha)_D = -5°$ (ethanol);
^1H NMR [276], IR [276], UV [276], MS [276].

1-(4-Hydroxyphenyl)-2-[(phenylmethyl)amino]ethanone

$C_{15}H_{15}NO_2$ mol.wt. 241.29



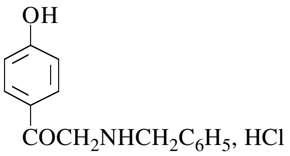
Synthesis

-Obtained by adding ammonia to an aqueous solution of its hydrochloride [504].

m.p. 132-133° [504].

1-(4-Hydroxyphenyl)-2-[(phenylmethyl)amino]ethanone *(Hydrochloride)*

$C_{15}H_{15}NO_2$, HCl mol.wt. 277.75



Synthesis

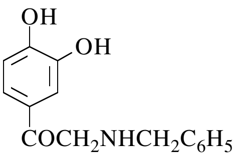
-Obtained by reductive condensation of p-hydroxyphenylglyoxal hydrate and benzylamine under hydrogen in the presence of Raney nickel in ethanol at 40°. Then, treatment of the mixture with 6 N ethanolic hydrogen chloride (82%) [504].

N.B.: The same reaction from p-hydroxyphenylglyoxal-potassium bisulfite at 45° gave a 79% yield [504].

m.p. 240° [504].

1-(3,4-Dihydroxyphenyl)-2-[(phenylmethyl)amino]ethanone

$C_{15}H_{15}NO_3$ mol.wt. 257.29



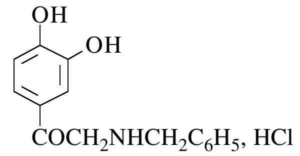
Syntheses

-Obtained by reaction of α-chloro-3,4-dihydroxyacetophenone with benzylamine [357].
-Also obtained by adding ammonia to an aqueous solution of its hydrochloride [504].

m.p. 147-148° [504].

1-(3,4-Dihydroxyphenyl)-2-[(phenylmethyl)amino]ethanone *(Hydrochloride)*

$C_{15}H_{15}NO_3$, HCl mol.wt. 293.75



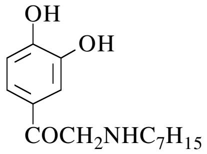
Synthesis

-Obtained by reductive condensation of 3,4-dihydroxyphenylglyoxal and benzylamine under hydrogen in the presence of Raney nickel in ethanol at 45°. Then, treatment of the mixture with ethanolic hydrogen chloride (73%) [504].

m.p. 220-221° [504].

1-(3,4-Dihydroxyphenyl)-2-(heptylamino)ethanone

$C_{15}H_{23}NO_3$ mol.wt. 265.35



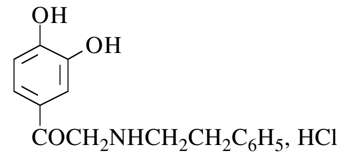
Synthesis

-Preparation by reaction of excess heptylamine with α-chloro-3,4-diacetoxyacetophenone [357].

m.p. 125° [357].

1-(3,4-Dihydroxyphenyl)-2-[2-(phenylethyl)amino]ethanone *(Hydrochloride)*

$C_{16}H_{17}NO_3$, HCl mol.wt. 307.78



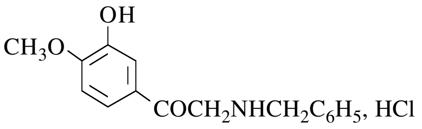
Synthesis

-Obtained by total demethylation of 1-(3,4-dimethoxyphenyl)-2-[(phenylethyl)amino]ethanone hydrochloride (m.p. 219-222°), (79%) [1018] according to [1017].

monohydrate [1018]; m.p. 220-222° (d) [1018].

1-(3-Hydroxy-4-methoxyphenyl)-2-[(phenylmethyl)amino]ethanone *(Hydrochloride)*

$C_{16}H_{17}NO_3$, HCl mol.wt. 307.78



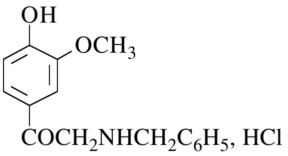
Synthesis

-Obtained by reductive condensation of 3-hydroxy-4-methoxyphenylglyoxal and benzylamine under hydrogen in the presence of Raney nickel in ethanol at 45° for 45 min. Then, elimination of the catalyst and acidification of the mixture with hydrochloric acid (54%) [504].

m.p. 226° [504].

1-(4-Hydroxy-3-methoxyphenyl)-2-[(phenylmethyl)amino]ethanone *(Hydrochloride)*

$C_{16}H_{17}NO_3$, HCl mol.wt. 307.78



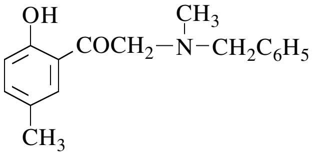
Synthesis

-Preparation by reductive condensation of 4-hydroxy-3-methoxyphenylglyoxal-potassium-bisulfite and benzylamine under hydrogen in the presence of Raney nickel in dilute ethanol at 45° for 1.75 h. Then, elimination of the catalyst and acidification of the mixture with hydrochloric acid (76%) [504].

m.p. 230° [504].

2-(Benzyl-methyl-amino)-1-(2-hydroxy-5-methylphenyl)ethanone

$C_{17}H_{19}NO_2$ mol.wt. 269.34

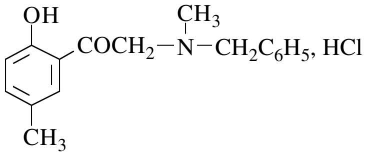


Synthesis

-Obtained by condensation of 2-hydroxy-5-methyl-α-bromoacetophenone with benzyl methyl amine in ethyl ether at r.t. for 24 to 72 h [67].

2-(Benzyl-methyl-amino)-1-(2-hydroxy-5-methylphenyl)ethanone *(Hydrochloride)*

$C_{17}H_{19}NO_2$, HCl mol.wt. 305.80



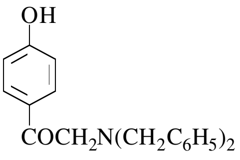
Synthesis

-Obtained by reaction of 2-hydroxy-5-methyl-α-bromoacetophenone with N-benzylmethylamine in ethyl ether at r.t. for 24 to 72 h, followed by treatment with hydrochloric acid [67].

m.p. 186°5-187° [67].

2-[Bis(phenylmethyl)amino]-1-(4-hydroxyphenyl)ethanone

[88693-95-2] $C_{22}H_{21}NO_2$ mol.wt. 331.41



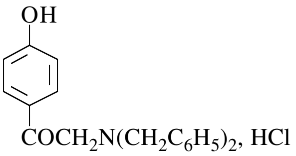
Synthesis

-Preparation by reaction of p-hydroxyphenacyl chloride (1 mol) with dibenzylamine (2 mol) in refluxing ethanol for 4 h [1363].

uncrystallizable oil [1363].

2-[Bis(phenylmethyl)amino]-1-(4-hydroxyphenyl)ethanone *(Hydrochloride)*

$C_{22}H_{21}NO_2$, HCl mol.wt. 367.87



Synthesis

-Preparation by adding a solution of ethanolic hydrogen chloride to a solution of α-dibenzylamino-p-hydroxyacetophenone in chloroform (77%) [1363].

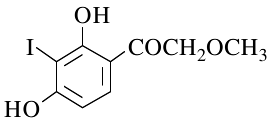
m.p. 239-241° (d) [1363].

Chapter 4. Compounds derived from alkoxyacetic acids

4.1. *Compounds derived from methoxyacetic acids*

1-(2,4-Dihydroxy-3-iodophenyl)-2-methoxyethanone

[72511-78-5] $C_9H_9IO_4$ mol.wt. 308.07



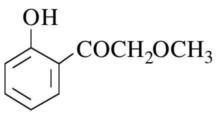
Synthesis

-Obtained by iodination of 2,4-dihydroxy-α-methoxy-acetophenone with iodine and periodic acid in ethanol for 2 h at r.t. (74%) [21].

m.p. 157-158° [21].

1-(2-Hydroxyphenyl)-2-methoxyethanone

[138206-45-8] $C_9H_{10}O_3$ mol.wt. 166.18



Syntheses

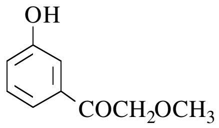
-Preparation by hydrogenolysis of 2-(benzyloxy)-α-methoxyacetophenone (SM) in the presence of Pd/C in ethanol for 1 h in hydrogen atmosphere (96%). SM was obtained by treatment of 2-(benzyloxy)phenylmagnesium bromide with methoxyacetonitrile in THF, first in an ice bath, then stirred for 2 h at r.t. (56%, colourless oil) [1113].

-Also obtained by decomposition of 1-(2-acetoxyphenyl)-2-diazoethanone in methanol with copper bronze (54%). The diazoketone (deep red thick oil) was prepared by reaction of diazomethane with 2-acetoxybenzoyl chloride in ethyl ether [1251].

colourless oil [1113], pale yellow liquid [1251]; b.p.$_{0.6-0.8}$ 76-77° [1251]; ^{1}H NMR [1113], IR [1113], MS [1113].

1-(3-Hydroxyphenyl)-2-methoxyethanone

[54794-31-9] $C_9H_{10}O_3$ mol.wt. 166.18



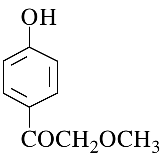
Syntheses

-Refer to: [621] and [1276] (Polish patent).

N.B.: K salt [622].

1-(4-Hydroxyphenyl)-2-methoxyethanone

[32136-81-5] $C_9H_{10}O_3$ mol.wt. 166.18



Syntheses

-Obtained by scission of 5-hydroxy-4-(4-hydroxyphenyl) 5*H*-furan-2-one with potassium hydroxide in methanol at 20° for 24 h (85%) [443].

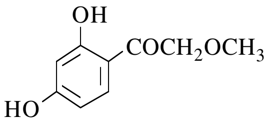
-Also obtained by catalytic debenzylation of 1-(4-benzyl-oxyphenyl)-2-methoxyethanone in methanol under hydrogen (5 bars) in the presence of 5% Pd/C for 24 h (81%) [443].

-Also obtained by methoxylation of the trimethylsilyl enol ether of 4-acetoxyacetophenone (SM) according to the procedure [1034], iodosobenzenediacetate replaced iodosobenzene, followed by hydrolysis of the ester complex formed (40%). SM was prepared in two steps from p-hydroxyacetophenone, namely acetylation, then trimethylsilylation (80%) [360].
-Also obtained by reaction of 2-chloro-1-(4-hydroxyphenyl)ethanone (m.p. 151°) with methanolic sodium methoxide at r.t. for 24 h (90%) [602].
-Also refer to: [3] [403] [473] [665] [1344] [1372].

m.p. 133-135° [602], 128-130° [443];
^{1}H NMR [443] [602], ^{13}C NMR [443], IR [443] [602],
MS [443] [602].

1-(2,4-Dihydroxyphenyl)-2-methoxyethanone

[57280-75-8] $C_9H_{10}O_4$ mol.wt. 182.18



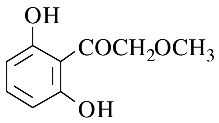
Syntheses

-Obtained by reaction of methoxyacetonitrile with resorcinol and subsequent hydrolysis of the ketimine hydrochloride (m.p. 205-207°) formed (Hoesch reaction) [34] [303] [378] [1371].
-Also obtained by decomposition of 1-(2,4-diacetoxyphenyl)-2-diazoethanone in methanol with copper bronze (43%). The diazoketone (brownish yellow glassy solid) was prepared by reaction of diazomethane with 2,4-diacetoxybenzoyl chloride in ethyl ether [1251].
-Also obtained by alkaline degradation of 7-acetoxy-3,4-dimethoxycoumarin (m.p. 123-124°) with sodium hydroxide or sodium carbonate [16].
-Also refer to: [17] [18] [21] [33] [123] [379] [592] [801] [803] [1123] [1154] [1253].

m.p. 138-139° [378], 136-138° [1251], 136° [1371];
^{1}H NMR [378], ^{13}C NMR [378], MS [378].

1-(2,6-Dihydroxyphenyl)-2-methoxyethanone

$C_9H_{10}O_4$ mol.wt. 182.18

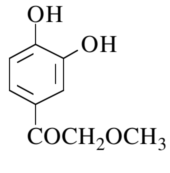


Synthesis

-Obtained by Fries rearrangement of 4-methylumbelliferone methoxyacetate, followed by alkaline hydrolysis of the resulting 8-(2-methoxyacetyl)-4-methylumbelliferone [726].

1-(3,4-Dihydroxyphenyl)-2-methoxyethanone

[64349-40-2] $C_9H_{10}O_4$ mol.wt. 182.18



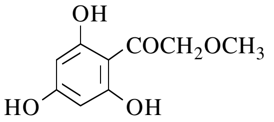
Syntheses

-Obtained by methoxylation of the trimethylsilyl enol ether of 3,4-diacetoxyacetophenone (SM) according to the procedure [1034], iodosobenzenediacetate replaced iodosobenzene, followed by hydrolysis of the ester complex formed (40%). SM was prepared in two steps from 3,4-dihydroxyacetophenone, namely acetylation (70%), then trimethylsilylation (88%) [361].

-Also refer to: [3] [450].

2-Methoxy-1-(2,4,6-trihydroxyphenyl)ethanone

[55317-02-7] $C_9H_{10}O_5$ mol.wt. 198.18



Syntheses

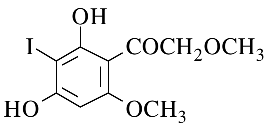
-Preparation by reaction of methoxyacetonitrile with phloroglucinol (Hoesch reaction) [34] [141] [215] [368] [470] [957] [1371], (80%) [192], (79%) [168], (77%) [378], (75-80%) [1240], (50%) [550].

-Also refer to: [15] [17] [18] [123] [234] [371] [372] [379] [464] [728] [789] [800] [801] [863] [933] [1050] [1078] [1126] [1222] [1230] [1255] [1362] [1460].

monohydrate [328074-83-5]: [957] [1371]; Crystal data [957];
m.p. 195-196° [368], 192-194° [192] [378], 192° [847] [1371], 191-194° [550];
^{1}H NMR [192] [378], ^{13}C NMR [192] [378] [1156], MS [192] [378].

1-(2,4-Dihydroxy-3-iodo-6-methoxyphenyl)-2-methoxyethanone

[74047-42-0] $C_{10}H_{11}IO_5$ mol.wt. 338.10



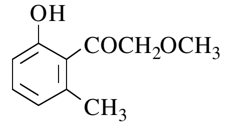
Synthesis

-Preparation by iodination of 2,4-dihydroxy-6,α-dimethoxyacetophenone with iodine and periodic acid in dilute ethanol for 2 h at 60-70° (78%) [22].

m.p. 191-193° [22];
N.B.: This ketone was characterized by its corresponding diacetate: m.p. 112-114° and ^{1}H NMR [22].

1-(2-Hydroxy-6-methylphenyl)-2-methoxyethanone

[75278-05-6] $C_{10}H_{12}O_3$ mol.wt. 180.20



Synthesis

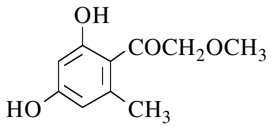
-Obtained by fission of 3-methoxy-5-methylflavone (m.p. 113-115°) with ethanolic potash (50%) [20].

N.B.: This compound could not be prepared by Hoesch condensation of m-cresol with methoxyacetonitrile [20].

oil [20]; ^{1}H NMR [20].

1-(2,4-Dihydroxy-6-methylphenyl)-2-methoxyethanone

[75278-00-1] $C_{10}H_{12}O_4$ mol.wt. 196.20



Syntheses

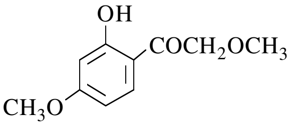
-Preparation by Hoesch condensation of orcinol with methoxyacetonitrile (53%) [20].

-Also refer to: [371].

m.p. 182-183° [20]; ^{1}H NMR [20].

1-(2-Hydroxy-4-methoxyphenyl)-2-methoxyethanone *(Fisetol dimethyl ether)*

[4940-44-7] $C_{10}H_{12}O_4$ mol.wt. 196.20



Syntheses

-Preparation by reaction of methoxyacetonitrile with resorcinol monomethyl ether (Hoesch reaction) [1371], (80%) [479].

-Also obtained by decomposition of 1-(2-acetoxy-4-methoxyphenyl)-2-diazoethanone in methanol with copper bronze for 30 min at 50-55°, followed by hydrolysis of the acetyl derivative (57%). The diazoketone (m.p. 102-105°) was prepared by reaction of diazomethane with 2-acetoxy-4-methoxybenzoyl chloride in ethyl ether for 12 h at -5° [1251].

-Obtained by alkaline degradation of different polymethoxyflavones with potassium hydroxide,

*From *fisetin tetramethyl ether* (3,7,3',4'-tetramethoxyflavone) [636] [637] [638] [639] [828] [1172] [1296] [1371];

*From 3,7,3',4',5'-pentamethoxyflavone (SM) (m.p. 149°) [223], (81%) [1296]. SM was prepared by methylation of 3,7,3',4',5'-pentahydroxyflavone, itself isolated from *Robinia pseudacacia* [1296];

*From *kanugin* (3,7,3'-trimethoxy-4',5'-methylenedioxyflavone) (m.p. 203-205°), isolated from the root bark of *Pongamia glabra* [1210];

*From *demethoxykanugin* (3,7-dimethoxy-3',4'-methylenedioxyflavone) (SM) (m.p. 142°), [1015], (86%) [1061]. SM was isolated from the seed oil of karanja (*Pongamia glabra*) [1061] or from fresh root bark and the stem bark of *Pongamia glabra* [1015].

-Also obtained by alkaline degradation of 3,7-dimethoxychromone with sodium ethoxide [488].

-Also obtained by alkaline degradation of 3,4,7-trimethoxycoumarin (m.p. 113-115°) with refluxing 5% aqueous sodium hydroxide for 1 h (60%) [16].

-Also obtained by partial methylation of α-methoxyresacetophenone with dimethyl sulfate,

*in the presence of potassium carbonate in refluxing benzene for 12 h (83%) [1253] or for 10 h (78%) [1123];

*in 5% aqueous sodium hydroxide [277] [1371], (70%) [303].

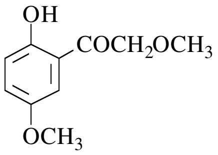
-Also refer to: [123] [592] [1022].

m.p. 132° [479], 69-70° [1251] [1253], 68-69° [1015], 67-68° [16], 67° [1061] [1296], 66° [223] [1123] [1371], 65-67° [1210], 65-66° [303]. One of the reported melting points is obviously wrong.

^{1}H NMR [479]; TLC [16].

1-(2-Hydroxy-5-methoxyphenyl)-2-methoxyethanone

[103323-12-2] $C_{10}H_{12}O_4$ mol.wt. 196.20



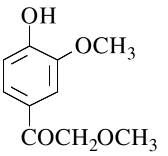
Synthesis

-Obtained by decomposition of 1-(2-acetoxy-5-methoxyphenyl)-2-diazoethanone in methanol with copper bronze (57%). The diazoketone (dark reddish liquid) was prepared by reaction of diazomethane with 2-acetoxy-5-methoxybenzoyl chloride in ethyl ether [1251].

reddish liquid [1251]; b.p.$_{0.3\text{-}0.4}$ 98-100° [1251].

1-(4-Hydroxy-3-methoxyphenyl)-2-methoxyethanone

[64349-38-8] $C_{10}H_{12}O_4$ mol.wt. 196.20

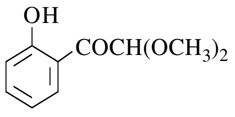


Synthesis

-Refer to: [3] (Japanese paper).

1-(2-Hydroxyphenyl)-2,2-dimethoxyethanone

[127255-97-4] $C_{10}H_{12}O_4$ mol.wt. 196.20



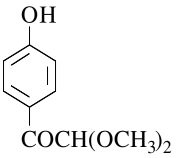
Synthesis

-Preparation by reaction of o-hydroxyacetophenone with catalytic amounts of diphenyl diselenide and excess of ammonium peroxydisulfate in refluxing methanol for 1.5 h (72%) [1458].

oil [1458]; TLC [1458]; GLC [1458];
^{1}H NMR [1458], ^{13}C NMR [1458], MS [1458].

1-(4-Hydroxyphenyl)-2,2-dimethoxyethanone

[144757-78-8] $C_{10}H_{12}O_4$ mol.wt. 196.20



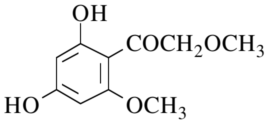
Syntheses

-Obtained by oxidation of p-hydroxyacetophenone with methyl nitrite gas in methanolic hydrogen chloride [1042], at 0 to 5° over 4 h (57%) [429].
N.B.: The reaction involves oxidation with a source of nitrosonium ion (NO^+) in the presence of an alcohol and a source of H^+ to give a phenylglyoxal acetal.
Experimental procedure: Preparation by reaction of methyl nitrite with p-hydroxyacetophenone in 1.25 N methanolic hydrogen chloride between 0 to 5° for 4 h (72%). The methyl nitrite source was supplied by adding gradually 33% aqueous sulfuric acid to a sodium nitrite solution in aqueous methanol (1:1) under nitrogen. **N.B.**: During the course of the reaction, the bath was maintained at about -20°. The methyl nitrite generator was not cooled [428].
-Also obtained from electrosynthesis by a selenium catalyzed transformation of p-hydroxyacetophenone in methanol at r.t. (22%) [1373].
-Also refer to: [983] [1042].

white solid [983];
^{1}H NMR [428] [1373], ^{13}C NMR [428], MS [428] [1373].

1-(2,4-Dihydroxy-6-methoxyphenyl)-2-methoxyethanone

[62330-14-7] $C_{10}H_{12}O_5$ mol.wt. 212.20



Syntheses

-Preparation by condensation of methoxyacetonitrile with phloroglucinol monomethyl ether (Hoesch reaction) (60%) [847].

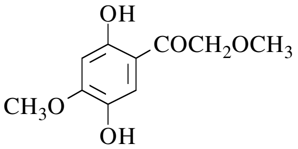
-Preparation by a three-step synthesis: first, tosylation of α-methoxyphloroacetophenone with p-toluenesulfonyl chloride in the presence of potassium carbonate in refluxing acetone for 4 h. Dimethyl sulfate and potassium carbonate were then added and the mixture refluxed for 36 h more. Finally, saponification of the residue isolated by distillation with refluxing 5% methanolic potassium hydroxide for 4 h (42%) [15].

-Also refer to: [17] [18] [22] [49].

m.p. 208° [847], 190-192° [15].

1-(2,5-Dihydroxy-4-methoxyphenyl)-2-methoxyethanone

[35930-51-9] $C_{10}H_{12}O_5$ mol.wt. 212.20



Syntheses

-Obtained on oxidation of 2-hydroxy-4,α-dimethoxyacetophenone with potassium persulfate in aqueous sodium hydroxide at 30-40° for 90 min and at r.t. for 36 h [532] (18%) [1253] (Elbs reaction).

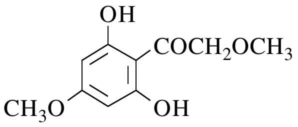
-Also obtained by reaction of methoxyacetonitrile with 1,4-dihydroxy-2-methoxybenzene (Hoesch reaction) (13%) [410].

-Also refer to: [563] [721].

trihydrate [1253];
m.p. 150° [410], 148-149° [532], 145-146° [1253].

1-(2,6-Dihydroxy-4-methoxyphenyl)-2-methoxyethanone

[70390-87-3] $C_{10}H_{12}O_5$ mol.wt. 212.20



Syntheses

-Obtained by alkaline degradation of quercetin 3,7,3',4'-tetramethyl ether (m.p. 159-160°) (5-hydroxy-3,7,3',4'-tetramethoxyflavone) (SM) with potassium hydroxide. SM was isolated from *citrus reticulata* Blanco (Rutaceae) [1292].

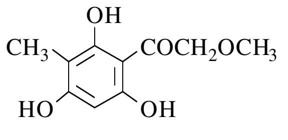
-Also obtained by partial methylation of α-methoxyphloroacetophenone with diazomethane in a methanol/ethyl ether mixture at 0° for 2 h (< 8%) [847].

-Also refer to: [674] [680] [1050].

m.p. 161-162° [847]; MS [1292].

2-Methoxy-1-(2,4,6-trihydroxy-3-methylphenyl)ethanone

[110333-13-6] $C_{10}H_{12}O_5$ mol.wt. 212.20



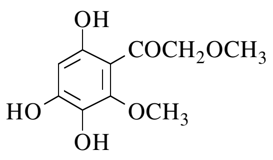
Syntheses

-Preparation by condensation of 2-methylphloroglucinol with methoxyacetic acid-boron trifluoride complex at 28-30° for 24 h (50%) [961].
-Preparation by reaction of methoxyacetonitrile with 2-methylphloroglucinol (28%) (Hoesch reaction) [708].
-Also refer to: [709].

m.p. 207° [961], 206-207° [708]; sesquihydrate [708].

2-Methoxy-1-(6-methoxy-2,4,5-trihydroxyphenyl)ethanone

[65039-95-4] $C_{10}H_{12}O_6$ mol.wt. 228.20



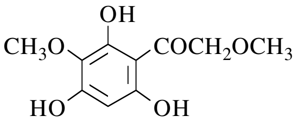
Syntheses

-Obtained by reaction of potassium persulfate with 2,4-dihydroxy-6,α-dimethoxyacetophenone in aqueous sodium hydroxide at r.t. under nitrogen for 38 h (11%) [49] (Elbs reaction).
-Also refer to: [1513] [1514].

m.p. 163° [49]; IR [49], UV [49].

2-Methoxy-1-(2,4,6-trihydroxy-3-methoxyphenyl)ethanone

[16297-02-2] $C_{10}H_{12}O_6$ mol.wt. 228.20



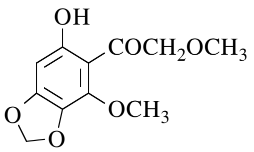
Synthesis

-Preparation by reaction of methoxyacetonitrile with iretol (Hoesch reaction) [535], (59%) [534].

m.p. 157-158° (anhydrous) [534] [535],
82-84° [1175], 79-80° (dihydrate) [534].

1-[6-Hydroxy-2-methoxy-3,4-(methylenedioxy)phenyl]-2-methoxyethanone

[91144-13-7] $C_{11}H_{12}O_6$ mol.wt. 240.21



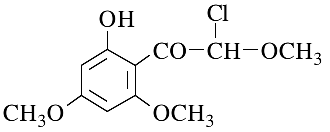
Syntheses

-Obtained by reaction of methoxyacetonitrile with 3-methoxy-4,5-(methylenedioxy)phenol (Hoesch reaction) [532], (41%) [527], (29%) [49].
-Also obtained (trace) by reaction of methylene iodide with 3,4,6-trihydroxy-2,α-dimethoxyacetophenone in the presence of potassium carbonate in refluxing acetone for 30 h (1%) [49].
-Also obtained by alkaline degradation of *meliternatin* with boiling alcoholic potassium hydroxide [234], for 7 h (65%) [233]. *Meliternatin* —3,5-dimethoxy-6,7,3',4'-bis(methylenedioxy)flavone —(m.p. 198-198°5) was first isolated from *Melicope ternata* (Rutaceae) [233], then from *Melicope mantelli* Buch [261].

m.p. 142-144° [233] [234], 140-142° [49] [527]; IR [49] [527].

2-Chloro-1-(2-hydroxy-4,6-dimethoxyphenyl)-2-methoxyethanone

[88092-53-9] $C_{11}H_{13}ClO_5$ mol.wt. 260.67



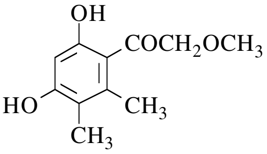
Synthesis

-Obtained (by-product) by reaction of 1-(2-hydroxy-4,6-dimethoxyphenyl)-2-methoxyethanone with iron complex $[Fe(DMF)_3Cl_2]$ $[FeCl_4]$ in refluxing dilute methanol for 4 h (< 3%) [1495].

semi-solid [1495]; column chromatography [1495];
^{1}H NMR [1495], UV [1495].

1-(4,6-Dihydroxy-2,3-dimethylphenyl)-2-methoxyethanone

[132020-84-9] $C_{11}H_{14}O_4$ mol.wt. 210.23

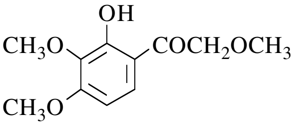


Syntheses

-Preparation by reaction of methoxyacetonitrile with 1,3-dihydroxy-4,5-dimethylbenzene (Hoesch reaction) (71%) [168].
-Also refer to: [371] [372].

1-(2-Hydroxy-3,4-dimethoxyphenyl)-2-methoxyethanone

[21417-76-5] $C_{11}H_{14}O_5$ mol.wt. 226.23



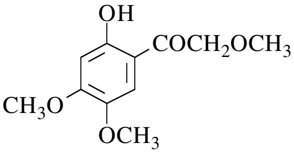
Syntheses

-Obtained by alkaline hydrolysis of 3,7,8,3',4'-pentamethoxyflavone (m.p. 153°) with 10% potassium hydroxide solution in boiling ethanol for 4 h (58%) [312].
-Also obtained by alkaline hydrolysis of O-pentamethyldihydromelanoxetin (3,7,8,3',4'-pentamethoxyflavanone) (m.p. 146-148°) with 8% potassium hydroxide solution in refluxing ethanol for 30 min [1252].

m.p. 85-86° [312], 82-84° [1252]; ^{1}H NMR [312].

1-(2-Hydroxy-4,5-dimethoxyphenyl)-2-methoxyethanone

$C_{11}H_{14}O_5$ mol.wt. 226.23



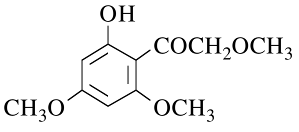
Synthesis

-Preparation by partial methylation of 4,α-dimethoxy-2,5-dihydroxyacetophenone with dimethyl sulfate in the presence of potassium carbonate in refluxing benzene for 12 h (38%) [1253].

m.p. 90-91° [1253].

1-(2-Hydroxy-4,6-dimethoxyphenyl)-2-methoxyethanone

[17874-42-9] $C_{11}H_{14}O_5$ mol.wt. 226.23



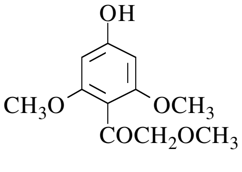
Syntheses

-Preparation by partial methylation of α-methoxyphloroacetophenone [1222],
*with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone/benzene mixture for 12 h (60%) [1255], (38%) [1050];
*with methyl iodide in the presence of potassium carbonate in refluxing acetone for 3 h [708];
*with diazomethane (1 mol) in a methanol/ethyl ether mixture at 0° for 2 h [847].
-Also obtained by condensation of phloroglucinol dimethyl ether with methoxyacetonitrile (Hoesch reaction) (45%) [168], (25%) [1255].
-Also obtained by alkaline degradation of various polymethoxyflavones,
*From *izalpinin* dimethyl ether (m.p. 194°) (3,5,7-trimethoxyflavone) on boiling with 10% ethanolic potassium hydroxide for 3 h (52%) [793];
*From *kaempferide* trimethyl ether (m.p. 153-154°) (SM) (3,5,7,4'-tetramethoxyflavone) with potassium hydroxide. SM was isolated from *Citrus reticulata* Blanco (Rutaceae) [1292];
*From *populnetin* tetramethyl ether, so called *kaempferol* tetramethyl ether (m.p. 165-166°) (3,5,7,4'-tetramethoxyflavone) by refluxing with 8% ethanolic potassium hydroxide for 6 h [1222];
*From *morin* pentamethyl ether (m.p. 154-157°) (3,5,7,2',4'-pentamethoxyflavone) by heating at reflux with 20% ethanolic potassium hydroxide for 8-10 h [636];
*From *quercetin* pentamethyl ether (m.p. 148-150°) (3,5,7,3',4'-pentamethoxyflavone) with ethanolic potassium hydroxide [636] [1172] or with boiling dilute ethanolic sodium hydroxide (54%) [662];
*From *oxyayanin-A* trimethyl ether (m.p. 190-193°) (3,5,7,2',4',5'-hexamethoxyflavone) [951], with potassium hydroxide in boiling ethanol for 8 h (57%) [800];
*From *myricetin* hexamethyl ether (m.p. 153°) (3,5,7,3',4',5'-hexamethoxyflavone) with boiling 10% ethanolic potassium hydroxide [791] [1172].
-Also obtained by alkaline degradation of 3,4,5,7-tetramethoxycoumarin with refluxing 5% aqueous sodium hydroxide for 1 h [16].
-Also refer to: [68] [123] [157] [234] [464] [592] [792] [794] [795] [1076] [1078] [1371] [1495].

m.p. 104-106° [1222], 104-105° [708], 103-104° [800] [1255], 102-104° [16] [636] [951] [1172], 102° [662] [791] [793], 98-100° [1050], 98° [847];
^{1}H NMR [1050], ^{13}C NMR [1156], IR [662] [1050], MS [1292];
TLC [16]; GLC [151].

1-(4-Hydroxy-2,6-dimethoxyphenyl)-2-methoxyethanone

$C_{11}H_{14}O_5$ mol.wt. 226.23



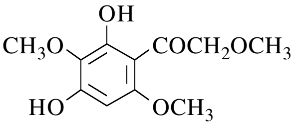
Synthesis

-Obtained (by-product) by condensation of phloroglucinol dimethyl ether with methoxyacetonitrile (Hoesch reaction) (< 2%) [1255].

m.p. 259-260° [1255].

1-(2,4-Dihydroxy-3,6-dimethoxyphenyl)-2-methoxyethanone

[42923-40-0] $C_{11}H_{14}O_6$ mol.wt. 242.23



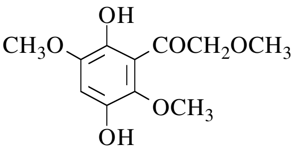
Syntheses

-Obtained by reaction of methoxyacetonitrile with 2,5-dimethoxyresorcinol (Hoesch reaction) [1223], (82%) [120], (62%) [1058] [1225].
-Also obtained by debenzylation of 4-benzyloxy-2-hydroxy-3,6,α-trimethoxyacetophenone in acetic acid in the presence of hydrochloric acid (d = 1.16) on a boiling water bath for 1 h [1288].
-Also refer to: [531] [649] [1142].

m.p. 150-151° [120] [1058] [1225], 149-150° [1288].

1-(2,5-Dihydroxy-3,6-dimethoxyphenyl)-2-methoxyethanone

$C_{11}H_{14}O_6$ mol.wt. 242.23



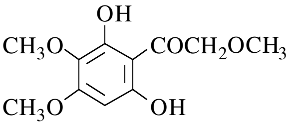
Synthesis

-Obtained by reduction of 2-(2-methoxyacetyl)-3,6-dimethoxy-1,4-benzoquinone (m.p. 222-224°) with sulfur dioxide in ethanol (40%). This quinone was prepared by oxidation of 2-hydroxy-3,5,6,α-tetramethoxyacetophenone with fuming nitric acid in ethyl ether [122].

m.p. 175-177° [122].

1-(2,6-Dihydroxy-3,4-dimethoxyphenyl)-2-methoxyethanone

[100059-77-6] $C_{11}H_{14}O_6$ mol.wt. 242.23



Synthesis

-Preparation by reaction of methoxyacetonitrile with 4,5-dimethoxyresorcinol (Hoesch reaction) [120] [286] [566].

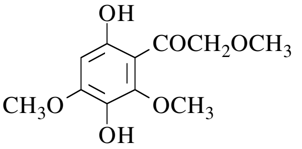
Isolation from natural sources

-Preparation by hydrolysis of *Casticin* (m.p. 186-187°) (5,3'-dihydroxy-3,6,7,4'-tetramethoxyflavone) with potassium hydroxide in refluxing ethanol for 4 h under nitrogen (66%) [155].
-Also by degradation of *Gnaphaliin* monomethyl ether (SM) (m.p. 176-178°) (5-hydroxy-3,7,8-trimethoxyflavone) with 10% ethanolic potassium hydroxide for 2 h under nitrogen. SM was prepared by partial methylation of *Gnaphaliin* (m.p. 174-175°) (3,5-dihydroxy-7,8-dimethoxyflavone), itself isolated from the aerial parts of *Gnaphalium obtusifolium* [610].
-Also refer to: [1255].

m.p. 129-130° [155] [286].

1-(3,6-Dihydroxy-2,4-dimethoxyphenyl)-2-methoxyethanone

[14639-73-7] $C_{11}H_{14}O_6$ mol.wt. 242.23



Syntheses

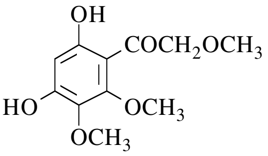
-Preparation from 2-hydroxy-4,6,α-trimethoxyacetophenone by Elbs reaction (22%) [168],
*with sodium persulfate in aqueous sodium hydroxide at 15-20° for 23 h [800] [1336], (23%) [1255], (32%) [1362];
*with potassium persulfate in aqueous sodium hydroxide at 15-20° for 20 h (26%) [951].

-Also refer to: [175] [176] [563] [647] [721] [1078] [1513] [1514] [1515].

m.p. 139-140° [1362], 135-136° [951] [1255];
sublimation at 115-130°/0.2 mm [1362]; ^{1}H NMR [1336], ^{13}C NMR [1156].

1-(4,6-Dihydroxy-2,3-dimethoxyphenyl)-2-methoxyethanone

$C_{11}H_{14}O_6$ mol.wt. 242.23



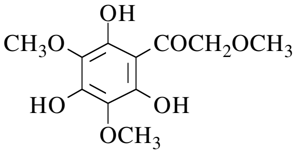
Synthesis

-Preparation by reaction of methoxyacetonitrile with 4,5-dimethoxyresorcinol, according to the Hoesch method [286].

m.p. 129-130° [286].

2-Methoxy-1-(2,4,6-trihydroxy-3,5-dimethoxyphenyl)ethanone

[85950-49-8] $C_{11}H_{14}O_7$ mol.wt. 258.23



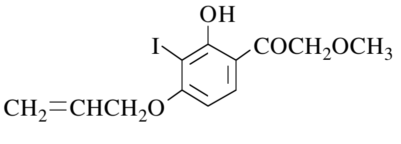
Synthesis

-Obtained by condensation of methoxyacetonitrile with 1,3,5-trihydroxy-2,4-dimethoxybenzene (m.p. 98°) (Hoesch reaction) [1157], (85%) [431].

m.p. 152-153° [1157];
IR [431], UV [431], MS [431].

1-[2-Hydroxy-3-iodo-4-(2-propenyloxy)phenyl]-2-methoxyethanone

[72511-79-6] $C_{12}H_{13}IO_4$ mol.wt. 348.14



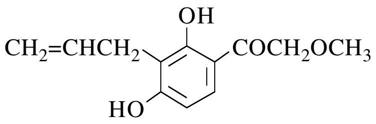
Synthesis

-Obtained by allylation of 2,4-dihydroxy-3-iodo-α-methoxyacetophenone with allyl bromide in the presence of potassium carbonate in refluxing acetone for 4-5 h (53%) [21].

m.p. 88-90° [21]; ^{1}H NMR [21].

1-[2,4-Dihydroxy-3-(2-propenyl)phenyl]-2-methoxyethanone

$C_{12}H_{14}O_4$ mol.wt. 222.24



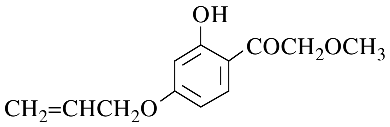
Synthesis

-Obtained by Claisen rearrangement of 2-hydroxy-4-allyloxy-α-methoxyacetophenone by heating for 2 h at 190-195° under reduced pressure (67%) [51].

m.p. 139-139°5 [51].

1-[2-Hydroxy-4-(2-propenyloxy)phenyl]-2-methoxyethanone

[57280-73-6] $C_{12}H_{14}O_4$ mol.wt. 222.24



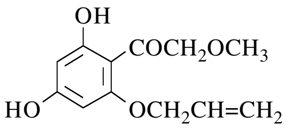
Syntheses

-Obtained by reaction of allyl bromide with α-methoxyresacetophenone in the presence of potassium carbonate in refluxing acetone for 5 h (52%) [51].
-Also refer to: [16].

pale yellow viscous liquid [51].

1-[2,4-Dihydroxy-6-(2-propenyloxy)phenyl]-2-methoxyethanone

[62330-10-3] $C_{12}H_{14}O_5$ mol.wt. 238.24



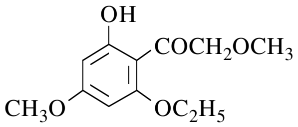
Synthesis

-Preparation by a three-step synthesis: first, tosylation of α-methoxyphloroacetophenone with p-toluenesulfonyl chloride in the presence of potassium carbonate in refluxing acetone for 4 h. Allyl bromide and potassium carbonate were then added to the reaction mixture and refluxed for 30 h. Finally, saponification of the residue, isolated by distillation, with refluxing 5% methanolic potassium hydroxide for 4 h (38%) [15].

m.p. 184-186° [15].

1-(2-Ethoxy-6-hydroxy-4-methoxyphenyl)-2-methoxyethanone

[21587-55-3] $C_{12}H_{16}O_5$ mol.wt. 240.26



Syntheses

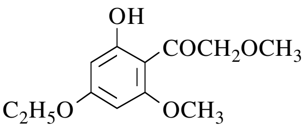
-Obtained by alkaline degradation of various flavones,
-with *potassium hydroxide* in boiling ethanol for 8 h,
*From 5-ethoxy-3,7,3',4'-tetramethoxyflavone (20%) [662];
*From 5-ethoxy-3,7,2',4',5'-pentamethoxyflavone [951];
*From 5,2'-diethoxy-3,7,4',5'-tetramethoxyflavone [951];
*From 5,2',5'-triethoxy-3,7,4'-trimethoxyflavone (*oxyayanin-A triethyl ether*) (57%) [800];
-with *sodium hydroxide* in boiling ethanol for 1 h,
*From 5,3',5'-triethoxy-3,7,4'-trimethoxyflavone (33%) [284]. This flavone (m.p. 139°) was prepared from *myricetin*, first by selective methylation, then ethylation of the obtained *myricetin 3,7,4'-trimethyl ether* (m.p. 207-208°) [284];

*From 5,3'-diethoxy-3,7,4'-trimethoxyflavone. This flavone was prepared from *quercetin*, first by selective methylation, then ethylation of the obtained *quercetin 3,7,4'-trimethyl ether* (m.p. 174°) [284].

m.p. 110° [951], 109-110° [800], 106-107° [662], 95° [284];
^{1}H NMR [284], MS [284].

1-(4-Ethoxy-2-hydroxy-6-methoxyphenyl)-2-methoxyethanone

[91555-84-9] $C_{12}H_{16}O_5$ mol.wt. 240.26



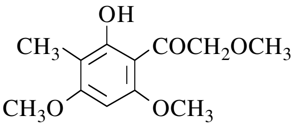
Syntheses

-Obtained by alkaline degradation of various polysubstituted flavones with potassium hydroxide in refluxing ethanol,
*From 7-ethoxy-3,5-dimethoxyflavone (m.p. 128-129°) (81%) [1212];
*From 7-ethoxy-3,5,4'-trimethoxyflavone [1222];
*From 7-ethoxy-3,5,3',4'-tetramethoxyflavone (m.p. 158-160°) (81%) [1212].

m.p. 108-110° [1222], 105-106° [1212].

1-(2-Hydroxy-4,6-dimethoxy-3-methylphenyl)-2-methoxyethanone

$C_{12}H_{16}O_5$ mol.wt. 240.26



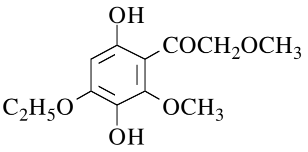
Syntheses

-Obtained by treatment of α-methoxyphloracetophenone with methyl iodide in the presence of potassium carbonate in refluxing acetone for 3 h [708] [1501], (18%) [930].
-Also obtained by condensation of methoxyacetonitrile with 2-hydroxy-4,6-dimethoxytoluene (Hoesch reaction) [930].
-Also obtained (by-product) by treatment of α-methoxyphloracetophenone with dimethyl sulfate in the presence of potassium carbonate by refluxing in an acetone and benzene mixture (1:3, v/v) for 12 h (< 3%) [1050].
-Also obtained by alkaline degradation of 8-methylquercetin pentamethyl ether (m.p. 213-215°) with boiling ethanolic potash [1174].
-Also refer to: [709].

m.p. 176-177° [708] [1501] (anhydrous); 148-149° [930] [1174],
141-142° [708] [1501], 140-142° [1050] (hydrate);
^{1}H NMR [1050], IR [1050].

1-(4-Ethoxy-3,6-dihydroxy-2-methoxyphenyl)-2-methoxyethanone

$C_{12}H_{16}O_6$ mol.wt. 256.26

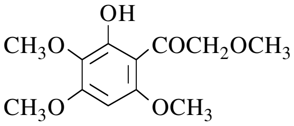


Synthesis

-Obtained by reaction of potassium persulfate with 4-ethoxy-2-hydroxy-6,α-dimethoxyacetophenone in aqueous sodium hydroxide at r.t. for 24 h (23%) (Elbs reaction) [1212].

1-(2-Hydroxy-3,4,6-trimethoxyphenyl)-2-methoxyethanone *(Gossypetol tetramethyl ether)*

[7741-43-7] $C_{12}H_{16}O_6$ mol.wt. 256.26



Syntheses

-Preparation by partial methylation of 2,4-dihydroxy-3,6,α-trimethoxyacetophenone,
*with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 12 h (63%) [1058];
*with diazomethane in acetone (82%) [531].

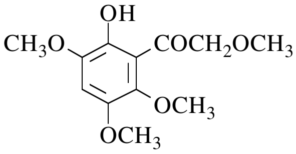
Isolation from natural sources

-Also obtained by alkaline degradation of various polymethoxyflavones with potassium hydroxide,
*From *chlorflavonin dimethyl ether* (3'-chloro-3,5,7,8,2'-pentamethoxyflavone) (m.p. 114-115°) (SM), (35%). SM was obtained by methylation of *chlorflavonin* (3'-chloro-5,2'-dihydroxy-3,7,8-trimethoxyflavone) (m.p. 212°), itself isolated from cultures of *Aspergillus candidus* [184];
*From *Herbacetin pentamethyl ether* (3,5,7,8,4'-pentamethoxyflavone) (m.p. 156-158°) [1223];
*From *Gossypetin hexamethyl ether* (3,5,7,8,3',4'-hexamethoxyflavone) (m.p. 170-172°) [1173]; [123] [1058], (85%) [634], (63%) [1058];
*From 3,5,7,8,3',4',5'-heptamethoxyflavone (m.p. 194-194°5) (SM), (51%) [1314]. SM was prepared according to different methods:
-by methylation of 5,7,3'-trihydroxy-3,8,4',5'-tetramethoxyflavone (m.p. 214-216°), itself isolated from *Beyeria brevifolia* (Muell. Arg.) Benth. [305];
-by methylation of 5,7-dihydroxy-3,8,3',4',5'-pentamethoxyflavone (m.p. 204-205°), itself isolated from the whole plant of *Conyza stricta* Willd. (Compositae) [1314];
-from *hibiscetin heptamethyl ether* (m.p. 194-196°). *Hibiscetin* is an aglycone of *Hibiscitrin* (3,5,7,8,3',4',5'-heptahydroxyflavone). It was isolated from the flowers of *Hibiscus sabdariffa* [1224].
-Also refer to: [470].

m.p. 116-118° [1058], 115-116° [184] [305] [531] [634] [1223] [1224] [1314];
UV [531]; GLC [151].

1-(2-Hydroxy-3,5,6-trimethoxyphenyl)-2-methoxyethanone

[62953-05-3] $C_{12}H_{16}O_6$ mol.wt. 256.26



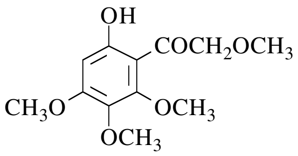
Syntheses

-Preparation in numerous steps starting from 2,6-dihydroxy-α-methoxyacetophenone. No data [726].
-Also obtained by alkaline degradation of some flavones with refluxing ethanolic potassium hydroxide,
*From 3,5,6,8,4'-pentamethoxyflavone (m.p. 158-159°) (SM). SM was prepared by methylation of 5,6-dihydroxy-3,8,4'-trimethoxyflavone (m.p. 178-179°), itself isolated from the whole plant of *Conyza stricta* Willd. (Compositae) [1314];
*From *methyl gardenin* (3,5,6,8,3',4',5'-heptamethoxyflavone) (m.p. 116-117°) (SM) [123], (84%) [122]. SM was prepared by methylation of *gardenin* (m.p. 163-164°), itself isolated from Dikamali gum (gum of *Gardenia lucida*) [122].

m.p. 110-112° [1314], 88-89° [122]. One of the reported melting points is obviously wrong.

1-(6-Hydroxy-2,3,4-trimethoxyphenyl)-2-methoxyethanone *(Quercetagetol tetramethyl ether)*

[14290-59-6] $C_{12}H_{16}O_6$ mol.wt. 256.26



Syntheses

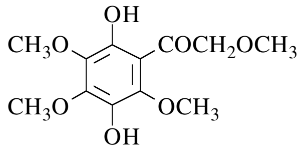
-Obtained by partial methylation of 2,5-dihydroxy-α,4,6-trimethoxyacetophenone with dimethyl sulfate [1336], in the presence of potassium carbonate,
*in boiling acetone/benzene (1:1) for 8.5 h (53%) [1362];
*in refluxing benzene for 10 h (47%) [1255].

-Also obtained by alkaline degradation of various polymethoxyflavones,
*From *mikanin dimethyl ether* so-called *Tangeretin* [1236] (3,5,6,7,4'-pentamethoxyflavone) (SM) (m.p. 157-158°) [789], (m.p. 155-156°) [199] with potassium hydroxide in refluxing ethanol for 6.5 h (29%) [789] or for 8 h [199]; SM was isolated from oil of the bark of bitter orange [199];
*From *alnusin trimethyl ether* (3,5,6,7-tetramethoxyflavone) (m.p. 112-112°5) (SM) refluxing in a mixture of 50% potassium hydroxide solution and ethanol for 20 h under nitrogen (50%). SM was prepared by methylation of *alnusin* (6-methoxy-3,5,7-trihydroxyflavone) (m.p. 239-241°). *Alnusin* was the main flavonoid isolated from *Alnus sieboldiana* (Betulaceae) [88];
*From *vogeletin tetramethyl ether* with potassium hydroxide in refluxing ethanol for 6 h (81%) [1216], (98%) [1315];
N.B.: The *mikanin dimethyl ether* is identical with *penduletin dimethyl ether* and *vogeletin tetramethyl ether*.
*From *apulein* (2',5'-dihydroxy-3,5,6,7,4'-pentamethoxyflavone) (m.p. 211-213°) with 20% sodium hydroxide in refluxing dilute methanol (1:1) for 4 h [489]. The *apulein* was isolated from the wood of *Apuleia leiocarpa* (Vog.) Macbr. (= *Apuleia praecox M*art.) (Leguminosae, subfamily Caesalpinioideae);
*From *apulein diethyl ether* (2',5'-diethoxy-3,5,6,7,4'-pentamethoxyflavone) (m.p. 129-131°) with 10% ethanolic potassium hydroxide at reflux for 10 h under nitrogen [489];
*From *quercetagetin* hexamethyl ether (3,5,6,7,3',4'-hexamethoxyflavone) (m.p. 141-142°) [1255];
*From *patuletin hexamethyl ether* (3,5,6,7,3',4'-hexamethoxyflavone) (m.p. 141-142°) [1254],
-with refluxing (150-155°) 50% aqueous potash for 8 h(21%);
-with refluxing 7% ethanolic potash for 6 h (94%);
*From methyl 3,5,6,7,3',4'-hexamethoxyflavone-2'-carboxylate (m.p. 151-152°) (SM1) with potassium hydroxide in refluxing dilute ethanol for 8 h (78%) [801]. SM1 was obtained by prolonged methylation of *distemonanthin*, itself isolated from the wood of *distemonanthus benthamianus;*
*From (3,5,6,7,2',3',4'-heptamethoxyflavone) (m.p. 191-192°) [951];
*From *apulein dimethyl ether* (3,5,6,7,2',4',5'-heptamethoxyflavone) (m.p. 159-160°) with 50% aqueous potassium hydroxide in refluxing ethanol for 8 h [489];
*From 3,5,6,7,3',4',5'-heptamethoxyflavone (m.p. 155-156°) (SM2) with potassium hydroxide in boiling ethanol for 7 h, under nitrogen [728]. SM2 was isolated from *Eremophila fraseri* F. Muell.

oil [199];
m.p. 77-78° [1255], 75-76° [951] [1254], 72-73° [1315],
71-72° [497] [801] [1216] [1362], 70-71° [728] [789], 69-71° [88] [489];
^{1}H NMR [88] [1336], IR [88] [489] [1362], UV [88] [489], MS [489];
TLC [489]; GLC [151].

1-(2,5-Dihydroxy-3,4,6-trimethoxyphenyl)-2-methoxyethanone

$C_{12}H_{16}O_7$ mol.wt. 272.25



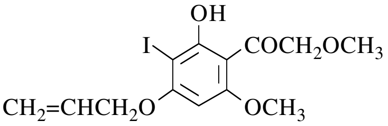
Syntheses

-Obtained by oxidation of 2-hydroxy-3,4,6,α-tetramethoxyacetophenone with alkali persulfate (Elbs reaction) (14%) [1058].
-Also refer to: [468] [469].

m.p. 102-103° [1058].

1-[2-Hydroxy-3-iodo-6-methoxy-4-(2-propenyloxy)phenyl]-2-methoxyethanone

[74047-41-9] $C_{13}H_{15}IO_5$ mol.wt. 378.16



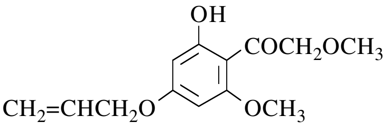
Synthesis

-Obtained by treatment of 2,4-dihydroxy-3-iodo-6,α-dimethoxyacetophenone with allyl bromide in the presence of potassium carbonate in refluxing acetone for 4-5 h (54%) [22].

m.p. 167-168° [22]; ^{1}H NMR [22].

1-[2-Hydroxy-6-methoxy-4-(2-propenyloxy)phenyl]-2-methoxyethanone

[62330-15-8] $C_{13}H_{16}O_5$ mol.wt. 238.24



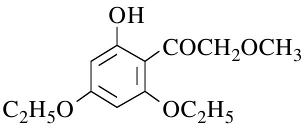
Synthesis

-Preparation by partial alkylation of 2,4-dihydroxy-6,α-dimethoxyacetophenone with allyl bromide in the presence of potassium carbonate in refluxing acetone for 4 h (80%) [15].

m.p. 87-89° [15].

1-(2,4-Diethoxy-6-hydroxyphenyl)-2-methoxyethanone

[2495-77-4] $C_{13}H_{18}O_5$ mol.wt. 254.28



Syntheses

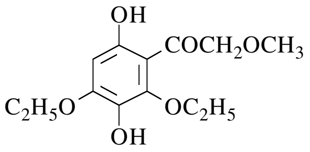
-Obtained by partial ethylation of 2,4,6-trihydroxy-α-methoxyacetophenone,
*with diethyl sulfate in the presence of potassium carbonate in boiling acetone for 5 h (78%) [789] or for 16 h [368];
*with ethyl iodide in the presence of potassium carbonate in refluxing acetone for 6 h [1222].
-Also obtained by alkaline degradation of some polysubstituted flavones with potassium hydroxide,
*From 3,4'-dimethoxy-5,7,3'-triethoxyflavone (m.p. 108-109°) (SM). SM was prepared by total ethylation of 3,4'-dimethoxy-5,7,3'-trihydroxyflavone (m.p. 235-236°), itself isolated from *Baccharis sarothroides* A. Gray (Compositae) [860];
*From 3-methoxy-5,7,3',4'-tetraethoxyflavone (m.p. 146-148°) (SM) in boiling ethanol for 6 h (35%). SM was prepared by total ethylation of *quercetin 3-methyl ether* (m.p. 261-263°), itself obtained by hydrolysis of its glycoside (m.p. 165-167°). This one (*stizoloside*) was isolated from

the aerial parts of *Stizolophus balsamita* (Lam.) A. Takht, so-called *Centaurea balsamita* Lam. (Compositae) [1488].

m.p. 111-112° [789], 110-112° [1222], 110-111° [1488], 109-111° [368], 109-110° [860];
^{1}H NMR [860], IR [860], UV [860].

1-(2,4-Diethoxy-3,6-dihydroxyphenyl)-2-methoxyethanone

[4324-58-7] $C_{13}H_{18}O_6$ mol.wt. 270.28



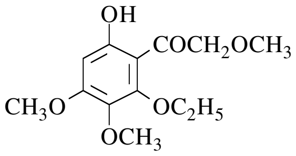
Synthesis

-Obtained by reaction of potassium persulfate with 2,4-diethoxy-6-hydroxy-α-methoxyacetophenone in the presence of aqueous sodium hydroxide (Elbs reaction), (33%) [789], (25%) [368].

m.p. 102-103° [368], 101-103° [789]; ^{1}H NMR [368].

1-(2-Ethoxy-6-hydroxy-3,4-dimethoxyphenyl)-2-methoxyethanone

[14965-23-2] $C_{13}H_{18}O_6$ mol.wt. 270.28



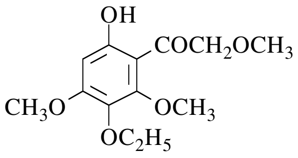
Syntheses

-Obtained by alkaline degradation of two flavones with potassium hydroxide in refluxing ethanol for 12 h under nitrogen,
*From 5,3',4'-triethoxy-3,6,7-trimethoxyflavone (m.p. 96-97°) (98%) [558];
*From 5,3',5'-triethoxy-3,6,7,4'-tetramethoxyflavone (m.p. 120-121°) [728].

m.p. 82-83° [558] [728].

1-(3-Ethoxy-6-hydroxy-2,4-dimethoxyphenyl)-2-methoxyethanone

$C_{13}H_{18}O_6$ mol.wt. 270.28



Syntheses

-Obtained by alkaline degradation of two flavones with potassium hydroxide in boiling ethanol for 7 h,
*From 6,3'-diethoxy-3,5,7,4'-tetramethoxyflavone (di-O-ethyl-O-methyl *oxyayanin-B*) (73%) [800];
*From 6,2'-diethoxy-3,5,7,4',5'-pentamethoxyflavone (m.p. 136-137°) [951].

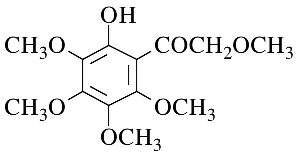
-Also obtained by reaction of ethyl iodide with 3,6-dihydroxy-2,4-dimethoxy-α-methoxyacetophenone in the presence of potassium carbonate in refluxing acetone for 18 h [800].

m.p. 78-79° [800], 78° [951].

1-(2-Hydroxy-3,4,5,6-tetramethoxyphenyl)-2-methoxyethanone

(Calycopterol pentamethyl ether)

[5071-47-6] $C_{13}H_{18}O_7$ mol.wt. 286.28



Syntheses

-Obtained by alkaline degradation of *Calycopterin dimethyl ether* or *Thapsin dimethyl ether* (SM) both 3,5,6,7,8,4'-hexamethoxyflavone (m.p. 133-134°) [123] [1323], (89%) [769], (54%) [1322]. SM was prepared by total methylation of *Thapsin*, itself isolated from *Digitalis Thapsi*, L. [769].

-Also obtained by alkaline degradation of *purpurascenin* (3,5,6,7,8,2',4',5'-octamethoxyflavone) (m.p. 132-133°) with refluxing ethanolic potassium hydroxide for 15 h (24%) [1158]. *Purpurascenin* was isolated from the roots, stem, leaves and flowers of *Pogostemon purpurascens* (Labiatae).

-Also obtained by alkaline degradation of *Digicitrine dimethyl ether* (3,5,6,7,8,3',4',5'-octamethoxyflavone) (m.p. 126°) with potassium hydroxide in refluxing 80% ethanol for 4 h (ca. 115°) (75%) [990]. The *Digicitrine dimethyl ether* was prepared by methylation of *Digicitrine* (5,3'-dihydroxy-3,6,7,8,4',5'-hexamethoxyflavone) (m.p. 178-179°), itself isolated from the leaves of *Digitalis purpurea* L.

-Also obtained by alkaline degradation of *Melibentin* with potassium hydroxide in refluxing dilute ethanol for 5 h (73%) [1237]. *Melibentin* (3,5,6,7,8-pentamethoxy-3',4'-methylenedioxyflavone) (m.p. 134-135°) was isolated from the bark and the wood of *Melicope broadbentiana* F. M. Bail (Rutaceae).

-Also obtained by alkaline degradation of *Natsudaidain methyl ether* (3,5,6,7,8,3',4'-heptamethoxyflavone) (SM) (m.p. 130-131°) [199], (m.p. 128°) [808] with potassium hydroxide in refluxing ethanol [199], (75%) [808]. SM was isolated from oil of the bark of bitter orange [199] or was prepared by methylation of *Natsudaidain* (3-hydroxy-5,6,7,8,3',4'-hexamethoxyflavone) (m.p. 146°), itself isolated from the peel oil of *Citrus natsudaidai* HAYATA [808].

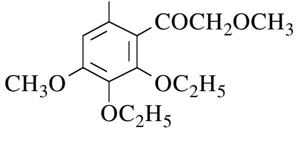
-Also obtained by partial methylation of 2,5-dihydroxy-3,4,6,α-tetramethoxyacetophenone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 1 h [110] [469], (29%) [468].

-Also refer to: [1143] [1211] [1324].

gum [1158]; sublimation at 40°/0.01 mm [990];
m.p. 85-87° [1237], 66-67° [769], 65-67° [1322], 65-66° [990], 64-66° [199], 64° [808], 62-64° [468]. One of the described melting points is obviously wrong.
GLC [151]; TLC [990] [1158].
^{1}H NMR [1158] [1237], IR [1237], UV [990] [1237], MS [1158].

1-(2,3-Diethoxy-6-hydroxy-4-methoxyphenyl)-2-methoxyethanone

$C_{14}H_{20}O_6$ mol.wt. 284.31



Syntheses

-Obtained by alkaline degradation of various polyalkylated flavones with potassium hydroxide in refluxing ethanol,

*From (5,6,3'-triethoxy-3,7,4'-trimethoxyflavone) *oxyayanin-B* triethyl ether (72%) [800];

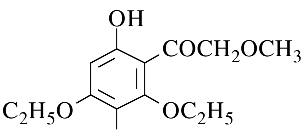
*From 5,6-diethoxy-3,7,3',4'-tetramethoxyflavone (SM). SM was prepared by ethylation of 5,6-dihydroxy-3,7,3',4'-tetramethoxyflavone (m.p. 211-213°), itself isolated from the heartwood of *Distemonanthus benthamianus* Baillon [951];

*From 5,6-diethoxy-3,7,2',4',5'-pentamethoxyflavone (m.p. 97-99°) (SM1). SM1 was prepared by ethylation of 5,6-dihydroxy-3,7,2',4',5'-pentamethoxyflavone (m.p. 142-145°), itself isolated from the heartwood of *Distemonanthus benthamianus* (Leguminosae) [950].

m.p. 80° [951], 79-80° [800] [950]; ^{1}H NMR [950].

1-(2,4-Diethoxy-6-hydroxy-3-methoxyphenyl)-2-methoxyethanone

[4324-59-8] $C_{14}H_{20}O_6$ mol.wt. 284.31



Syntheses

-Obtained by reaction of dimethyl sulfate with 2,4-diethoxy-3,6-dihydroxy-α-methoxyacetophenone in the presence of potassium carbonate in refluxing acetone for 2.5 h [950], (27%) [789] or for 12 h [368].

-Preparation by Friedel-Crafts acylation of 3,5-diethoxy-4-methoxyphenol with methoxyacetyl chloride in ethyl ether in the presence of aluminium chloride, first at 10°, then at 20° for 3 h (72%) [534].

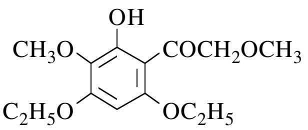
-Also obtained by reaction of methoxyacetonitrile with 3,5-diethoxy-4-methoxyphenol (Hoesch reaction) [535], (7%) [534].

-Also obtained by alkaline degradation of 5,7-diethoxy-3,6,4'-trimethoxyflavone (SM) (m.p. 123-124°) with sodium hydroxide in refluxing dilute ethanol for 20 h under nitrogen (71%). SM was prepared by ethylation of 5,7-dihydroxy-3,6,4'-trimethoxyflavone (m.p. 164-165°), itself isolated from the leaves and terminal branches of *Dodonaea attenuata* var. linearis [1163].

m.p. 65-66° [1163], 60-62° [368], 57-58° [789], 56-57° [950];
b.p.$_{0.2}$ 145-146° [534] [535];
^{1}H NMR [368] [950], IR [534].

1-(4,6-Diethoxy-2-hydroxy-3-methoxyphenyl)-2-methoxyethanone

[5128-46-1] $C_{14}H_{20}O_6$ mol.wt. 284.31



Syntheses

-Obtained by alkaline degradation of some polyalcoxy-flavones with potassium hydroxide,

*From 5,7-diethoxy-3,8,4'-trimethoxyflavone (m.p. 106-108°) (SM) (91%). SM was obtained by ethylation of 5,7-dihydroxy-3,8,4'-trimethoxyflavone (m.p. 173-175°), itself isolated from *Beyeria* sp [368];

*From 5,7,3'-triethoxy-3,8,4',5'-tetramethoxyflavone (m.p. 138-139°) (89%) [305];

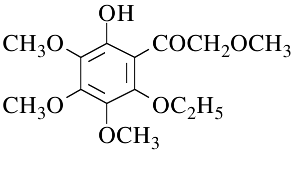
*From 5,7,4'-triethoxy-3,8-dimethoxyflavone (m.p. 128-129°) (71%) [558];

*From 5,7,4'-triethoxy-3,8,3'-trimethoxyflavone (m.p. 110-111°) (23%) [558].

m.p. 125-126° [558], 124-125° [305] [368]; ^{1}H NMR [368].

1-(2-Ethoxy-6-hydroxy-3,4,5-trimethoxyphenyl)-2-methoxyethanone

$C_{14}H_{20}O_7$ mol.wt. 300.31



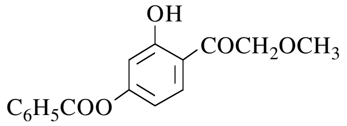
Synthesis

-Obtained by alkaline degradation of *Calycopterin diethyl ether* (m.p. 131-132°) [1323], so called *Thapsin diethyl ether* (m.p. 130°) [769] (5,4'-diethoxy-3,6,7,8-tetramethoxyflavone) with refluxing ethanolic potash [1323], (86%) [769].

m.p. 75-77° [1323], 63-64° [769].

1-[(4-Benzoyloxy)-2-hydroxyphenyl]-2-methoxyethanone

$C_{16}H_{14}O_5$ mol.wt. 286.28



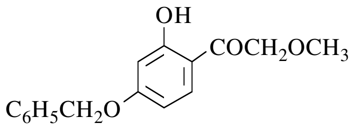
Synthesis

-Formed (by-product) by simple hydrolysis of 2,4-dibenzoyloxy-α-methoxyacetophenone with potassium ethoxide in pyridine at r.t. for 1 min (11%) [1123].

m.p. 122° [1123].

1-[2-Hydroxy-4-(phenylmethoxy)phenyl]-2-methoxyethanone

[62952-90-3] $C_{16}H_{16}O_4$ mol.wt. 272.30



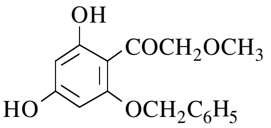
Synthesis

-Obtained by partial benzylation of α-methoxyresacetophenone with benzyl chloride in the presence of potassium carbonate and potassium iodide in refluxing acetone for 5 h (47%) [17].

m.p. 67-68° [17].

1-[2,4-Dihydroxy-(6-phenylmethoxy)phenyl]-2-methoxyethanone

[62952-93-6] $C_{16}H_{16}O_5$ mol.wt. 288.30



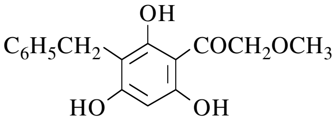
Synthesis

-Preparation in one pot by tosylation of α-methoxyphloracetophenone with 2 mol of p-toluenesulfonyl chloride, subsequent benzylation and final detosylation (35%) [17].

m.p. 227-228° [17].

1-[2,4,6-Trihydroxy-3-(phenylmethyl)phenyl]-2-methoxyethanone

$C_{16}H_{16}O_5$ mol.wt. 288.30



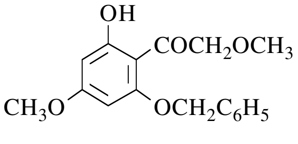
Synthesis

-Obtained by total hydrogenolysis of 1-[2-hydroxy-4,6-bis(phenylmethoxy)-3-(phenylmethyl)phenyl]-2-methoxyethanone in methanol in the presence of Pd/C under hydrogen atmosphere [302].

m.p. 98° (monohydrate) [302]; IR [302], UV [302].

1-[2-Hydroxy-4-methoxy-6-(phenylmethoxy)phenyl]-2-methoxyethanone

[62952-92-5] $C_{17}H_{18}O_5$ mol.wt. 302.33



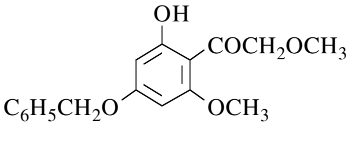
Synthesis

-Preparation by partial methylation of 6-(benzyloxy)-2,4-dihydroxy-α-methoxyacetophenone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 4 h (86%) [17].

m.p. 122-124° [17].

1-[2-Hydroxy-6-methoxy-4-(phenylmethoxy)phenyl]-2-methoxyethanone

[62952-91-4] $C_{17}H_{18}O_5$ mol.wt. 302.33



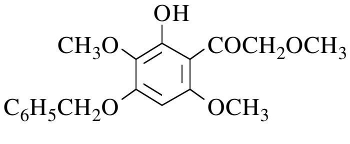
Synthesis

-Obtained by reaction of benzyl chloride with 2,4-dihydroxy-6,α-dimethoxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone for 5 h [17].

m.p. 101-102° [17].

1-[2-Hydroxy-3,6-dimethoxy-4-(phenylmethoxy)phenyl]-2-methoxyethanone

$C_{18}H_{20}O_6$ mol.wt. 332.35



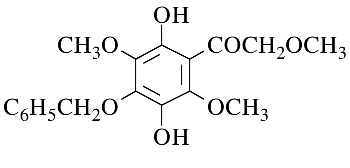
Syntheses

-Obtained (by-product) during the condensation of methoxyacetonitrile with 1,3-bis(benzyloxy)-2,5-dimethoxybenzene (Hoesch reaction) (32%) [1288].
-Also refer to: [460] [464] [531].

m.p. 109-110° [1288].

1-[2,5-Dihydroxy-3,6-dimethoxy-4-(phenylmethoxy)phenyl]-2-methoxyethanone

$C_{18}H_{20}O_7$ mol.wt. 348.35



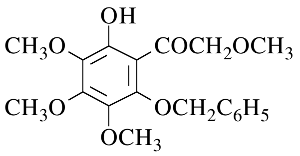
Syntheses

-Obtained by oxidation of 4-(benzyloxy)-2-hydroxy-3,6,α-trimethoxyacetophenone in alkaline solution with potassium persulfate (Elbs reaction) (10%) [1288].
-Also refer to: [611].

deep yellow viscous oil [1288].

1-[2-Hydroxy-6-(phenylmethoxy)-3,4,5-trimethoxyphenyl]-2-methoxyethanone

[94385-86-1] $C_{19}H_{22}O_7$ mol.wt. 362.38



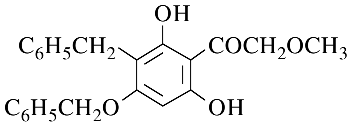
Synthesis

-Obtained by alkaline degradation of *Digicitrine dibenzyl ether* [5,3'-bis(benzyloxy)-3,6,7,8,4',5'-hexamethoxyflavone] (m.p. 75-76°) with potassium hydroxide in refluxing 80% ethanol for 3 h (85%) [990].

m.p. 64°5-65° [990]; UV [990].

1-[2,6-Dihydroxy-4-(phenylmethoxy)-3-(phenylmethyl)phenyl]-2-methoxyethanone

[18074-51-6] $C_{23}H_{22}O_5$ mol.wt. 378.42



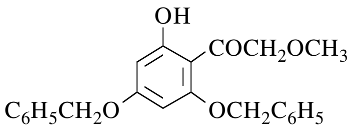
Synthesis

-Obtained from 1-[2-hydroxy-4,6-bis(phenylmethoxy)-3-(phenylmethyl)phenyl]-2-methoxyethanone by partial hydrogenolysis in methanol in the presence of Pd/C [302].

m.p. 203-205° [302]; IR [302], UV [302].

1-[2-Hydroxy-4,6-bis(phenylmethoxy)phenyl]-2-methoxyethanone

[18074-53-8] $C_{23}H_{22}O_5$ mol.wt. 378.42



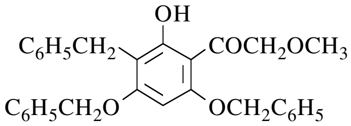
Synthesis

-Obtained (poor yield) by reaction of benzyl chloride with α-methoxyphloracetophenone in the presence of potassium carbonate in refluxing acetone (5%) [302].

m.p. 124° [302]; IR [302], UV [302].

1-[2-Hydroxy-4,6-bis(phenylmethoxy)-3-(phenylmethyl)phenyl]-2-methoxyethanone

$C_{30}H_{28}O_5$ mol.wt. 468.55



Synthesis

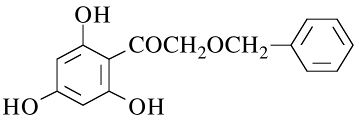
-Preparation by benzylation of α-methoxyphloracetophenone with benzyl chloride in the presence of sodium iodide and potassium carbonate in boiling acetone for 3 h (34%) [302].

m.p. 147-148° [302]; IR [302], UV [302].

4.2. *Compounds derived from phenylmethoxyacetic acids*

2-(Phenylmethoxy)-1-(2,4,6-trihydroxyphenyl)ethanone

[322405-72-1] $C_{15}H_{14}O_5$ mol.wt. 274.27

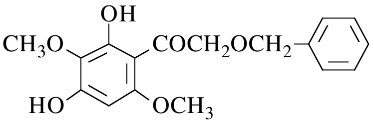


Synthesis

-Preparation by reaction of benzyloxyacetonitrile with phloroglucinol (Hoesh reaction) (91%) [1440].

1-(2,4-Dihydroxy-3,6-dimethoxyphenyl)-2-(phenylmethoxy)ethanone

$C_{17}H_{18}O_6$ mol.wt. 318.33



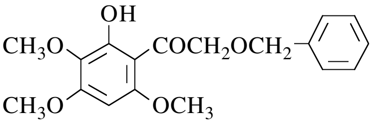
Synthesis

-Obtained by hydrogenation of 2-(benzyloxy)-1-[4-(benzyloxy)-2-hydroxy-3,6-dimethoxyphenyl]ethanone in ethyl acetate over Pd/C [531].

m.p. 175-176° [531].

1-(2-Hydroxy-3,4,6-trimethoxyphenyl)-2-(phenylmethoxy)ethanone

$C_{18}H_{20}O_6$ mol.wt. 332.35



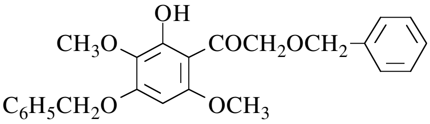
Synthesis

-Obtained by partial methylation of 2-(benzyloxy)-1-(2,4-dihydroxy-3,6-dimethoxyphenyl)ethanone with diazomethane [531].

m.p. 172-174° [531].

1-[2-Hydroxy-3,6-dimethoxy-4-(phenylmethoxy)phenyl]-2-(phenylmethoxy)ethanone

$C_{24}H_{24}O_6$ mol.wt. 408.45



Synthesis

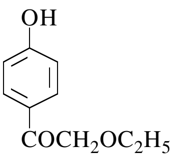
-Obtained by reaction of (benzyloxy)-acetonitrile with 2,5-dimethoxyresorcinol dibenzyl ether (Hoesch reaction) (33%) [531].

m.p. 150-151° [531].

4.3. *Compounds derived from ethoxyacetic acids*

2-Ethoxy-1-(4-hydroxyphenyl)ethanone

[91061-33-5] $C_{10}H_{12}O_3$ mol.wt. 180.20



Synthesis

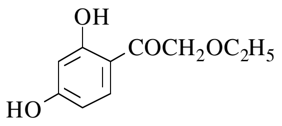
-Obtained by adding ethanol (0.1 ml) and boron trifluoride etherate to a suspension of resin **6** (52 mg) in methylene chloride, and stirring the mixture at r.t. for 1 h. The compound was isolated by usual method and purified by preparative TLC (52%) [682].

N.B.: Resin **6** (resin-bound α-TMS diazoketone **6**) (preparation given).

^{1}H NMR [682], ^{13}C NMR [682], IR [682], MS [682].

1-(2,4-Dihydroxyphenyl)-2-ethoxyethanone

$C_{10}H_{12}O_4$ mol.wt. 196.20



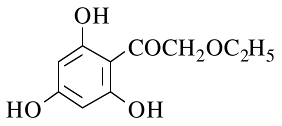
Synthesis

-Obtained by reaction of ethoxyacetonitrile with resorcinol [310], (97%) [1382], (28%) (Hoesch reaction) [1257].

m.p. 136-137° [1382], 135-136° [1257], 132-133° [310];
b.p.$_{10}$ 195-200° [1257].

2-Ethoxy-1-(2,4,6-trihydroxyphenyl)ethanone

$C_{10}H_{12}O_5$ mol.wt. 212.201



Syntheses

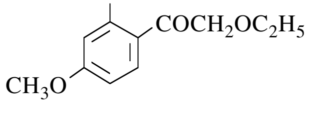
-Preparation by reaction of ethoxyacetonitrile with phloroglucinol (Hoesch reaction) (64%) [1256].

-Also refer to: [600] [1257].

m.p. 197-198° [1256].

2-Ethoxy-1-(2-hydroxy-4-methoxyphenyl)ethanone

[34811-99-9] $C_{11}H_{14}O_4$ mol.wt. 210.23



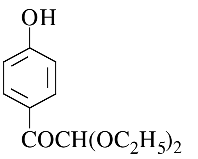
Synthesis

-Obtained by partial methylation of α-ethoxy-2,4-dihydroxyacetophenone (SM) with diazomethane in ethyl ether [311], (18%) [310]. SM was prepared by reaction of ethoxyacetonitrile with resorcinol (Hoesch reaction) [311].

oil [311]; m.p. 30-31° [310]; b.p.$_{0.02}$ 80-85° [310]; ^{1}H NMR [310], IR [310].

2,2-Diethoxy-1-(4-hydroxyphenyl)ethanone

[200420-28-6] $C_{12}H_{16}O_4$ mol.wt. 224.26

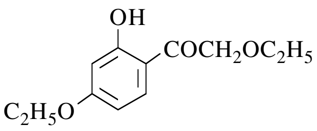


Synthesis

-Refer to: [941] (Japanese patent).

2-Ethoxy-1-(4-ethoxy-2-hydroxyphenyl)ethanone

$C_{12}H_{16}O_4$ mol.wt. 224.26



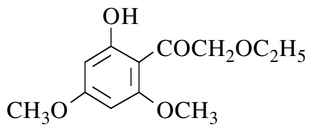
Synthesis

-Obtained by treatment of *fisetin* tetraethyl ether (3,7,3',4'-tetraethoxyflavone) with boiling alcoholic potassium hydroxide solution [637] [638] [828] [1371].

m.p. 42-44° [638].

2-Ethoxy-1-(2-hydroxy-4,6-dimethoxyphenyl)ethanone

[21587-57-5] $C_{12}H_{16}O_5$ mol.wt. 240.26



Syntheses

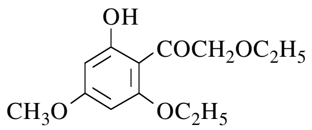
-Obtained by partial methylation of α-ethoxyphloroacetophenone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 12 h (62%) [1257].

-Also obtained by degradation of 3-ethoxy-5,7,3',4'-tetramethoxyflavone with sodium hydroxide in boiling dilute ethanol for 16 h (9%) [662].

m.p. 103-104° [1257], 99-100° [662].

2-Ethoxy-1-(2-ethoxy-6-hydroxy-4-methoxyphenyl)ethanone

[21587-58-6] $C_{13}H_{18}O_5$ mol.wt. 254.28



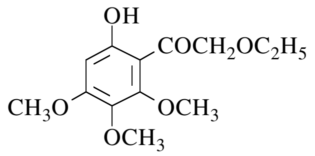
Synthesis

-Obtained (poor yield) by degradation of 3,5-diethoxy-7,3',4'-trimethoxyflavone (m.p. 164-165°) with sodium hydroxide in refluxing ethanol (3%) [662].

m.p. 82-83° [662]; IR [662].

2-Ethoxy-1-(6-hydroxy-2,3,4-trimethoxyphenyl)ethanone

[19598-24-4] $C_{13}H_{18}O_6$ mol.wt. 270.28



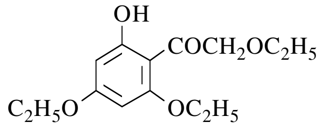
Synthesis

-Obtained by alkaline degradation of *Eupatoretin* diethyl ether (m.p. 119-120°) (3,3'-diethoxy-5,6,7,4'-tetramethoxyflavone) with potassium hydroxide in refluxing ethanol under nitrogen for 17 h (46%) [861].

m.p. 60-61° [861];
^{1}H NMR [861], IR [861], UV [861], MS [861].

1-(2,4-Diethoxy-6-hydroxyphenyl)-2-ethoxyethanone

[64184-96-9] $C_{14}H_{20}O_5$ mol.wt. 268.31



Syntheses

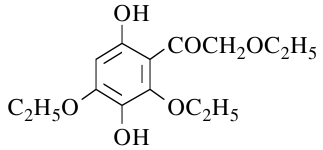
-Obtained by partial ethylation of α-ethoxyphloroacetophenone with ethyl iodide in the presence of potassium carbonate in refluxing acetone for 12 h (53%) [1256].

-Also obtained by degradation of various polyethoxyflavones with boiling ethanolic potash,
*From 3,5,7,3'-tetraethoxy-4'-methoxyflavone (m.p. 136-137°) (8% potassium hydroxide, reflux 6 h) [600];
*From 3,5,7,3',4'-pentaethoxyflavone (*quercetin* pentaethyl ether) (7% potassium hydroxide, reflux 6 h) (good yield) [1256];
*From 3,5,7,3',5'-pentaethoxy-4'-methoxyflavone (m.p. 160°) (*4'-methylmyricetin pentaethyl ether*) (SM). SM was obtained by total ethylation of *4'-methylmyricetin*, itself isolated from the leaves of *Elaeocarpus lanceofolius* Roxb. (Elaeocarpaceae) [365] [1228];
*From 3,5,7,3',4',5'-hexaethoxyflavone (m.p. 149-151°) (*myricetin* hexaethyl ether) [365] [1172]. *Myricetin* is the 3,5,7,3',4',5'-hexahydroxyflavone.
N.B.: Na salt [1256].

m.p. 97-98° [600], 96-97° [1172] [1256], 96° [365];
^{1}H NMR [365], UV [365], MS [365].

1-(2,4-Diethoxy-3,6-dihydroxyphenyl)-2-ethoxyethanone

$C_{14}H_{20}O_6$ mol.wt. 284.31



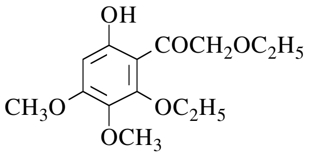
Synthesis

-Obtained by reaction of potassium persulfate with 2-hydroxy-4,6,α-triethoxyacetophenone in 5% aqueous sodium hydroxide, first at 15°, then at r.t. for 20 h (30%) (Elbs reaction) [1256].

m.p. 103-104° [1256].

2-Ethoxy-1-(2-ethoxy-6-hydroxy-3,4-dimethoxyphenyl)ethanone

[4324-56-5] $C_{14}H_{20}O_6$ mol.wt. 284.31



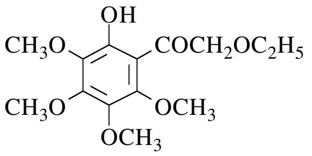
Syntheses

-Obtained by alkaline degradation of various substituted flavones with potassium hydroxide in refluxing ethanol,
*From *Mikanin* diethyl ether (m.p. 94-95°) (3,5-diethoxy-6,7,4'-trimethoxyflavone) [789];
*From *Eupatin* triethyl ether (m.p. 105-106°) (3,5,3'-triethoxy-6,7,4'-trimethoxyflavone) (26%) [861];
*From *Eupalitin* triethyl ether (m.p. 80-81°) (3,5,4'-triethoxy-6,7-dimethoxyflavone) (88%) [1204];
*From *Eupatolitin* tetraethyl ether (m.p. 120-121°) (3,5,3',4'-tetraethoxy-6,7-dimethoxyflavone) (97%) [1204].

m.p. 61-62° [789], 59-60° [861] [1204];
^1H NMR [861], IR [1204], UV [861], MS [861] [1204].

2-Ethoxy-1-(2-hydroxy-3,4,5,6-tetramethoxyphenyl)ethanone

$C_{14}H_{20}O_7$ mol.wt. 300.31



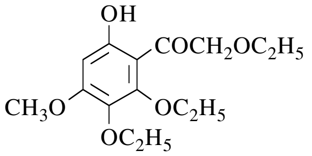
Synthesis

-Obtained by alkaline degradation of *Natsudaidain ethyl ether* (3-ethoxy-5,6,7,8,3',4'-hexamethoxyflavone) (m.p. 118°) with potassium hydroxide in refluxing ethanol [808].

m.p. 47° [808]; ^1H NMR [808], IR [808], MS [808].

2-Ethoxy-1-(2,3-diethoxy-6-hydroxy-4-methoxyphenyl)ethanone

$C_{15}H_{22}O_6$ mol.wt. 298.34

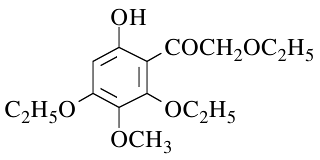


Synthesis

-Refer to: [1256].

2-Ethoxy-1-(2,4-diethoxy-6-hydroxy-3-methoxyphenyl)ethanone

$C_{15}H_{22}O_6$ mol.wt. 298.34



Syntheses

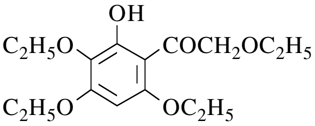
-Obtained from ethyl 3,5,7,3',4'-pentaethoxy-6-methoxyflavone-2'-carboxylate (m.p. 111-112°) (SM) by hydrolysis with 20% ethanolic potassium hydroxide at reflux for 8 h (73%). SM was obtained by ethylation of *distemonanthin*, itself isolated from the wood of *distemonanthus benthamianus* [801].

-Also obtained by alkaline degradation of *patuletin* pentaethyl ether (3,5,7,3',4'-pentaethoxy-6-methoxyflavone) (m.p. 127-128°) with refluxing 7% ethanolic potash on a water bath for 6 h (40%) [1256].
-Also obtained by partial methylation of α,4,6-triethoxy-2,5-dihydroxyacetophenone with dimethyl sulfate in the presence of potassium carbonate in refluxing benzene for 12 h (38%) [1256].

m.p. 88-89° [801], 86-87° [1256].

2-Ethoxy-1-(2-hydroxy-3,4,6-triethoxyphenyl)ethanone *(Gossypitol tetraethyl ether)*

$C_{16}H_{24}O_6$ mol.wt. 312.36



Synthesis

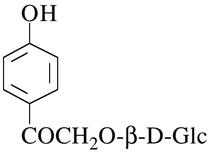
-Obtained by alkaline degradation of *Gossypetin* hexaethyl ether (m.p. 144-146°) (3,5,7,8,3',4'-hexaethoxyflavone) with potassium hydroxide in refluxing dilute ethanol for 6 h (84%) [1173].

m.p. 110-111° [1173].

4.4. *Miscellaneous*

2-(β-D-Glucopyranosyloxy)-1-(4-hydroxyphenyl)ethanone

[167638-61-1] $C_{14}H_{18}O_8$ mol.wt. 314.29



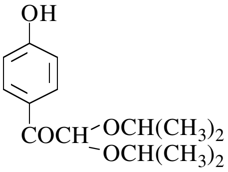
Isolation from natural sources

-From the fresh root bark of *Picea abies* (Pinaceae) (compound 4) [1131].

$(\alpha)_D$ = -33° (c = 0.2 methanol) [1131];
^{1}H NMR [1131], ^{13}C NMR [1131], UV [1131].

1-(4-Hydroxyphenyl)-2,2-bis(1-methylethoxy)ethanone

[144757-80-2] $C_{14}H_{20}O_4$ mol.wt. 252.31



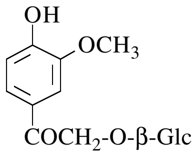
Syntheses

-Obtained by gradually adding a 33% hydrogen chloride solution in isopropanol to a solution of p-hydroxyphenylglyoxal and isopropyl nitrite in isopropanol cooled to 0°. Hydrogen chloride solution was added at such a speed to maintain a temperature of less than 25° [428].
-Also refer to: [429].

solid [428]; ^{1}H NMR [428], ^{13}C NMR [428], MS [428].

2-(β-D-Glucopyranosyloxy)-1-(4-hydroxy-3-methoxyphenyl)ethanone

[178959-37-0] $C_{15}H_{20}O_9$ mol.wt. 344.32

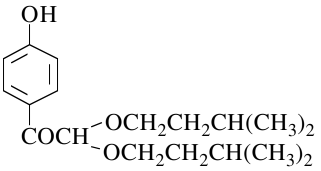


Isolation from natural sources

-From inner bark of *Pinus sylvestris* (compound 4) [1132].

1-(4-Hydroxyphenyl)-2,2-bis(3-methylbutoxy)ethanone

[144757-79-9] $C_{18}H_{28}O_4$ mol.wt. 308.42



Syntheses

-Obtained by slowly adding isoamyl nitrite to a solution of p-hydroxyacetophenone in isoamyl alcohol acidified with anhydrous hydrogen chloride at temperature < 25° (62%) [428].
-Also refer to: [429].

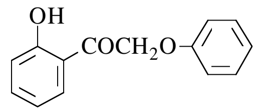
^1H NMR [428], ^{13}C NMR [428], MS [428].

Chapter 5. Compounds derived from aryloxyacetic acids

5.1. *Compounds derived from phenoxyacetic acid*

1-(2-Hydroxyphenyl)-2-phenoxyethanone

[73014-18-3] $C_{14}H_{12}O_3$ mol.wt. 228.25



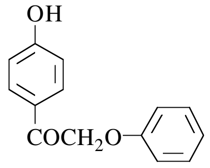
Syntheses

-Preparation by hydrogenolysis of 2-benzyloxy-α-phenoxyacetophenone in ethanol/dioxane (1:1) in the presence of Pd/C under hydrogen (85%) [1417].
-Also obtained by acidic hydrolysis of 4-hydroxy-3-phenoxycoumarin (m.p. 216°) [810] according to [996].
-Also prepared by reaction of phenoxyacetonitrile with phenol (Hoesch reaction) [1025].
-Also refer to: [160].

m.p. 115-115°5 [1417], 115° [810]; UV [1417].

1-(4-Hydroxyphenyl)-2-phenoxyethanone

[41978-29-4] $C_{14}H_{12}O_3$ mol.wt. 228.25



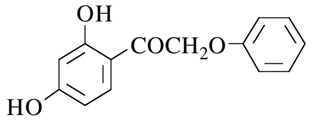
Synthesis

-Refer to: [1234] [1267] (Japanese papers).

m.p. 159-160° [1267]; b.p.$_2$ 212-220° [1267].

1-(2,4-Dihydroxyphenyl)-2-phenoxyethanone

[73014-19-4] $C_{14}H_{12}O_4$ mol.wt. 244.25



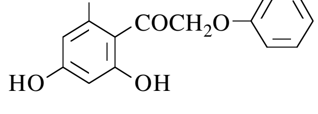
Syntheses

-Obtained by reaction of phenoxyacetonitrile with resorcinol (Hoesch reaction) [78] [1382] [1498] [1499], (88%) [1496], (82%) [1417].
-Also refer to: [540] [567].

m.p. 209°5-210° [1417], 207-208° [1496], 204-205° [1382];
^{1}H NMR [1496], UV [1417].

2-Phenoxy-1-(2,4,6-trihydroxyphenyl)ethanone

[72023-07-1] $C_{14}H_{12}O_5$ mol.wt. 260.25



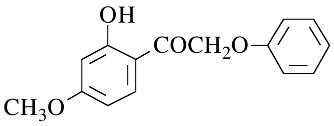
Syntheses

-Preparation by reaction of phenoxyacetonitrile with phloroglucinol (Hoesch reaction), (84%) [1417], (80%) [541], (48%) [1575].
-Also refer to: [1185] [1545] [1559].

m.p. 275° (d) [1575], 244-245° [1417], 234° [541].
One note a very large dispersion of the various melting points.
^{1}H NMR [541], UV [1417].

1-(2-Hydroxy-4-methoxyphenyl)-2-phenoxyethanone

[73023-08-2] $C_{15}H_{14}O_4$ mol.wt. 258.27



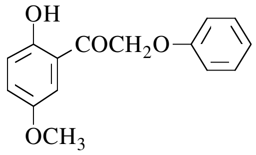
Syntheses

-Obtained by partial methylation of 2,4-dihydroxy-α-phenoxyacetophenone with dimethyl sulfate in the presence of potassium carbonate in boiling acetone for 2.5 h (83%) [1417].
-Also refer to: [1498].

m.p. 86°5-87° [1417]; UV [1417].

1-(2-Hydroxy-5-methoxyphenyl)-2-phenoxyethanone

[137612-24-9] $C_{15}H_{14}O_4$ mol.wt. 258.27

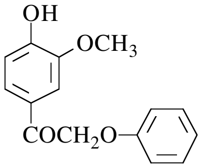


Syntheses

-Obtained by acylation of hydroquinone monomethyl ether with phenoxyacetonitrile in the presence of boron trichloride and aluminium chloride in ethylene dichloride (44%) [1026].
-Also refer to: [1025].

1-(4-Hydroxy-3-methoxyphenyl)-2-phenoxyethanone

[41978-28-3] $C_{15}H_{14}O_4$ mol.wt. 258.27



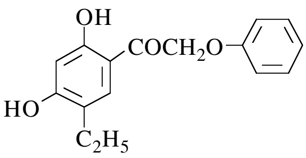
Syntheses

-Obtained (by-product, unusual result) by methylation of 2-(3-chlorophenoxy)-1-(4-hydroxy-3-methoxyphenyl)-ethanone [397].
-Also refer to: [1267] (Japanese paper).

m.p. 94°5-95° [1267]; b.p.$_2$ 218-225° [1267].

1-(5-Ethyl-2,4-dihydroxyphenyl)-2-phenoxyethanone

[243465-56-7] $C_{16}H_{16}O_4$ mol.wt. 272.30

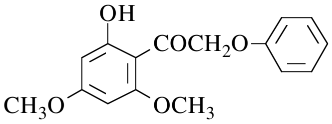


Synthesis

-Obtained [540] by previously described methods [1185].

1-(2-Hydroxy-4,6-dimethoxyphenyl)-2-phenoxyethanone

[73023-09-3] $C_{16}H_{16}O_5$ mol.wt. 288.30



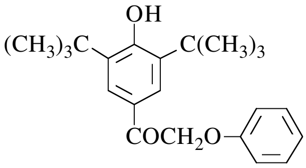
Synthesis

-Obtained by partial methylation of 2,4,6-trihydroxy-α-phenoxyacetophenone with dimethyl sulfate in the presence of potassium carbonate in boiling acetone for 8 h (63%) [1417].

m.p. 122-123° [1417]; UV [1417].

1-[3,5-Bis-(1,1-dimethylethyl)-4-hydroxyphenyl]-2-phenoxyethanone

[41978-27-2] $C_{22}H_{28}O_3$ mol.wt. 340.46



Synthesis

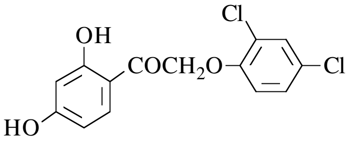
-Refer to: [1267] (Japanese paper).

m.p. 111°5-112° [1267].

5.2. *Compounds derived from substituted phenoxyacetic acids*

2-(2,4-Dichlorophenoxy)-1-(2,4-dihydroxyphenyl)ethanone

[137987-83-8] $C_{14}H_{10}Cl_2O_4$ mol.wt. 313.14



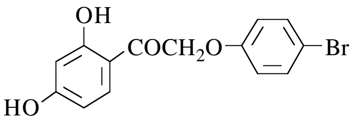
Synthesis

-Obtained by reaction of 2,4-dichlorophenoxy-acetonitrile with resorcinol (Hoesch reaction) (85%) [1496].

m.p. 192° [1496]; ^1H NMR [1496].

2-(4-Bromophenoxy)-1-(2,4-dihydroxyphenyl)ethanone

[243465-55-6] $C_{14}H_{11}BrO_4$ mol.wt. 323.14

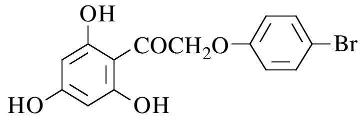


Synthesis

-Obtained [540] by previously described method [1185].

2-(4-Bromophenoxy)-1-(2,4,6-trihydroxyphenyl)ethanone

[243657-60-5] $C_{14}H_{11}BrO_5$ mol.wt. 339.14



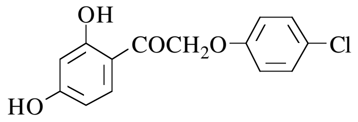
Synthesis

-Preparation by Hoesch condensation of p-bromophenoxyacetonitrile with phloroglucinol in benzene/ethyl ether in the presence of zinc chloride and hydrogen chloride at 0° (82%) [541].

m.p. 256° [541]; ^{1}H NMR [541].

2-(4-Chlorophenoxy)-1-(2,4-dihydroxyphenyl)ethanone

[115781-11-8] $C_{14}H_{11}ClO_4$ mol.wt. 278.69



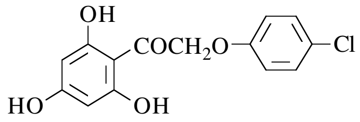
Syntheses

-Obtained by reaction of 4-chlorophenoxyacetonitrile with resorcinol (Hoesch reaction) (84%) [1496].
-Also refer to: [1431] (Japanese patent).

m.p. 187°5 [1496]; ^{1}H NMR [1496].

2-(4-Chlorophenoxy)-1-(2,4,6-trihydroxyphenyl)ethanone

[243657-59-2] $C_{14}H_{11}ClO_5$ mol.wt. 294.69



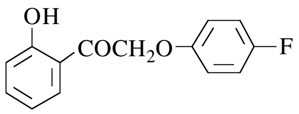
Synthesis

-Preparation by Hoesch condensation of p-chlorophenoxyacetonitrile with phloroglucinol in benzene/ethyl ether in the presence of zinc chloride and hydrogen chloride at 0° (85%) [541].

m.p. 251° [541]; ^{1}H NMR [541].

2-(4-Fluorophenoxy)-1-(2-hydroxyphenyl)ethanone

[137612-30-7] $C_{14}H_{11}FO_3$ mol.wt. 246.24

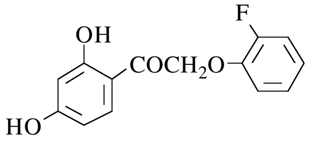


Syntheses

-Obtained by reaction of p-fluorophenoxyacetonitrile with phenol (Hoesch reaction) [1025].
-Also refer to: [1026].

1-(2,4-Dihydroxyphenyl)-2-(2-fluorophenoxy)ethanone

[137987-82-7] $C_{14}H_{11}FO_4$ mol.wt. 262.24



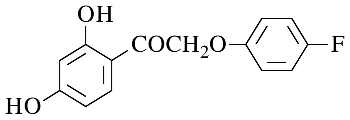
Synthesis

-Obtained by reaction of 2-fluorophenoxyacetonitrile with resorcinol (Hoesch reaction) (87%) [1496].

m.p. 163° [1496]; ^{1}H NMR [1496].

1-(2,4-Dihydroxyphenyl)-2-(4-fluorophenoxy)ethanone

[121361-56-6] $C_{14}H_{11}FO_4$ mol.wt. 262.24



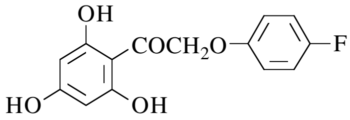
Syntheses

-Obtained by reaction of p-fluorophenoxyacetonitrile with resorcinol (Hoesch reaction), (86%) [1496], (63%) [1187].
-Also refer to: [540] [1499].

m.p. 165° [1187] [1496]; ^{1}H NMR [1187] [1496], IR [1187].

2-(4-Fluorophenoxy)-1-(2,4,6-trihydroxyphenyl)ethanone

[127526-42-5] $C_{14}H_{11}FO_5$ mol.wt. 278.24



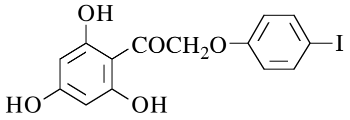
Synthesis

-Preparation by Hoesch condensation of p-fluorophenoxyacetonitrile with phloroglucinol in benzene/ethyl ether in the presence of zinc chloride and hydrogen chloride at 0° (81%) [541].

m.p. 242° [541]; ^{1}H NMR [541].

2-(4-Iodophenoxy)-1-(2,4,6-trihydroxyphenyl)ethanone

[243657-61-6] $C_{14}H_{11}IO_5$ mol.wt. 386.14



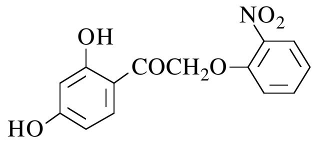
Synthesis

-Preparation by Hoesch condensation of p-iodophenoxyacetonitrile with phloroglucinol in benzene/ethyl ether in the presence of zinc chloride and hydrogen chloride at 0° (80%) [541].

m.p. 269° [541]; ^{1}H NMR [541].

1-(2,4-Dihydroxyphenyl)-2-(2-nitrophenoxy)ethanone

[137987-91-8] $C_{14}H_{11}NO_6$ mol.wt. 289.24



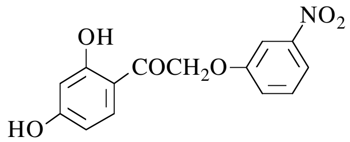
Synthesis

-Obtained by reaction of o-nitrophenoxyacetonitrile with resorcinol (Hoesch reaction) (84%) [1496].

m.p. 287° [1496]; ^{1}H NMR [1496].

1-(2,4-Dihydroxyphenyl)-2-(3-nitrophenoxy)ethanone

[137987-90-7] $C_{14}H_{11}NO_6$ mol.wt. 289.24



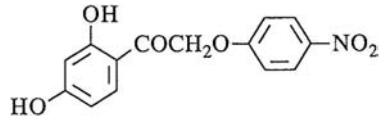
Synthesis

-Obtained by reaction of m-nitrophenoxyacetonitrile with resorcinol (Hoesch reaction) (81%) [1496].

m.p. 275° [1496]; ^{1}H NMR [1496].

1-(2,4-Dihydroxyphenyl)-2-(4-nitrophenoxy)ethanone

[137987-89-4] $C_{14}H_{11}NO_6$ mol.wt. 289.24



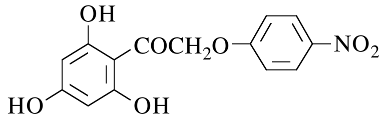
Synthesis

-Obtained by reaction of p-nitrophenoxyacetonitrile with resorcinol (Hoesch reaction) (86%) [1496].

m.p. 281° [1496]; ^{1}H NMR [1496].

2-(4-Nitrophenoxy)-1-(2,4,6-trihydroxyphenyl)ethanone

[243657-68-3] $C_{14}H_{11}NO_7$ mol.wt. 305.24



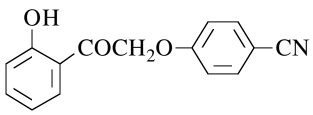
Synthesis

-Preparation by Hoesch condensation of p-nitrophenoxyacetonitrile with phloroglucinol in benzene/ethyl ether in the presence of zinc chloride and hydrogen chloride at 0° (87%) [541].

m.p. 295° [541]; ^{1}H NMR [541].

2-(4-Cyanophenoxy)-1-(2-hydroxyphenyl)ethanone

$C_{15}H_{11}NO_3$ mol.wt. 253.26

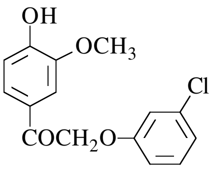


Syntheses

-Refer to: [1114] [1115].

2-(3-Chlorophenoxy)-1-(4-hydroxy-3-methoxyphenyl)ethanone

[107602-85-7] $C_{15}H_{13}ClO_4$ mol.wt. 292.72



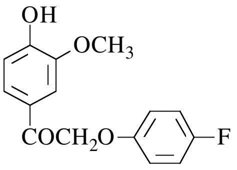
Synthesis

-Obtained by saponification of 1-(4-acetoxy-3-methoxyphenyl)-2-(3-chlorophenoxy)ethanone with sodium methoxide in refluxing methanol for 2.5 h (82%) [397].

m.p. 118-119° [397];
^1H NMR [397], IR [397], MS [397].

2-(4-Fluorophenoxy)-1-(4-hydroxy-3-methoxyphenyl)ethanone

[104972-13-6] $C_{15}H_{13}FO_4$ mol.wt. 276.26



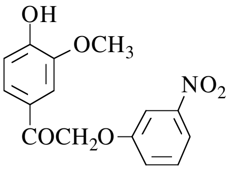
Synthesis

-Preparation by treatment of 1-(4-isopropoxy-3-methoxyphenyl)-2-(4-fluorophenoxy)ethanone (viscous liquid) (1 mol) with aluminium chloride (4 mol) in benzene for 2 h at r.t. (95%) [1243].

^1H NMR [1243], ^{13}C NMR [1243],
^{19}F NMR [1243], IR [1243]; TLC [1243].

1-(4-Hydroxy-3-methoxyphenyl)-2-(3-nitrophenoxy)ethanone

[107584-70-3] $C_{15}H_{13}NO_6$ mol.wt. 303.27



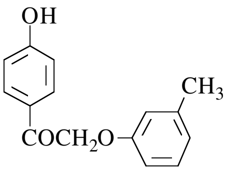
Synthesis

-Obtained by saponification of 1-(4-acetoxy-3-methoxyphenyl)-2-(3-nitrophenoxy)ethanone (m.p. 130-133°) with sodium methoxide in refluxing methanol for 2.5 h (65%) [397].

m.p. 187°5-189°5 [397];
^1H NMR [397], IR [397], MS [397].

1-(4-Hydroxyphenyl)-2-(3-methylphenoxy)ethanone

[107584-64-5] $C_{15}H_{14}O_3$ mol.wt. 242.27



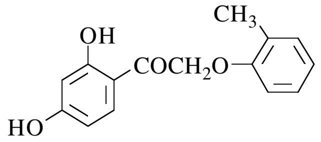
Synthesis

-Obtained by coupling 4-hydroxy-α-bromoacetophenone with m-cresol (44%) [397].

m.p. 170°5-172°5 [397];
^1H NMR [397], IR [397], MS [397].

1-(2,4-Dihydroxyphenyl)-2-(2-methylphenoxy)ethanone

[137987-86-1] $C_{15}H_{14}O_4$ mol.wt. 258.27



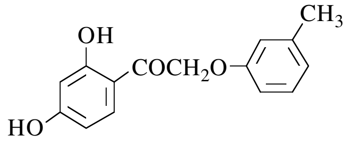
Synthesis

-Obtained by reaction of o-methylphenoxyacetonitrile with resorcinol (Hoesch reaction) (82%) [1496].

m.p. 182° [1496];
^{1}H NMR [1496].

1-(2,4-Dihydroxyphenyl)-2-(3-methylphenoxy)ethanone

[137987-85-0] $C_{15}H_{14}O_4$ mol.wt. 258.27



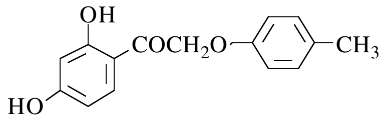
Synthesis

-Obtained by reaction of 3-methylphenoxyacetonitrile with resorcinol (Hoesch reaction) (82%) [1496].

m.p. 162° [1496];
^{1}H NMR [1496].

1-(2,4-Dihydroxyphenyl)-2-(4-methylphenoxy)ethanone

[137987-84-9] $C_{15}H_{14}O_4$ mol.wt. 258.27



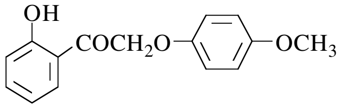
Synthesis

-Obtained by condensation of (p-methylphenoxy)-acetonitrile with resorcinol in ethyl ether/benzene in the presence of zinc chloride according to Houben-Hoesch method (95%) [78], (87%) [1496].

m.p. 171-172° [78], 167° [1496];
^{1}H NMR [78] [1496].

1-(2-Hydroxyphenyl)-2-(4-methoxyphenoxy)ethanone

$C_{15}H_{14}O_4$ mol.wt. 258.27

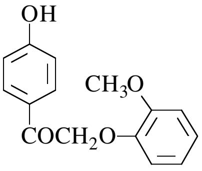


Syntheses

-Refer to: [1114] (compound **1d**) and [1115].

1-(4-Hydroxyphenyl)-2-(2-methoxyphenoxy)ethanone

[143486-72-0] $C_{15}H_{14}O_4$ mol.wt. 258.27



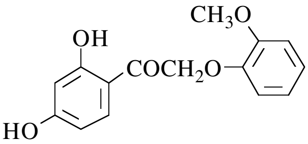
Synthesis

-Preparation by saponification of 1-(4-acetoxyphenyl)-2-(2-methoxyphenoxy)ethanone (SM) with potassium hydroxide in ethanol for 3 h at temperature < 30° under nitrogen (90%) [1500]. SM was obtained by alkylation of sodium 2-methoxyphenoxide with p-acetoxy-α-bromo-acetophenone (Williamson synthesis) (96%, m.p. 67°5-68°5).

m.p. 159-160° [1500]; ^{1}H NMR [1500].

1-(2,4-Dihydroxyphenyl)-2-(2-methoxyphenoxy)ethanone

[137987-88-3] $C_{15}H_{14}O_5$ mol.wt. 274.27



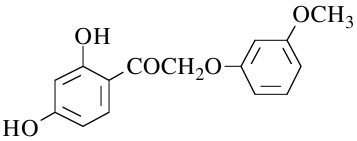
Synthesis

-Obtained by reaction of o-methoxyphenoxyacetonitrile with resorcinol (Hoesch reaction) (87%) [1496].

m.p. 193° [1496]; ^{1}H NMR [1496].

1-(2,4-Dihydroxyphenyl)-2-(3-methoxyphenoxy)ethanone

[137987-87-2] $C_{15}H_{14}O_5$ mol.wt. 274.27



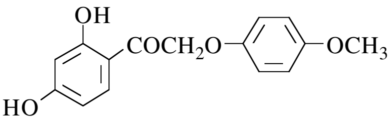
Synthesis

-Obtained by reaction of m-methoxyphenoxy-acetonitrile with resorcinol (Hoesch reaction) (85%) [1496].

m.p. 145° [1496]; ^{1}H NMR [1496].

1-(2,4-Dihydroxyphenyl)-2-(4-methoxyphenoxy)ethanone

[121361-55-5] $C_{15}H_{14}O_5$ mol.wt. 274.27



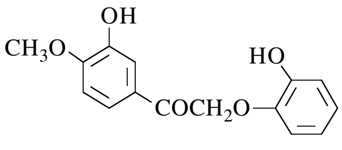
Syntheses

-Obtained by reaction of p-methoxyphenoxy-acetonitrile with resorcinol (Hoesch reaction) (89%) [1496], (73%) [1187].
-Also refer to: [1182].

m.p. 179° [1182] [1187], 175° [1496];
^{1}H NMR [1182] [1187] [1496], IR [1182] [1187].

1-(3-Hydroxy-4-methoxyphenyl)-2-(2-hydroxyphenoxy)ethanone

[99783-86-5] $C_{15}H_{14}O_5$ mol.wt. 274.27



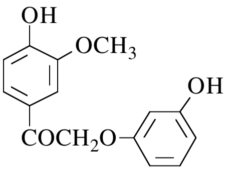
Syntheses

-Preparation by reaction of 3-hydroxy-4-methoxy-α-chloroacetophenone,
*with pyrocatechol monosodium salt in DMF at r.t. for 3 h (51%) [84];
*with pyrocatechol in the presence of potassium carbonate in 2-butanone [83].
-Also refer to: [81].

m.p. 154° [84]; ^{1}H NMR [84], MS [84].

1-(4-Hydroxy-3-methoxyphenyl)-2-(3-hydroxyphenoxy)ethanone

[107584-71-4] $C_{15}H_{14}O_5$ mol.wt. 274.27



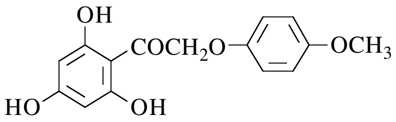
Syntheses

-Obtained by saponification of 1-(4-acetoxy-3-methoxyphenyl)-2-(3-hydroxyphenoxy)ethanone with sodium methoxide in refluxing methanol for 2.5 h [397].
-Also obtained by coupling reaction of 4-hydroxy-3-methoxy-α-bromoacetophenone with sodium m-acetoxyphenolate [397].

m.p. 145-146° [397]; ^{1}H NMR [397], IR [397], MS [397].

2-(4-Methoxyphenoxy)-1-(2,4,6-trihydroxyphenyl)ethanone

[243657-65-0] $C_{15}H_{14}O_6$ mol.wt. 290.27



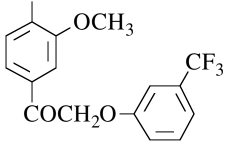
Synthesis

-Preparation by Hoesch condensation of p-methoxyphenoxyacetonitrile with phloroglucinol in benzene/ethyl ether in the presence of zinc chloride and hydrogen chloride at 0° (78%) [541].

m.p. 259° [541]; ^{1}H NMR [541].

1-(4-Hydroxy-3-methoxyphenyl)-2-[3-(trifluoromethyl)phenoxy]ethanone

[107584-69-0] $C_{16}H_{13}F_3O_4$ mol.wt. 326.27



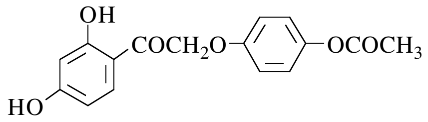
Synthesis

-Obtained by saponification of 1-(4-acetoxy-3-methoxyphenyl)-2-[3-(trifluoromethyl)phenoxy]ethanone with sodium methoxide in refluxing methanol for 2.5 h (88%) [397].

m.p. 107°5-108°5 [397] ; ^{1}H NMR [397], IR [397], MS [397].

2-(4-Acetoxyphenoxy)-1-(2,4-dihydroxyphenyl)ethanone

[137987-93-0] $C_{16}H_{14}O_6$ mol.wt. 302.28

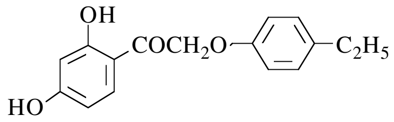


Synthesis

-Refer to: [1496].

1-(2,4-Dihydroxyphenyl)-2-(4-ethylphenoxy)ethanone

[201284-76-6] $C_{16}H_{16}O_4$ mol.wt. 272.30



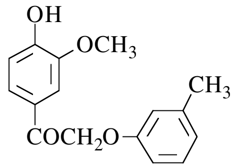
Synthesis

-Obtained by condensation of (p-ethylphenoxy)-acetonitrile with resorcinol in ethyl ether/benzene in the presence of zinc chloride according to Houben-Hoesch method (84%) [78].

m.p. 147-148° [78]; ^{1}H NMR [78].

1-(4-Hydroxy-3-methoxyphenyl)-2-(3-methylphenoxy)ethanone

[107584-67-8] $C_{16}H_{16}O_4$ mol.wt. 272.30



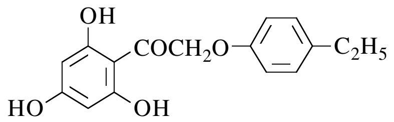
Synthesis

-Obtained by saponification of 1-(4-acetoxy-3-methoxyphenyl)-2-(3-methylphenoxy)ethanone with sodium methoxide in refluxing methanol for 2.5 h (53%) [397].

m.p. 170°5-172°5 [397];
^{1}H NMR [397], IR [397], MS [397].

2-(4-Ethylphenoxy)-1-(2,4,6-trihydroxyphenyl)ethanone

[243657-62-7] $C_{16}H_{16}O_5$ mol.wt. 288.30



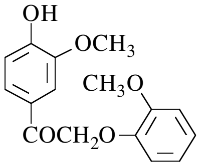
Synthesis

-Preparation by Hoesch condensation of p-ethylphenoxyacetonitrile with phloroglucinol in ethyl ether/benzene in the presence of zinc chloride and hydrogen chloride at 0° (88%) [541].

m.p. 247° [541]; ^{1}H NMR [541].

1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)ethanone

[22317-35-7] $C_{16}H_{16}O_5$ mol.wt. 288.30



Syntheses

-Preparation by treatment of 1-(4-acetoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)ethanone in chloroform solution with sodium methoxide in methanol, followed by acidification with dilute sulfuric acid (92%) [1309].

-Also obtained by hydrogenolysis of 1-[4-(benzyloxy)-3-methoxyphenyl]-2-(2-methoxyphenoxy)ethanone in methanol in the presence of 5% Pd on barium sulfate under hydrogen pressure (72%) [1124].

-Preparation by treatment of 1-(4-isopropoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)ethanone (m.p. 70°) (1 mol) with aluminium chloride (4 mol) in benzene for 2 h at r.t. (95%) [1243].

-Also obtained by oxidative degradation with 3% peracetic acid of 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)ethanol and 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanol (used as softwood lignin model compounds) in 10% acetic acid or 50% ethanol for 48 h at 30° [1119].

-Also obtained by degradation of 1-(4-benzyloxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)ethanol in the presence of *Aspergillus flavus*. Initial reactions in the degradation of this compound were oxidation of the α-hydroxy group to the corresponding ketone and debenzylation of the benzyloxy group [167].

-Formation from kraft lignin in sulfate cooking [1437] [1450].

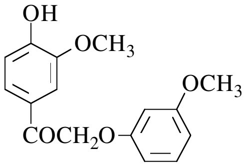
-Also obtained from the cleavage of the β-ether bond in the guaiacylglycol-β-guaiacyl ether (SM) with the water solution of phthalocyanine complex trisodium tetra-4-sulfonatophthalocyanine-iron (III) (Fe(TSPc)). Fe(TSPc) catalyzed formation of oxidized products in the absence of oxygen. The radical derived from SM then undergoes further single electron oxidation and deprotonation to give the titled compound [1523].

-Also refer to: [272] [317] [398] [562] [654] [673] [1451].

m.p. 94-95° [1124], 93° [1309], 65-67° [1450].
One the reported melting points is obviously wrong.
^{1}H NMR [167] [1124] [1243], ^{13}C NMR [1243], IR [167] [1243], UV [1124],
MS [167] [1124]; TLC [167] [1243]; GC [167].

1-(4-Hydroxy-3-methoxyphenyl)-2-(3-methoxyphenoxy)ethanone

[107584-68-9] $C_{16}H_{16}O_5$ mol.wt. 288.30



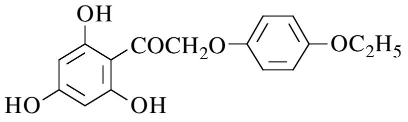
Synthesis

-Obtained by saponification of 1-(4-acetoxy-3-methoxyphenyl)-2-(3-methoxyphenoxy)ethanone with sodium methoxide in refluxing methanol for 2.5 h (75%) [397].

m.p. 109-110° [397];
^{1}H NMR [397], IR [397], MS [397].

2-(4-Ethoxyphenoxy)-1-(2,4,6-trihydroxyphenyl)ethanone

[243657-66-1] $C_{16}H_{16}O_6$ mol.wt. 304.30



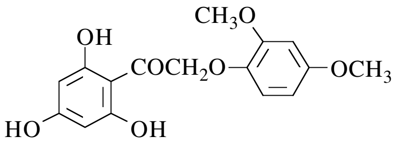
Synthesis

-Preparation by Hoesch condensation of p-ethoxyphenoxyacetonitrile with phloroglucinol in benzene/ethyl ether in the presence of zinc chloride and hydrogen chloride at 0° (81%) [541].

m.p. 223° [541]; ^1H NMR [541].

2-(2,4-Dimethoxyphenoxy)-1-(2,4,6-trihydroxyphenyl)ethanone

[149312-75-4] $C_{16}H_{16}O_7$ mol.wt. 320.30



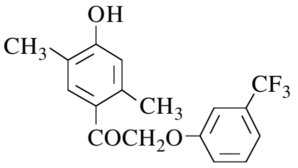
Synthesis

-Obtained by reaction of 2,4-dimethoxyphenoxyacetonitrile with phloroglucinol in THF in the presence of zinc chloride and hydrogen chloride in an ice bath for 4 h (53%) (Hoesch reaction) [1575].

m.p. 105-107° [1575]; monohydrate [1575];
^1H NMR [1575], ^{13}C NMR [1575], IR [1575], UV [1575], MS [1575].

1-(4-Hydroxy-2,5-dimethylphenyl)-2-[3-(trifluoromethyl)phenoxy]ethanone

[107584-80-5] $C_{17}H_{15}F_3O_3$ mol.wt. 324.30



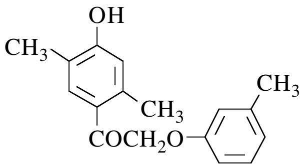
Synthesis

-Obtained by coupling 2,5-dimethyl-4-hydroxy-α-bromoacetophenone with m-(trifluoromethyl)phenol (87%) [397].

m.p. 191-194° [397];
^1H NMR [397], IR [397], MS [397].

1-(4-Hydroxy-2,5-dimethylphenyl)-2-(3-methylphenoxy)ethanone

[107584-79-2] $C_{17}H_{18}O_3$ mol.wt. 270.33



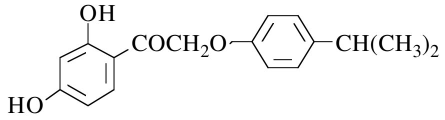
Synthesis

-Obtained by coupling 2,5-dimethyl-4-hydroxy-α-bromoacetophenone with m-cresol (54%) [397].

m.p. 188°5-190°5 [397];
^1H NMR [397], IR [397], MS [397].

1-(2,4-Dihydroxyphenyl)-2-[4-(1-methylethyl)phenoxy]ethanone

[201284-86-8] $C_{17}H_{18}O_4$ mol.wt. 286.33



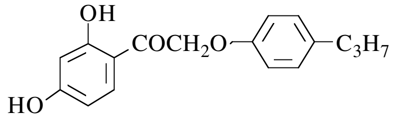
Synthesis

-Obtained by condensation of (p-isopropylphenoxy)acetonitrile with resorcinol in ethyl ether/benzene in the presence of zinc chloride according to Houben-Hoesch method (90%) [78].

m.p. 167° [78]; ^{1}H NMR [78].

1-(2,4-Dihydroxyphenyl)-2-(4-propylphenoxy)ethanone

[201283-81-3] $C_{17}H_{18}O_4$ mol.wt. 286.33



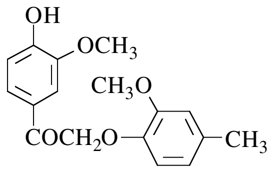
Synthesis

-Obtained by condensation of (p-propylphenoxy)-acetonitrile with resorcinol in ethyl ether/benzene in the presence of zinc chloride according to Houben-Hoesch method (88%) [78].

m.p. 149-150° [78]; ^{1}H NMR [78].

1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxy-4-methylphenoxy)ethanone

[152306-57-5] $C_{17}H_{18}O_5$ mol.wt. 302.33



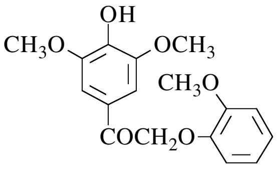
Synthesis

-Obtained by coupling α-bromoacetoguaiacone (1 equiv) with sodium creosolate (8 equiv) (compound 8) (19%) [395].

m.p. 109-111° [395];
^{1}H NMR [395], ^{13}C NMR [395], IR [395], MS [395].

1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanone

[18167-90-3] $C_{17}H_{18}O_6$ mol.wt. 318.33



Syntheses

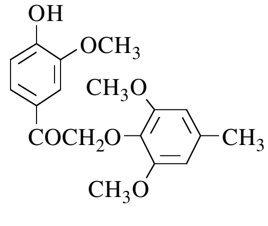
-Preparation by reaction of α-bromoacetosyringone (m.p. 130°) with guaiacol in the presence of sodium hydroxide in refluxing ethanol for 3 h (64%) [809].
-From degradation of the lignin model compound syringylglycol β-guaiacyl ether (m.p. 70-71°) (SM) by *Polyporus versicolor* and *Stereum frustulatum* [809].

SM was obtained by reduction of α-guaiacoxyacetosyringone in ethyl acetate with hydrogen over 10% Pd/C or with sodium borohydride in isopropanol (almost quantitative yield).

m.p. 85-86° [809].

2-(2,6-Dimethoxy-4-methylphenoxy)-1-(4-hydroxy-3-methoxyphenyl)ethanone

[105153-11-5] $C_{18}H_{20}O_6$ mol.wt. 332.35

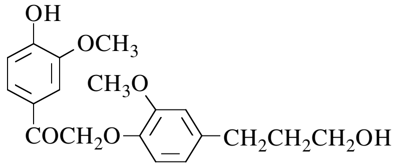


Synthesis

-Refer to: [396].

1-(4-Hydroxy-3-methoxyphenyl)-2-[4-(3-hydroxypropyl)-2-methoxyphenoxy]ethanone

[120936-27-8] $C_{19}H_{22}O_6$ mol.wt. 346.38

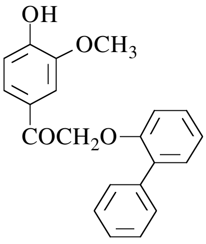


Synthesis

-Refer to: [62].

2-([1,1'-Biphenyl]-2-yloxy)-1-(4-hydroxy-3-methoxyphenyl)ethanone

[108434-12-4] $C_{21}H_{18}O_4$ mol.wt. 334.37



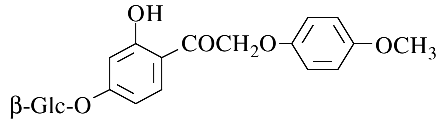
Synthesis

-Obtained by degradation of 1-(4-benzyloxy-3-methoxyphenyl)-2-(2-phenylphenoxy)ethanol in the presence of *Aspergillus flavus*. Initial reactions in the degradation of this compound were oxidation of the α-hydroxy group to the corresponding ketone and debenzylation of the benzyloxy group [167].

^{1}H NMR [167], IR [167], MS [167];
TLC [167]; GC [167].

1-[4-(β-D-Glucopyranosyloxy)-2-hydroxyphenyl]-2-(4-methoxyphenoxy)ethanone

[121361-58-8] $C_{21}H_{24}O_{10}$ mol.wt. 436.42



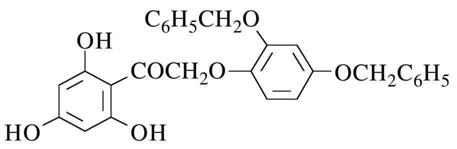
Synthesis

-Obtained by hydrolysis of 1-[2-hydroxy-4-[(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)oxy]phenyl]-2-(4-methoxyphenoxy)ethanone with 2 N sodium hydroxide in refluxing dilute methanol for 30 min (93%) [1187].

m.p. 144° [1187]; $(\alpha)_D^{23}$ = -38° (c = 0.7 in acetone) [1187]; IR [1187].

2-[2,4-Bis(phenylmethoxy)phenoxy]-1-(2,4,6-trihydroxyphenyl)ethanone

[149312-76-5] $C_{28}H_{24}O_7$ mol.wt. 472.49



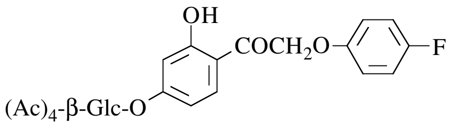
Synthesis

-Obtained by reaction of 2,4-(dibenzyloxy)phenoxyacetonitrile with phloroglucinol in THF in the presence of zinc chloride and hydrogen chloride in an ice bath for 4 h (57%) (Hoesch reaction) [1575].

m.p. 91-92° [1575]; monohydrate [1575];
^{1}H NMR [1575], ^{13}C NMR [1575], IR [1575], UV [1575], MS [1575].

2-(4-Fluorophenoxy)-1-[2-hydroxy-4-[(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)oxy]-phenyl]ethanone

[121377-35-3] $C_{28}H_{29}FO_{13}$ mol.wt. 592.53



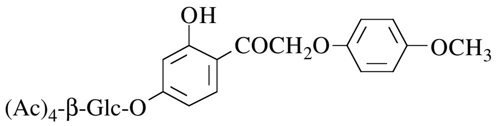
Synthesis

-Obtained by glycosylation of 1-(2,4-dihydroxyphenyl)-2-(4-fluorophenoxy)-ethanone with acetobromoglucose (34%) [1187].

m.p. 174° [1187]; $(\alpha)_D^{23} = -28°$ (c = 1 in chloroform) [1187];
^{1}H NMR [1187], IR [1187].

1-[2-Hydroxy-4-[(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)oxy]phenyl]-2-(4-methoxyphenoxy)ethanone

[121361-57-7] $C_{29}H_{32}O_{14}$ mol.wt. 604.56



Synthesis

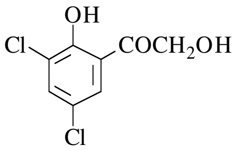
-Obtained by glycosylation of 1-(2,4-dihydroxyphenyl)-2-(4-methoxyphenoxy)ethanone with acetobromoglucose (45%) [1187].

m.p. 180° [1187]; $(\alpha)_D^{23} = -27°$ (c = 1 in chloroform) [1187];
^{1}H NMR [1187], IR [1187].

Chapter 6. Compounds derived from hydroxyacetic acids

1-(3,5-Dichloro-2-hydroxyphenyl)-2-hydroxyethanone

[58483-53-7] $C_8H_6Cl_2O_3$ mol.wt. 221.04

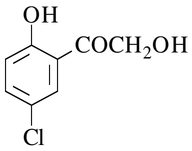


Synthesis

-Refer to: [268] (Romanian patent).

1-(5-Chloro-2-hydroxyphenyl)-2-hydroxyethanone

[52728-05-9] $C_8H_7ClO_3$ mol.wt. 186.59



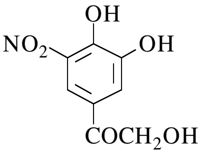
Synthesis

-Obtained by oxidative rearrangement of 5-chloro-2-hydroxy-α-bromoacetophenone in moist DMSO for 16 h at 20° (56%) [416].

m.p. 98-99° [416]; ^{1}H NMR [416].

1-(3,4-Dihydroxy-5-nitrophenyl)-2-hydroxyethanone

[134612-56-9] $C_8H_7NO_6$ mol.wt. 213.15

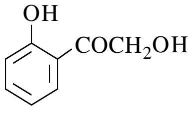


Synthesis

-Refer to: [163].

2-Hydroxy-1-(2-hydroxyphenyl)ethanone

[17375-96-1] $C_8H_8O_3$ mol.wt. 152.15



Syntheses

-Preparation by treatment of 2-hydroxy-α-bromoacetophenone with refluxing water for 16 h (88%) [145].

-Also obtained by hydrolysis of 2-hydroxy-α-(benzoyloxy)-acetophenone with 50% aqueous potassium hydroxide in refluxing ethanol for 34 h (73%) [416].

-Also obtained by oxidative rearrangement of 2-hydroxy-α-bromoacetophenone in moist DMSO for 16 h at 20° (31%) [416].

-Also obtained by action of hot aqueous sodium carbonate on 2,3-dihydro-2-hydroxybenzo[b]furan-3-one (m.p. 108°) (SM) at 100° for 1 h (33%). SM was obtained by oxidation of 2-hydroxyacetophenone with selenium dioxide [658].

-Also obtained by hypervalent iodine oxidation of 1-(trimethylsilyloxy)-1-[2-(trimethylsilyloxy)-phenyl]ethene with iodosobenzene, boron trifluoride etherate and water. The mixture was stirred at -40° for 1 h, then the temperature was slowly (1 h) raised to r.t. and stirring was continued for 30 min (25%) [1033].

-Also obtained by a selective one-step synthesis from phenoxymagnesium bromide (1 mol) and anhydrous monomeric glyoxal (1 mol) in boiling benzene for 20 h (24%) [271].

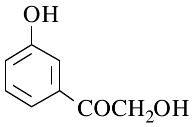
-Also obtained from α-chloro-o-hydroxyacetophenone by hydrolysis with boiling water for 15-20 h (20%) [1524].

-Also refer to: [23] [24] [341] [390] [524] [823] [847].

m.p. 66-67° [658], 65° [271] [1524], 64-65° [145] [416] [1033];
^{1}H NMR [271] [416] [658], IR [271], UV [271].

2-Hydroxy-1-(3-hydroxyphenyl)ethanone

[131341-58-7] $C_8H_8O_3$ mol.wt. 152.15

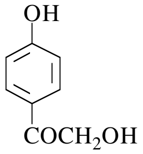


Synthesis

-Refer to: [607].

2-Hydroxy-1-(4-hydroxyphenyl)ethanone

[5706-85-4] $C_8H_8O_3$ mol.wt. 152.15



Syntheses

-Preparation by reaction of p-hydroxy-α-bromoacetophenone with formic acid in the presence of DBU,
*in benzene at 0°, followed by saponification of the intermediate formate ester with sodium hydroxide in methanol (99%) [1139];
*in methylene chloride, with the same treatment (49%) [560].

-Preparation by demethylation of α-acetoxy-p-methoxyacetophenone (SM) with aluminium chloride in refluxing benzene for 3 h (80%). In the reaction, deacetylation takes place simultaneously. SM was obtained by treatment of α-chloro-p-methoxyacetophenone with potassium acetate in ethanol [279].

-Preparation by action of boron trifluoride etherate with p-hydroxyphenyl diazomethyl ketone (SM1) in nitromethane under nitrogen at 22° for 15 min (81%). SM1, preparation given, melted at 145-150° (d) [143].

-Preparation from α-acetoxy-4-hydroxyacetophenone (m.p. 133°),
*by heating with 16% aqueous sodium hydroxide for 15 min on a steam bath (quantitative yield) [1238];
*in methanolic solution by treatment with 0.5 N aqueous sodium hydroxide at r.t. for 15 min (67%) [1577].

-Preparation by adding excess of concentrated hydrochloric acid to a warm concentrated aqueous solution of the potassium salt and cooling the solution [902].

-Preparation by treatment of the sodium salt with aqueous hydrochloric acid [1445].

-Also obtained from p-acetoxybenzoylcarbinol (SM2) by heating with 4% ethanolic potassium hydroxide for 45 min on a water bath (20%). SM2 was prepared from p-acetoxyphenyl diazomethyl ketone (m.p. 109-110°) after treatment in dioxane with 2 N sulfuric acid at r.t. for 20 min, then at 40° until no more nitrogen evolved [931].

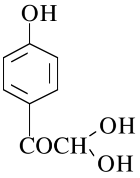
-Also obtained by condensation of glyoxal with phenol,
*in the presence of butylamine at 33° for 3 h (29%) [1039];
*in the presence of aqueous sodium hydroxide at 33° for 6 h (25%) [948];
*in the presence of hydrogen chloride at 80° for 4 h (< 5%) [947].

-Also obtained by reductive condensation of p-hydroxyphenylglyoxal potassium bisulfite with diethylamine under hydrogen in the presence of Raney nickel in dilute ethanol for 1.5 h at 45° [504].
-Also obtained from bisphenol A which is metabolized by a Gram-negative aerobic bacterium *via* a novel pathway involving oxidative skeletal rearrangement of the bisphenol A [1387].
-Also obtained by peroxidatic degradation of 7,4'-dihydroxyflavanone or 7,4'-dihydroxy-3'-methoxyflavanone [1159].
-Also refer to: [823] [1038].
N.B.: Na salt [1238] [1445], K salt [902].

m.p. 177-178° [279] [902], 173-174° [931], 173° [1577], 170-177° [504], 170-172° [1445], 170-171° [143], 165-167° [560] [1139];
^{1}H NMR [143] [1139], IR [143] [1139], MS [1139].

2,2-Dihydroxy-1-(4-hydroxyphenyl)ethanone

[197447-05-5] $C_8H_8O_4$ mol.wt. 168.15

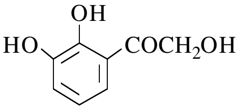


Syntheses

-Obtained by oxidation of p-hydroxyacetophenone with selenium oxide [1560].
-Also refer to: [296] (compound 1d) and [1521] [1522].

1-(2,3-Dihydroxyphenyl)-2-hydroxyethanone

[58483-49-1] $C_8H_8O_4$ mol.wt. 168.15

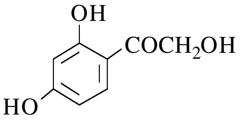


Synthesis

-Refer to: [851].

1-(2,4-Dihydroxyphenyl)-2-hydroxyethanone *(Fisetol)*

[487-47-8] $C_8H_8O_4$ mol.wt. 168.15



Syntheses

-Obtained by hydrolysis of α-acetoxyresacetophenone (m.p. 164°5) [287],
*with 5% aqueous sodium carbonate on a steam bath for 3 h (35%) [287];
*with 10% aqueous sodium hydroxide for 2 h at r.t. (38%) [287].
-Also obtained by hydrolysis of 2,4,α-triacetoxyacetophenone (m.p. 94°) [287],
*with 2 N sodium hydroxide [287];
*with 5 N methanolic ammonia for 8 days in the cold [1090].
-Also obtained by demethylation of α-methoxyresacetophenone with 40% hydrobromic acid for 3 h on a boiling water bath (16%) [592].
-Also obtained by treatment of α-[(methoxycarbonyl)oxy]resacetophenone (m.p. 157-158°) or

α-[(ethoxycarbonyl)oxy]resacetophenone (m.p. 107°) with 2 N sodium hydroxide for 2 h at r.t. [1380].

-Also obtained by reaction of hydroxyacetonitrile with resorcinol [803], (41%) (Hoesch reaction) [768].

-Also obtained by a selective one-step synthesis from 3-hydroxyphenoxymagnesium bromide (0.1 mol) and anhydrous monomeric glyoxal (0.1 mol) in boiling benzene for 20 h (35%) [271].

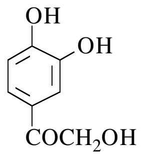
-Also obtained by treatment of *Fisetin* (3,7,3',4'-tetrahydroxyflavone) — m.p. 330° (d) — with boiling ethanolic potassium hydroxide [637].

-Also refer to: [303] [593] [691] [1028] [1371].

m.p. 191° [803], 189° [287] [768] [1090] [1380], 187-188° [592], 185-186° [271]; ^{1}H NMR [271], IR [271], UV [271] [592] [1574].

1-(3,4-Dihydroxyphenyl)-2-hydroxyethanone *(DOPKET)*

[29477-54-1] $C_8H_8O_4$ mol.wt. 168.15



Syntheses

-Obtained by saponification of its triacetate (SM) (m.p. 94°) with sodium hydroxide (or sodium ethoxide) in ethanol in a water bath for 20 min (33%). SM was prepared by treatment of 3,4-dihydroxy-α-chloroacetophenone with potassium acetate in refluxing acetic anhydride for 15 min (quantitative yield) [1510].

-Also obtained by heating N-acetyldopamine with 1 N hydrochloric acid [1031].

-Also obtained by hydrolysis of 2-(3',4'-dihydroxyphenyl)-3-acetylamino-6 (or 7)-(N-acetyl-2''-aminoethyl)-2,3-dihydro-1,4-benzodioxine (SM) with refluxing 1 N hydrochloric acid for 3 h. SM was formed by incubation of N-acetyldopamine with locust cuticle [48].

-Also obtained from the quinone of 3,4-dihydroxyphenylglycol by attack with isomerase (SM). This enzyme (SM) has been purified from the hemolymph of *Sarcophaga bullata* [1290].

Isolation from natural sources

-From sclerotization of the adult cuticle *(Leucophaea maderae)* [354].

-Also obtained by mild acid hydrolysis of sclerotized cuticles from locusts *(Schistocerca gregaria)*and beetles *(Pachynoda sinuata)* [45].

-From acid hydrolysates of insect hard cuticle [44].

-From acid hydrolysates of insect sclerotized cuticle in refluxing 1 N formic acid for 1 h. The cuticle used was obtained from the desert locust *(Schistocerca gregaria)* [46].

-By acid hydrolysis from exuviae of last instar larvae of the cicada *Tibicen pruinosa* [140].

-From the seed coat tamarind (*Tamarindus indica* L.) [1472].

-From the skins of tamarind seeds [1548].

-From mild acid hydrolysates of tanning pharate pupae cuticle from *Manduca Sexta* [1120].

-In hydrolysates of the wing-scales of butterfly (*Eurema hecabe*) in 1 N hydrochloric acid. This compound was also present in the hydrolyzate of wing-scales of *Catopsilia crocale, Appias indra and Morpho rhetenor* [1486].

-In aqueous extracts from cockroach and locust exuviae of various **Orthoptera** in refluxing water for 1 h *(Periplaneta americana, Periplaneta brunnea, Chortoicetes terminifera* and *Austracris guttulosa)* [91].

-in acidic extracts of insect cuticles (exuviae) in refluxing 1 N hydrochloric acid for 1.5 h, i. e.:

*__Orthoptera__ *(Periplaneta americana, Periplaneta brunnea, Blattella germanica, Nauphoeta cinerea, Chortoicetes terminifera* and *Austracris guttulosa)* [91];

*__Hemiptera__ *(Nezara viridula)* [91];

*__Lepidoptera__ *(Papilio aegeus* and *Antheraea helena)* [91];

*__Coleoptera__ *(Anthrenus australis)* [91].

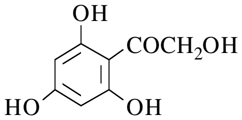
-in acidic extracts of insect cuticles (preparia) in refluxing 1 N hydrochloric acid for 1.5 h, i. e.:

***Diptera** *(Lucilia cuprina)* [91].
-in acid extracts of insect cuticles (prepal cuticles):
***Lepidoptera** *(Papilio aegeus)* [91].
-Also refer to: [326] [645] [890] [1411] [1470] [1471].

m.p. 195° [1510]; UV [44] [45], MS [44] [45] [1242];
electrophoresis [354]; column chromatography [45];
TLC [44] [45] [354]; LCEC chromatography [354]; GC [91]; HPLC [1120] [1290];
HPLC-MS [1031].

2-Hydroxy-1-(2,4,6-trihydroxyphenyl)ethanone

[55313-03-6] $C_8H_8O_5$ mol.wt. 184.15



Syntheses

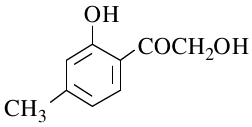
-Preparation according to Hoesch reaction from phloroglucinol,
*with acetoxyacetonitrile (81%) [291];
*with hydroxyacetonitrile (63%) [1574].

-Also obtained from dihydrokaempferol (3,5,7,4'-tetrahydroxyflavanone) *(Aromadendrin)* by basic hydrolysis and subsequent oxidation [1091].
-Dihydrokaempferol yields kaempferol (3,5,7,4'-tetrahydroxyflavone) with peroxides and alkaline conditions; subsequent thermolysis produces the titled ketone [1091].
-Quercetin (3,5,7,3',4'-pentahydroxyflavone) yields the same product under alkaline thermolysis (80°) [1091].
-Also refer to: [800].

m.p. 226° [1574], 224° [291]; UV [1574]; GC-MS [1091].

2-Hydroxy-1-(2-hydroxy-4-methylphenyl)ethanone

[55960-03-7] $C_9H_{10}O_3$ mol.wt. 166.18



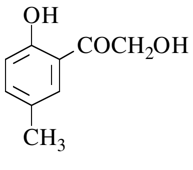
Syntheses

-Obtained by a selective one-step synthesis from 3-methylphenoxymagnesium bromide (1 mol) and anhydrous monomeric glyoxal (1 mol) in boiling benzene for 20 h (48%) [271].
-Also refer to: [851].

m.p. 68-69° [271]; ^1H NMR [271], IR [271], UV [271].

2-Hydroxy-1-(2-hydroxy-5-methylphenyl)ethanone

$C_9H_{10}O_3$ mol.wt. 166.18



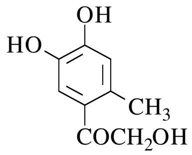
Synthesis

-Obtained by hydrolysis of 2-hydroxy-5-methyl-α-chloroacetophenone with boiling water for 15-20 h (40%) [1524].

m.p. 76-77° [1524].

1-(4,5-Dihydroxy-2-methylphenyl)-2-hydroxyethanone

[61407-16-7] $C_9H_{10}O_4$ mol.wt. 182.18



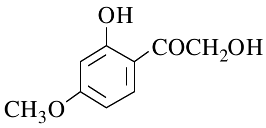
Synthesis

-Obtained (trace amounts) by heating D-fructose or D-glucose in 0.3 M acetate buffer of pH 4.5 at 96° for 48 h under nitrogen or D-fructose in 0.3 M acetate buffer of pH 4.5 in a stainless autoclave at 160° for 4 h [1190].

amorphous [1190]; ^{1}H NMR [1190], MS [1190].

2-Hydroxy-1-(2-hydroxy-4-methoxyphenyl)ethanone

[55960-07-1] $C_9H_{10}O_4$ mol.wt. 182.18



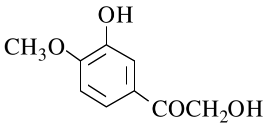
Syntheses

-Preparation from 2-hydroxy-4-methoxy-α-bromoacetophenone with refluxing water for 20 h (76%) [24].
-Also obtained from fisetol 4-monomethyl ether diacetate (m.p. 86°) by heating with ethanolic potassium hydroxide [1438].
-Also obtained by a selective one-step synthesis from 3-methoxyphenoxymagnesium bromide (1 mol) and anhydrous monomeric glyoxal (1 mol) in boiling benzene for 20 h (45%) [271].
-Also obtained by action of 40% aqueous hydrobromic acid with 2-hydroxy-4,α-dimethoxyacetophenone in acetic acid on a boiling water bath for 3 h (22%) [592].
-Also refer to: [23] [303] [561] [593] [1371] [1382].

m.p. 128° [1438], 127° [592], 126-128° [24], 126-127° [271];
^{1}H NMR [24] [271], IR [24] [271], UV [271] [592], MS [24].

2-Hydroxy-1-(3-hydroxy-4-methoxyphenyl)ethanone

[90536-46-2] $C_9H_{10}O_4$ mol.wt. 182.18



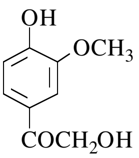
Syntheses

-Preparation by total hydrolysis of 4-methoxy-3,α-diacetoxyacetophenone (m.p. 82-83°) [478], (m.p. 81-82°) [454] in methanol with concentrated hydrochloric acid,
*for 4-5 h at r.t. (75%) [478];
*for 30 min at reflux (56%) [454].

m.p. 177-178° [454], 176-177° [478]; IR [454], UV [454].

2-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)ethanone

[18256-48-9] $C_9H_{10}O_4$ mol.wt. 182.18



Syntheses

-Preparation by total hydrolysis of 3-methoxy-4,α-diacetoxyacetophenone (m.p. 77-78°) [478], (m.p. 75-76°) [454] in methanol with concentrated hydrochloric acid,
*for 4-5 h at r.t. (78%) [478], (25%) [1124];
*during 14 h at 20°, then for 30 min at reflux (67%) [454].

-Obtained by photorelease of l-glutamic acid from 5-[2-(4-hydroxy-3-methoxyphenyl)-2-oxoethyl] l-glutamate, mono(trifluoroacetate) [284043-07-8] with either 300 or 350 nm lamps in water or in deuterium oxide [324].
-Also obtained by photorelease of γ-aminobutyric acid from 2-(4-hydroxy-3-methoxyphenyl)-2-oxoethyl γ-aminobutyrate [284043-11-4] with either 300 or 350 nm lamps in water or in deuterium oxide [324].

N.B.: Details of the synthesis and ^{1}H NMR, ^{13}C NMR, IR, UV and HRMS data are available free of charge *via* the Internet at http://pubs.acs.org. Complete experimental details are provided in the full paper [324].

-Also obtained by treatment of 2-(acetoxy)-1-(4-hydroxy-3-methoxyphenyl)ethanone,
*with boiling aqueous barium carbonate for 2 h [1198];
*with 16% aqueous sodium hydroxide on the steam bath. The obtained sodium salt was treated with 2 N acetic acid (62%) [909].

N.B.: Na salt sesquihydrate (70%) [909].
-Also refer to: [1101].

Isolation from natural sources

-From cell cultures of *Solanum khasianum* (Solanaceae) [1043] [1044].

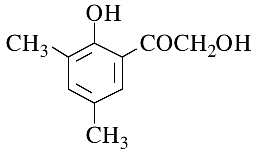
N.B.: Microsomal preparations from heterotropic cell cultures of *Solanum khasianum* catalyse the hydroxylation of the α-methyl group of acetovanillone. The reaction requires both oxygen and NADPH [1043].

-From the Namibian shrub *Salsola tuberculatiformis* [1415].
-From the suprarenal capsules [454].
-Also refer to: [1386].

m.p. 160-161° [454] [1124], 159-160° [478], 158-160° (anhydrous) [909];
^{1}H NMR [1044] [1124], ^{13}C NMR [1044], IR [454] [1124],
UV [454] [1044], MS [1044] [1124] [1386];
fluorescence spectroscopy [938]; HPLC [1044]; GC/MS [1044] [1386].

2-Hydroxy-1-(2-hydroxy-3,5-dimethylphenyl)ethanone

[55960-05-9] $C_{10}H_{12}O_3$ mol.wt. 180.20



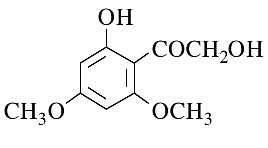
Synthesis

-Obtained by a selective one-step synthesis for 2,4-dimethylphenoxymagnesium bromide (1 mol) and anhydrous monomeric glyoxal (1 mol) in boiling benzene for 20 h (35%) [271].

m.p. 100-101° [271];
^{1}H NMR [271], IR [271], UV [271].

2-Hydroxy-1-(2-hydroxy-4,6-dimethoxyphenyl)ethanone

[83768-75-6] $C_{10}H_{12}O_5$ mol.wt. 212.20



Syntheses

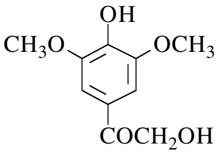
-Preparation by hydrolysis of 2-(2-hydroxy-4,6-dimethoxyphenyl)-2-oxoethyl benzoate in pyridine with aqueous sodium hydroxide under nitrogen atmosphere at r.t. for 1 h (80%) [1085].

-Also obtained by degradation of 2-[2-(2-hydroxy-4,6-dimethoxyphenyl)-2-oxoethoxy]-2-methylpropionic acid in refluxing mixture of concentrated hydrochloric acid/methanol (1 vol/5 vol) for 1 h (42%) [61].
-Also obtained by action of 40% hydrobromic acid with 2-hydroxy-α,4,6-trimethoxyacetophenone in acetic acid by heating on a boiling water bath for 3 h (32%) [592].
-Also refer to: [593].

m.p. 140-142° [61], 139-140° [592], 131-132° [1085]; TLC [1085];
^{1}H NMR [61] [1085], IR [1085], UV [592], MS [1085].

2-Hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone *(Danielone)*

[90426-22-5] $C_{10}H_{12}O_5$ mol.wt. 212.20



Syntheses

-Preparation by an efficient simple three-step synthesis: First, slowly adding a methanolic 3,5-dimethoxy-4-(methoxymethoxy)acetophenone to a cooled methanolic potassium hydroxide solution. Then iodosobenzene diacetate was added and the reaction mixture stirred at r.t. overnight, cooled in an ice bath and 6% hydrochloric acid was added. After refluxing at 60° for 1 h, the reaction mixture was cooled at r.t. and water was added (60%) [935].
-Obtained by hydrolysis of its diacetate (SM) with 5% hydrochloric acid in 70% dilute ethanol at 80° for 1.5 h [1378]. SM was prepared according to [757].
-Also obtained by photorelease of l-glutamic acid from 5-[2-(4-hydroxy-3,5-dimethoxyphenyl)-2-oxoethyl] l-glutamate, mono(trifluoroacetate) [284043-10-3] with either 300 or 350 nm lamps in water or in deuterium oxide [324].
-Also obtained by photorelease of γ-aminobutyric acid from 2-(4-hydroxy-3,5-dimethoxyphenyl)-2-oxoethyl γ-aminobutyrate [284043-12-5] with either 300 or 350 nm lamps, in water or in deuterium oxide [324].
N.B.: Details of the synthesis and ^{1}H NMR, ^{13}C NMR, IR, UV and HRMS data are available free of charge *via* the Internet at http://pubs.acs.org. Complete experimental details are provided in the full paper [324].
-Also obtained from 1,2-bis(4-hydroxy-3,5-dimethoxyphenyl)-propane-1,3-diol, a β-1-lignin substructure model compound, by degradation with laccase of *Coriolus versicolor* (Fr.) Quel. [775].
-Also refer to: [1116] [1379] [1464].

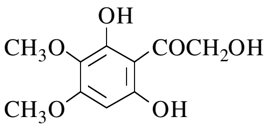
Isolation from natural sources

-From *Nicotiana tabacum* [1378] [1396] and *Atropa belladona* root cultures [1378].
-From cell. suspension cultures of *Hyoscyamus albus* [1004].
-From *Carica papaya* fruit slices (Caricaceae) [440].
-Isolated as virulence gene inducing compounds of *Agrobacterium* from the hairy root cultures of belladonna [1377].
-Also refer to: [1386].

m.p. 145° [440], 109-110° [1378]. One of the reported melting points is obviously wrong.
TLC [440]; GC/MS [1386] [1396];
^{1}H NMR [440] [1378], ^{13}C NMR [440] [1378], IR [440] [935],
UV [440] [1378] [1396], MS [440] [935] [1378] [1386] [1396].

1-(2,6-Dihydroxy-3,4-dimethoxyphenyl)-2-hydroxyethanone *(Methyldegeranylmelicopol)*

$C_{10}H_{12}O_6$ mol.wt. 228.20



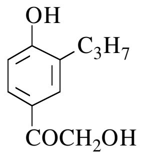
Synthesis

-Obtained by degradation of *methylmelicopol* (VII) (SM) with refluxing 2 N hydrochloric acid for 5 min in an atmosphere of nitrogen (16%) [1237]. SM was isolated from the leaves of *Melicope broadbentiana* F. M. Bail (Rutaceae) [128] [1237]. **N.B.**: In the paper [1237], the formulas (VII) as well as (XI) representing the titled compound were erroneous [128].

m.p. 181-183° [1237];
^{1}H NMR [1237], IR [1237], UV [1237].

2-Hydroxy-1-(4-hydroxy-3-propylphenyl)ethanone

[178978-33-1] $C_{11}H_{14}O_3$ mol.wt. 194.23

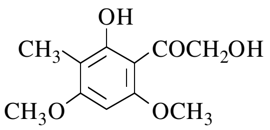


Synthesis

-Refer to: [616].

2-Hydroxy-1-(2-hydroxy-4,6-dimethoxy-3-methylphenyl)ethanone

[184706-61-4] $C_{11}H_{14}O_5$ mol.wt. 226.23



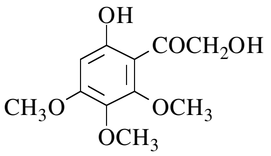
Isolation from natural sources

-From the stem wood of *Euphorbia quinquecostata* Volk. (Euphorbiaceae) [982].

m.p. 164-166° [982];
^{1}H NMR [982], ^{13}C NMR [982], IR [982], UV [982], MS [982].

2-Hydroxy-1-(6-hydroxy-2,3,4-trimethoxyphenyl)ethanone *(Dimethyldegeranylmelicopol)*

[51117-08-9] $C_{11}H_{14}O_6$ mol.wt. 242.23



Syntheses

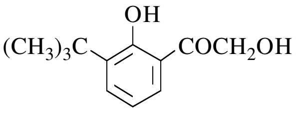
-Preparation by reaction of acetoxyacetonitrile with antiarol (Hoesch reaction), followed by heating the isolated intermediate compound in refluxing dilute ethanol for 8 h (32%) [128].

-Also obtained by hydrogenolysis of *dimethylmelicopol* (VIII) (SM) [1237]. SM was obtained by partial methylation of *methylmelicopol* (VII) [1237], itself isolated from the leaves of *Melicope broadbentiana* F. M. Bail. (Rutaceae) [128] [1237]. In the paper [1237], the formulas (VII) and (VIII), as well as (XIX) representing the titled compound were erroneous [128].

m.p. 87° [1237], 86-87° [128];
^{1}H NMR [1237], IR [1237], UV [1237].

1-[3-(Dimethylethyl)-2-hydroxyphenyl]-2-hydroxyethanone

[55960-04-8] $C_{12}H_{16}O_3$ mol.wt. 208.26



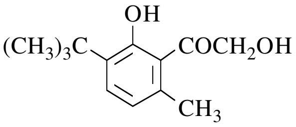
Synthesis

-Obtained by a selective one-step synthesis from 2-tert-butylphenoxymagnesium bromide (1 mol) and anhydrous monomeric glyoxal (1 mol) in boiling benzene for 20 h (45%) [271].

oil [271]; ^{1}H NMR [271], IR [271], UV [271].

1-[3-(Dimethylethyl)-2-hydroxy-6-methylphenyl]-2-hydroxyethanone

[55960-06-0] $C_{13}H_{18}O_3$ mol.wt. 222.28



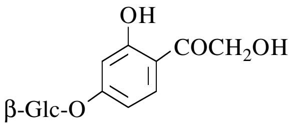
Synthesis

-Obtained by a selective one-step synthesis from 2-tert-butyl-5-methylphenoxymagnesium bromide (1 mol) and anhydrous monomeric glyoxal (1 mol) in boiling benzene for 20 h (25%) [271].

m.p. 76-77° [271]; ^{1}H NMR [271], IR [271], UV [271].

1-[4-(β-D-Glucopyranosyloxy)-2-hydroxyphenyl]-2-hydroxyethanone

$C_{14}H_{18}O_9$ mol.wt. 330.29

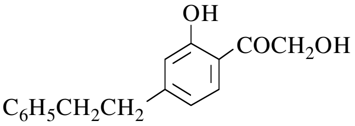


Synthesis

-Refer to: [1499].

2-Hydroxy-1-[2-hydroxy-4-(2-phenylethyl)phenyl]ethanone

[132197-47-8] $C_{16}H_{16}O_3$ mol.wt. 256.30

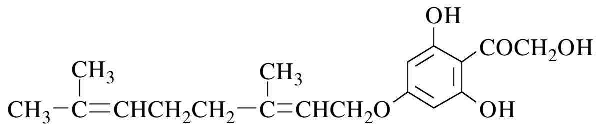


Synthesis

-Refer to: [523] (Japanese patent).

1-[4-[(3,7-Dimethyl-2,6-octadienyl)oxy]-2,6-dihydroxyphenyl]-2-hydroxyethanone

[142905-41-7] $C_{18}H_{24}O_5$ mol.wt. 320.38



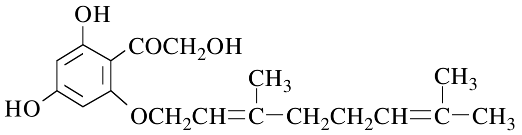
Isolation from natural source

-From the fruit of *Evodia Merrillii* Kanehira & Sasaki ex Kanehira (Rutaceae) [304].

m.p. 106-108° [304]; column chromatography [304];
^{1}H NMR [304], ^{13}C NMR [304], IR [304], UV [304], MS [304].

1-[2-[(3,7-Dimethyl-2,6-octadienyl)oxy]-4,6-dihydroxyphenyl]-2-hydroxyethanone *(E)*

[149492-42-2] $C_{18}H_{24}O_5$ mol.wt. 320.38



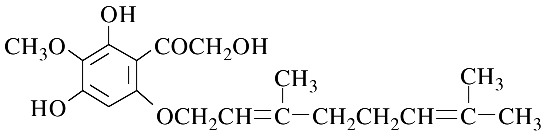
Isolation from natural source

-From the fruits of *Evodia merrillii* Kanehira & Sasaki ex Kanehira (Rutaceae) [926].

m.p. 144°5-146° [926];
^{1}H NMR [926], ^{13}C NMR [926], IR [926], UV [926], MS [926].

1-[6-[(3,7-Dimethyl-2,6-octadienyl)oxy]-2,4-dihydroxy-3-methoxyphenyl]-2-hydroxyethanone *(Melicopol)*

$C_{19}H_{26}O_6$ mol.wt. 350.41



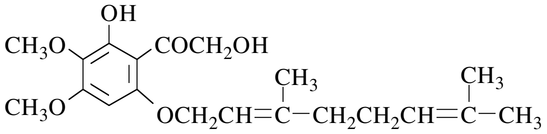
Isolation from natural source

-From the leaves of *Melicope broadbentiana* F. M. Bail. (Rutaceae) [128] [1237]. **N.B.**: In the paper [1237], the formula (VI) representing the titled compound was erroneous [128].

m.p. 133-134° [1237];
^{1}H NMR [1237], ^{1}H NMR NOE [128], IR [1237], UV [128] [1237].

1-[3,4-Dimethoxy-6-[(3,7-dimethyl-2,6-octadienyl)oxy]-2-hydroxyphenyl]-2-hydroxyethanone *(Methylmelicopol)*

$C_{20}H_{28}O_6$ mol.wt. 364.44



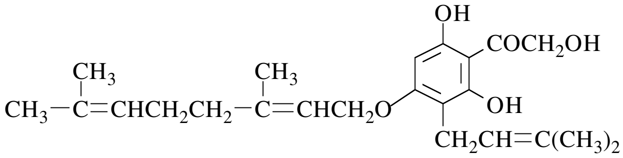
Isolation from natural source

-From the leaves of *Melicope broadbentiana* F. M. Bail. (Rutaceae) [128] [1237]. **N.B.**: In the paper [1237], the formula (VII) representing the titled compound was erroneous [128].

m.p. 103° [1237];
^{1}H NMR [1237], ^{1}H NMR NOE [128], IR [1237], UV [128] [1237].

1-[4-[(3,7-Dimethyl-2,6-octadienyl)oxy]-2,6-dihydroxy-3-(3-methyl-2-butenyl)phenyl]-2-hydroxyethanone *(E)*

[149492-41-1] $C_{23}H_{32}O_5$ mol.wt. 388.26



Isolation from natural source

-From the fruits of *Evodia merrillii* Kanehira & Sasaki ex Kanehira (Rutaceae) [926].

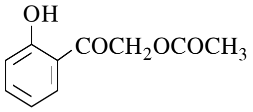
m.p. 136-137° [926];
^{1}H NMR [926], ^{13}C NMR [926], IR [926], UV [926], MS [926].

Chapter 7. Compounds derived from acyloxy- and aryloxyacetic acids

7.1. *Compounds derived from acetoxyacetic acids*

2-(Acetyloxy)-1-(2-hydroxyphenyl)ethanone

[40231-09-2]	$C_{10}H_{10}O_4$	mol.wt. 194.19



Syntheses

-Preparation by hydrolysis of o-acetoxy-α-acetoxy-acetophenone (SM) with aqueous potassium hydroxide solution by gently warming for 10-15 min on a water bath maintained at 80° (71%). SM was obtained by cupric chloride-catalyzed decomposition of o-acetoxy-α-diazoacetophenone in dioxane solution in the presence of acetic acid (65%, m.p. 161-162°) [879].

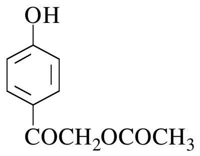
-Also obtained by oxidative rearrangement of 2-acetoxy-α-bromoacetophenone in moist DMSO for 28 h at 20° (49%) [416].

-Also obtained by reaction of potassium acetate with o-hydroxy-α-bromoacetophenone in acetone at r.t. for 90 min [1114].

m.p. 170-171° [879], 58-59° [416], 57° [1114]. One of the reported melting points is obviously wrong. Ogle and Main [1114] consider that the reported product of m.p. 171° [879], identified by only elemental and IR analysis, is not the titled product.
^{1}H NMR [416] [1114], ^{13}C NMR [1114], IR [879] [1114].

2-(Acetyloxy)-1-(4-hydroxyphenyl)ethanone

[20816-46-0]	$C_{10}H_{10}O_4$	mol.wt. 194.19



Syntheses

-Preparation by reaction of α-chloro-4-acetoxyacetophenone with potassium acetate in boiling ethanol for 4 h (quantitative yield) [1099].

-Preparation by reaction of acetic acid and potassium acetate with α-chloro-4-hydroxyacetophenone in refluxing ethanol for 1 h (80%) [1238].

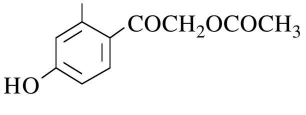
-Preparation by reaction of acetic acid with p-hydroxyphenacyl chloride in acetonitrile in the presence of triethylamine, first in an ice bath for 15 min, then at reflux for 3 h (50%) [1577].

-Also refer to: [917] [918].

m.p. 133° [1238] [1577], 127° [1099].

2-(Acetyloxy)-1-(2,4-dihydroxyphenyl)ethanone

[63124-23-2]	$C_{10}H_{10}O_5$	mol.wt. 210.19



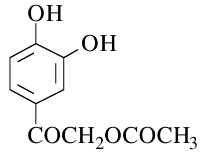
Synthesis

-Preparation by reaction of acetoxyacetonitrile with resorcinol (Hoesch reaction) (85%) [287], (40%) [1474].

m.p. 167-168° [1474], 164°5 [287];
^{1}H NMR [1474], IR [1474], UV [1574].

2-(Acetyloxy)-1-(3,4-dihydroxyphenyl)ethanone

[67083-58-3] $C_{10}H_{10}O_5$ mol.wt. 210.19



Synthesis

-Preparation by adding a solution of sodium acetate in aqueous acetic acid to an ethanolic solution of 3,4-dihydroxy-α-chloroacetophenone, and heating at reflux for 24 h (83%) [336].

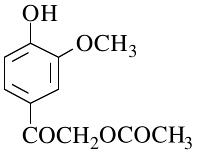
Isolation from natural sources

-Obtained by mild acid hydrolysis of sclerotized cuticles from locusts *(Schistocerca gregaria)* and beetles *(Pachynoda sinuata)* [45].

m.p. 157-160° [336]; UV [45], MS [45] [1242];
column chromatography [45]; TLC [45].

2-(Acetyloxy)-1-(4-hydroxy-3-methoxyphenyl)ethanone

[139473-80-6] $C_{11}H_{12}O_5$ mol.wt. 224.21



Syntheses

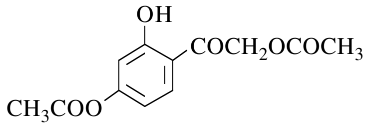
-Obtained by reaction of α-chloroacetovanillone with potassium acetate,
*in refluxing ethanol for 2 h (56%) [1198] or for 4 h (67%) [1099];
*in refluxing acetic acid and ethanol mixture for 1 h (57%) [909].

-Also obtained by partial hydrolysis of 4,α-diacetoxy-3-methoxyacetophenone (m.p. 75-76°) in the presence of potassium bicarbonate in methanol for 16 h at 20° (96%) [454].
-Also obtained from 4-hydroxy-3-methoxy-α-diazoacetophenone by slowly heating in acetic acid at 110° (29%) [454].
-Also refer to: [1447].

m.p. 113-114° [454], 110° [909] [1099].

2-(Acetyloxy)-1-[4-(acetyloxy)-2-hydroxyphenyl]ethanone

$C_{12}H_{12}O_6$ mol.wt. 252.22



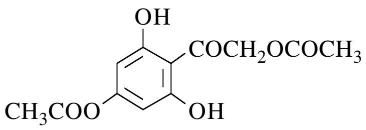
Syntheses

-Preparation by reaction of ammonia with fisetol triacetate (m.p. 94°) in ethanol for 30 min at r.t. (93%) [1574].
-Also obtained by adding acetic anhydride to a suspension of fisetol sodium salt in a water/ethyl ether mixture (27%) [1574].
-Also obtained by adding, with stirring and cooling, a solution of fisetol (m.p. 189-190°) in aqueous sodium hydroxide to a solution of acetic anhydride in chloroform (or benzene). Then, the mixture was maintained for 10 min at r.t. (19%) [1574].

m.p. 99-100° [1574]; UV [1574].

2-(Acetyloxy)-1-[4-(acetyloxy)-2,6-dihydroxyphenyl]ethanone

$C_{12}H_{12}O_7$ mol.wt. 268.22



Syntheses

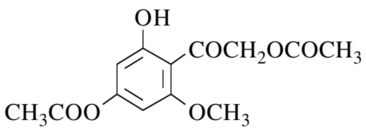
-Obtained by partial acetylation of α-hydroxyphloracetophenone with acetic anhydride in chloroform in the presence of aqueous sodium hydroxide, for 24 h at r.t. (31%) [1574].

-Also obtained by partial deacetylation of α-hydroxyphloracetophenone tetraacetate (m.p. 109-110°) in ethanol with ammonia, for 1.5 h at r.t. (30%) [1574].

m.p. 167-169° [1574]; UV [1574].

2-(Acetyloxy)-1-[4-(acetyloxy)-2-hydroxy-6-methoxyphenyl]ethanone

$C_{13}H_{14}O_7$ mol.wt. 282.25



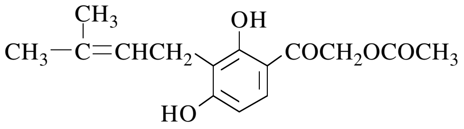
Synthesis

-Obtained by reaction of 4,α-diacetoxy-2,6-dihydroxyacetophenone with diazomethane in ethyl ether at 0° (37%) [1574].

m.p. 121° [1574].

2-(Acetyloxy)-1-[2,4-dihydroxy-3-(3-methyl-2-butenyl)phenyl]ethanone

[63124-25-4] $C_{15}H_{18}O_5$ mol.wt. 278.30



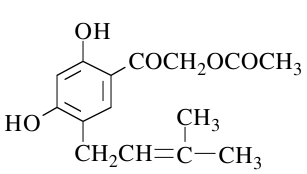
Synthesis

-Obtained (poor yield) by reaction of 2-methyl-3-buten-2-ol with 2,4-dihydroxy-α-(acetoxy)acetophenone in dioxane in the presence of boron trifluoride etherate at 50-60° for 3 h (6%) [1474].

m.p. 147-148° [1474]; ^{1}H NMR [1474], IR [1474].

2-(Acetyloxy)-1-[2,4-dihydroxy-5-(3-methyl-2-butenyl)phenyl]ethanone

[63124-24-3] $C_{15}H_{18}O_5$ mol.wt. 278.30



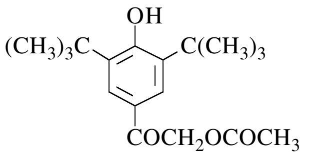
Synthesis

-Obtained by reaction of 2-methyl-3-buten-2-ol with 2,4-dihydroxy-α-(acetoxy)acetophenone in dioxane in the presence of boron trifluoride etherate at 50-60° for 3 h (20%) [1474].

m.p. 129-130° [1474]; ^{1}H NMR [1474], IR [1474].

2-(Acetyloxy)-1-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]ethanone

[28441-16-9] $C_{18}H_{26}O_4$ mol.wt. 306.40



Syntheses

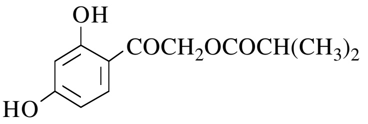
-Preparation by reaction of acetic acid with 3,5-di-tert-butyl-4-hydroxy-α-bromoacetophenone in toluene in the presence of DBU, first at 0° for 1 h, then at r.t. overnight (79%) [1577].
-Also refer to: [451].

m.p. 103-105° [451] [1577].

7.2. *Compounds derived from other acyloxy- and phenacyloxyacetic acids*

2-(2,4-Dihydroxyphenyl)-2-oxoethyl 2-methylpropanoate

[63124-27-6] $C_{12}H_{14}O_5$ mol.wt. 238.24



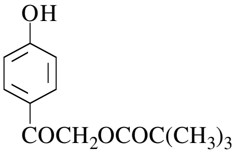
Synthesis

-Obtained by reaction of isobutyryloxyacetonitrile with resorcinol (Hoesch reaction) (40%) [1474].

m.p. 116-117° [1474];
^{1}H NMR [1474], IR [1474].

2-(4-Hydroxyphenyl)-2-oxoethyl 2,2-dimethylpropanoate

[230310-21-1] $C_{13}H_{16}O_4$ mol.wt. 236.27



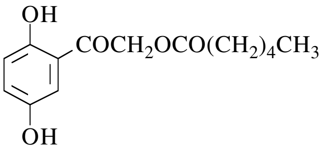
Synthesis

-Obtained by adding dropwise triethylamine over 15 min to a cooled solution of p-hydroxyphenacyl chloride and pivalic acid in acetonitrile in an ice bath and then refluxing for 3 h [1577].

m.p. 178°5 [1577]; ^{1}H NMR [1577].

2-(2,5-Dihydroxyphenyl)-2-oxoethyl hexanoate

[216301-66-5] $C_{14}H_{18}O_5$ mol.wt. 266.29



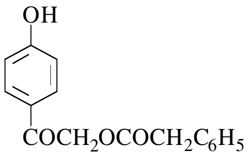
Synthesis

-Obtained by reaction of hexanoic acid with 2,5-dihydroxy-α-bromoacetophenone in acetonitrile in the presence of triethylamine at 70° for 4 h [216].

flash chromatography [216];
^{1}H NMR [216], IR [216], MS [216].

2-(4-Hydroxyphenyl)-2-oxoethyl benzeneacetate

[230310-20-0] $C_{16}H_{14}O_4$ mol.wt. 270.28



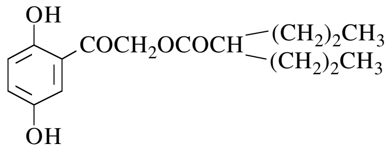
Synthesis

-Obtained by adding dropwise triethylamine over 15 min to a cooled solution of p-hydroxyphenacyl chloride and phenylacetic acid in acetonitrile in an ice bath and then refluxing for 3 h [1577].

m.p. 106-107° [1577]; ^{1}H NMR [1577].

2-(2,5-Dihydroxyphenyl)-2-oxoethyl 2-propylpentanoate *(so called Valproate)*

[216301-65-4] $C_{16}H_{22}O_5$ mol.wt. 294.35



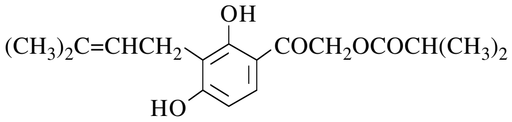
Synthesis

-Obtained by reaction of valproic acid with 2,5-dihydroxy-α-bromoacetophenone in acetonitrile in the presence of triethylamine at 70° for 4 h [216].

flash chromatography [216]; ^{1}H NMR [216], IR [216], MS [216].

2-[2,4-Dihydroxy-3-(3-methyl-2-butenyl)phenyl]-2-oxoethyl 2-methylpropanoate

[63124-29-8] $C_{17}H_{22}O_5$ mol.wt. 306.36



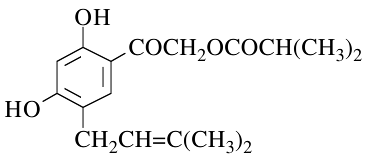
Synthesis

-Obtained (poor yield) by reaction of 2-methyl-3-buten-2-ol with 2,4-dihydroxy-α-(isobutyryloxy)-acetophenone in dioxane in the presence of boron trifluoride etherate at 50-60° for 3 h (5%) [1474].

m.p. 147-148° [1474]; ^{1}H NMR [1474], IR [1474].

2-[2,4-Dihydroxy-5-(3-methyl-2-butenyl)phenyl]-2-oxoethyl 2-methylpropanoate

[63124-28-7] $C_{17}H_{22}O_5$ mol.wt. 306.36



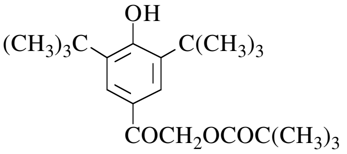
Synthesis

-Obtained by reaction of 2-methyl-3-buten-2-ol with 2,4-dihydroxy-α-(isobutyryloxy)acetophenone in dioxane in the presence of boron trifluoride etherate at 50-60° for 3 h (20%) [1474].

m.p. 122-123° [1474];
^{1}H NMR [1474], IR [1474].

2-[3,5-Bis(1,1-dimethylethyl)-4-hydroxyphenyl]-2-oxoethyl 2,2-dimethylpropanoate

[230310-24-4] $C_{21}H_{32}O_4$ mol.wt. 348.48



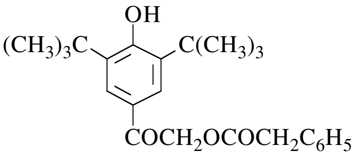
Synthesis

-Preparation by adding in one portion DBU to a solution of 2-bromo-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-ethanone and pivalic acid in toluene. The solution was stirred in ice for 1 h and then overnight at r.t. (70%) [1577].

m.p. 134-135°5 [1577]; ^{1}H NMR [1577].

2-[3,5-Bis(1,1-dimethylethyl)-4-hydroxyphenyl]-2-oxoethyl benzeneacetate

[230310-23-3] $C_{24}H_{30}O_4$ mol.wt. 382.50



Synthesis

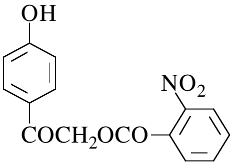
-Preparation by adding in one portion DBU to a solution of 2-bromo-1-(3,5-di-tert-butyl-4-hydroxyphenyl)ethanone and phenylacetic acid in toluene. The solution was stirred in an ice bath for 1 h and then at r.t. overnight (58%) [1577].

m.p. 63-63°5 [1577]; ^{1}H NMR [1577].

7.3. *Compounds derived from benzoyloxyacetic acids*

1-(4-Hydroxyphenyl)-2-[(2-nitrobenzoyl)oxy]ethanone

[130627-04-2] $C_{15}H_{11}NO_6$ mol.wt. 301.26

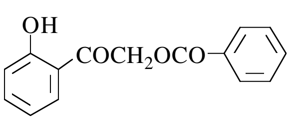


Syntheses

-Refer to: [1358] [1359].

2-(Benzoyloxy)-1-(2-hydroxyphenyl)ethanone

[52728-02-6] $C_{15}H_{12}O_4$ mol.wt. 256.26



Syntheses

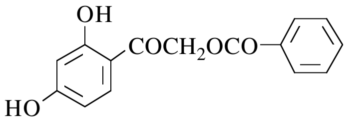
-Preparation by hydrolysis of 2-(benzoyloxy)-1-(2-acetoxyphenyl)ethanone (SM) with aqueous potassium hydroxide solution by gently warming for 10-15 min on a water bath maintained at 80° (75%) [879]. SM was obtained by cupric chloride-catalyzed decomposition of o-acetoxy-α-diazoacetophenone in dioxane solution in the presence of benzoic acid (86%, m.p. 110-111°).

-Also obtained by oxidative rearrangement of 2-benzoyloxy-α-bromoacetophenone in moist DMSO for 24 h at 20° (23%) [416].

m.p. 123-124° [879], 104-105° [416]. One of the reported melting points is obviously wrong. ^{1}H NMR [416].

2-(Benzoyloxy)-1-(2,4-dihydroxyphenyl)ethanone

[143091-87-6] $C_{15}H_{12}O_5$ mol.wt. 272.26



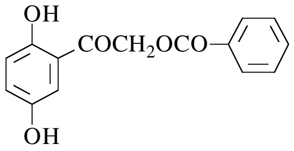
Syntheses

-Preparation by reaction of benzoyloxyacetonitrile (so called benzoylglycollonitrile) with resorcinol (Hoesch reaction), (79%) [626], (63%) [855].
-Also refer to: [390] [419] [730].

m.p. 202-203° [626], 200° [855].

2-(Benzoyloxy)-1-(2,5-dihydroxyphenyl)ethanone

[117421-24-6] $C_{15}H_{12}O_5$ mol.wt. 272.26



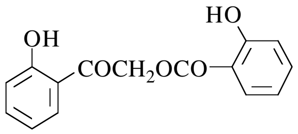
Synthesis

-Obtained by reaction of 2,5-dihydroxy-α-bromo-acetophenone with benzoic acid in the presence of triethylamine in acetonitrile at 45° for 4 h [1048].

MS [1048]; HPLC [1048].

2-(2-Hydroxyphenyl)-2-oxoethyl 2-hydroxybenzoate

[68176-44-3] $C_{15}H_{12}O_5$ mol.wt. 272.26



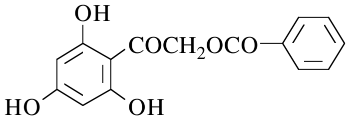
Synthesis

-Preparation by hydrolysis of 1-(2-acetoxyphenyl)-2-[(2-methoxybenzoyl)oxy]ethanone (SM) with aqueous potassium hydroxide solution by gently warming for 10-15 min on a water bath maintained at 80° (70%) [879]. SM was obtained by cupric chloride-catalyzed decomposition of o-acetoxy-α-diazoacetophenone in dioxane solution in the presence of o-acetoxybenzoic acid (35%, m.p. 124-125°).

m.p. 139-140° [879].

2-(Benzoyloxy)-1-(2,4,6-trihydroxyphenyl)ethanone

[65982-77-6] $C_{15}H_{12}O_6$ mol.wt. 288.26



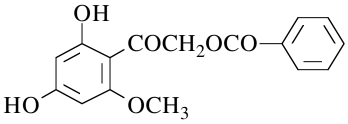
Syntheses

-Obtained by reaction of benzoyloxyacetonitrile with phloroglucinol (Hoesch reaction) [847] [933] [1257] [1362], (89%) [291], (67%) [626].
-Also refer to: [390] [589] [670] [856] [1126].

m.p. 235° [291], 234-235° [626], 220-225° [390].

2-(Benzoyloxy)-1-(2,4-dihydroxy-6-methoxyphenyl)ethanone

$C_{16}H_{14}O_6$ mol.wt. 302.28



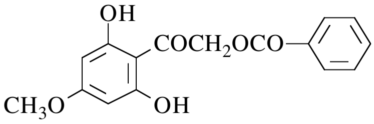
Synthesis

-Obtained by reaction of benzoyloxyacetonitrile with phloroglucinol monomethyl ether (Hoesch reaction) (68%) [847].

m.p. 145° [847].

2-(Benzoyloxy)-1-(2,6-dihydroxy-4-methoxyphenyl)ethanone

$C_{16}H_{14}O_6$ mol.wt. 302.28



Syntheses

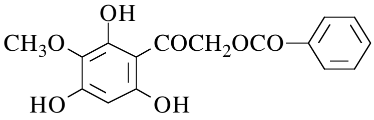
-Obtained by partial methylation of α-(benzoyloxy)phloroacetophenone with diazomethane in ethyl ether for 4 h at 5° (37%) [390] or in a methanol/ethyl ether mixture for 1 h at 0° (27%) [847].

-Also refer to: [1362].

m.p. 215-217° [390], 211° [847].

2-(Benzoyloxy)-1-(2,4,6-trihydroxy-3-methoxyphenyl)ethanone

[1162-73-8] $C_{16}H_{14}O_7$ mol.wt. 318.28



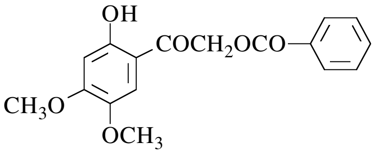
Syntheses

-Obtained by reaction of benzoyloxyacetonitrile with iretol (Hoesch reaction) [1087], (28%) [418].
-Also refer to: [648].

m.p. 227-229° [418];
^1H NMR [418], IR [418], UV [418].

2-(Benzoyloxy)-1-(2-hydroxy-4,5-dimethoxyphenyl)ethanone

$C_{17}H_{16}O_6$ mol.wt. 316.31



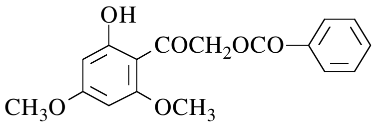
Synthesis

-Obtained by reaction of benzoyloxyacetonitrile with 3,4-dimethoxyphenol (Hoesch reaction) (17%) [739].

m.p. 128° [739].

2-(Benzoyloxy)-1-(2-hydroxy-4,6-dimethoxyphenyl)ethanone

[147437-71-6] $C_{17}H_{16}O_6$ mol.wt. 316.31



Syntheses

-Preparation by reaction of benzoyloxyacetonitrile with phloroglucinol dimethyl ether (Hoesch reaction) (56%) [847].

-Preparation by reaction of benzoyloxyacetonitrile with phloroglucinol (Hoesh reaction), followed by partial methylation of the obtained ketone with dimethyl sulfate [1085].

-Preparation by partial methylation of α-(benzoyloxy)phloroacetophenone with excess diazomethane in ethyl ether for 2 h (50%) [847] or for 4 h at 5° (6%) [390].

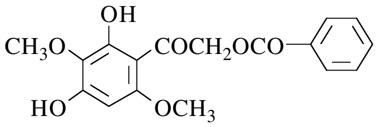
-Also refer to: [1141].

m.p. 135° [847], 132° [390], 120-122° [1141]. One of the reported melting points is obviously wrong.

^1H NMR [1141], ^{13}C NMR [1141], IR [1141], UV [1141], MS [1141].

2-(Benzoyloxy)-1-(2,4-dihydroxy-3,6-dimethoxyphenyl)ethanone

[7741-48-2] $C_{17}H_{16}O_7$ mol.wt. 332.31



Syntheses

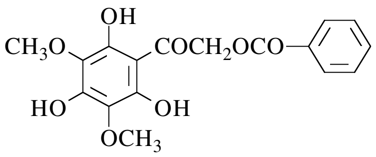
-Preparation by hydrogenation of 2-(benzoyloxy)-1-[4-(benzyloxy)-2-hydroxy-3,6-dimethoxyphenyl]ethanone in ethyl acetate in the presence of Pd/C (86%) [531].

-Also obtained by reaction of benzoyloxyacetonitrile with 2,5-dimethoxyresorcinol (Hoesch reaction) (51%) [651].

m.p. 177° [651], 175-176° [531]; UV [531] [651].

2-(Benzoyloxy)-1-(2,4,6-trihydroxy-3,5-dimethoxyphenyl)ethanone

[1167-74-4] $C_{17}H_{16}O_8$ mol.wt. 348.31



Syntheses

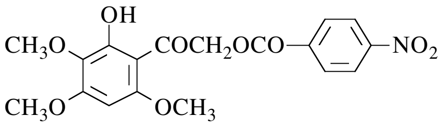
-Obtained by reaction of benzoyloxyacetonitrile with 2,4-dimethoxyphloroglucinol (Hoesch reaction) (12-15%) [418].

-Also refer to: [1056].

m.p. 139-142° [418]; ^1H NMR [418], IR [418], UV [418].

1-(2-Hydroxy-3,4,6-trimethoxyphenyl)-2-[(4-nitrobenzoyl)oxy]ethanone

[116512-01-7] $C_{18}H_{17}NO_9$ mol.wt. 391.33



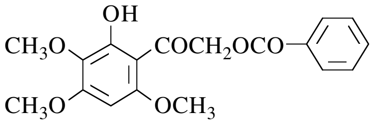
Synthesis

-Preparation by treatment of 2,3,4,6-tetramethoxy-α-(p-nitrobenzoyloxy)acetophenone with aluminium chloride in acetonitrile at 60° for 2 h (90%) [650].

m.p. 173-174° [650]; ^{1}H NMR [650].

2-(Benzoyloxy)-1-(2-hydroxy-3,4,6-trimethoxyphenyl)ethanone

[7741-49-3] $C_{18}H_{18}O_7$ mol.wt. 346.34



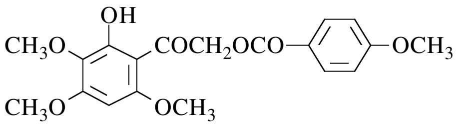
Synthesis

-Preparation by partial methylation of 2-(benzoyloxy)-1-(2,4-dihydroxy-3,6-dimethoxyphenyl)ethanone with diazomethane (71%) [531].

m.p. 172-174° [531]; UV [531].

2-(2-Hydroxy-3,4,6-trimethoxyphenyl)-2-oxoethyl 4-methoxybenzoate

[116512-00-6] $C_{19}H_{20}O_8$ mol.wt. 376.36



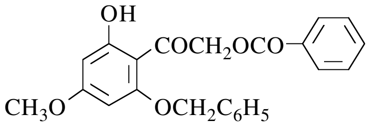
Synthesis

-Preparation by treatment of 2,3,4,6-tetramethoxy-α-(p-methoxybenzoyloxy)acetophenone with aluminium chloride in acetonitrile at 60° for 2 h (90%) [650].

m.p. 151-152° [650]; ^{1}H NMR [650].

2-(Benzoyloxy)-1-[2-hydroxy-4-methoxy-6-(phenylmethoxy)phenyl]ethanone

[14585-08-1] $C_{23}H_{20}O_6$ mol.wt. 392.41



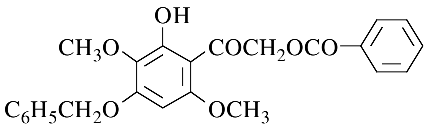
Synthesis

-Obtained by reaction of benzyl chloride with α-benzoyloxy-2,6-dihydroxy-4-methoxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone for 3.5 h (17%) [1362].

m.p. 151-153° [1362].

2-(Benzoyloxy)-1-[2-hydroxy-3,6-dimethoxy-4-(phenylmethoxy)phenyl]ethanone

[10048-37-0] $C_{24}H_{22}O_7$ mol.wt. 422.43



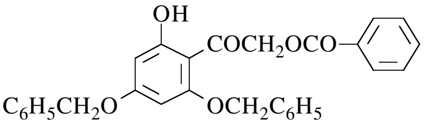
Synthesis

-Obtained by reaction of benzoyloxyacetonitrile with 1,3-bis(benzyloxy)-2,4-dimethoxybenzene (Hoesch reaction) (32%) [531].

m.p. 150-151° [531]; UV [531].

2-(Benzoyloxy)-1-[2-hydroxy-4,6-bis(phenylmethoxy)phenyl]ethanone

[14585-09-2] $C_{29}H_{24}O_6$ mol.wt. 468.51



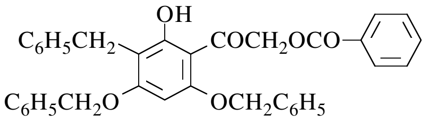
Synthesis

-Obtained by reaction of benzyl chloride with α-(benzoyloxy)phloroacetophenone in the presence of potassium carbonate in refluxing acetone for 2 h (12%) [1362] or for 26 h (13%) [589].

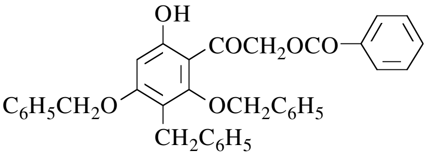
m.p. 140° [589], 136° [1362]; UV [589].

2-(Benzoyloxy)-1-[2-hydroxy-4,6-bis(phenylmethoxy)-3-(phenylmethyl)phenyl]ethanone
or
2-(Benzoyloxy)-1-[6-hydroxy-2,4-bis(phenylmethoxy)-3-(phenylmethyl)phenyl]ethanone

$C_{36}H_{30}O_6$ mol.wt. 558.63



or



Synthesis

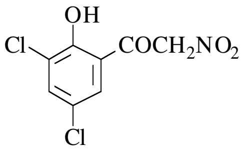
-Obtained by reaction of benzyl chloride with α-(benzoyloxy)phloracetophenone in refluxing acetone for 26 h in the presence of potassium carbonate (7%) or in the presence of potassium carbonate and sodium iodide in the same time (12%). The same result was obtained using only benzyl bromide [589].

m.p. 182° [589]; UV [589].

Chapter 8. Compounds derived from nitroacetic acids

1-(3,5-Dichloro-2-hydroxyphenyl)-2-nitroethanone

[60795-15-5] $C_8H_5Cl_2NO_4$ mol.wt. 250.04



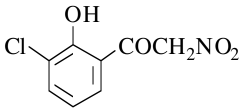
Synthesis

-Preparation by treatment of 6,8-dichloro-4-hydroxy-3-nitrocoumarin with 4% potassium hydroxide solution at r.t. for 24 h (85%) [1221].

m.p. 137° [1221]; IR [1221].

1-(3-Chloro-2-hydroxyphenyl)-2-nitroethanone

[60795-09-7] $C_8H_6ClNO_4$ mol.wt. 215.59



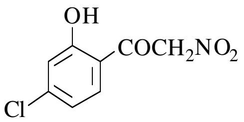
Synthesis

-Preparation by treatment of 8-chloro-4-hydroxy-3-nitrocoumarin with 4% potassium hydroxide solution at r.t. for 24 h (83%) [1221].

m.p. 103° [1221]; IR [1221].

1-(4-Chloro-2-hydroxyphenyl)-2-nitroethanone

[60795-11-1] $C_8H_6ClNO_4$ mol.wt. 215.59



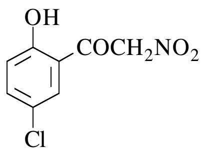
Synthesis

-Preparation by treatment of 7-chloro-4-hydroxy-3-nitrocoumarin with 4% potassium hydroxide solution at r.t. for 24 h (73%) [1221].

m.p. 117-118° [1221]; IR [1221].

1-(5-Chloro-2-hydroxyphenyl)-2-nitroethanone

[60795-14-4] $C_8H_6ClNO_4$ mol.wt. 215.59



Syntheses

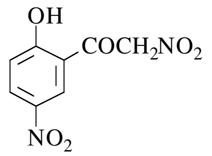
-Preparation by treatment of 6-chloro-4-hydroxy-3-nitrocoumarin with 4% potassium hydroxide solution at r.t. for 24 h (65%) [1221].

-Also refer to: [1134].

m.p. 112° [1221]; IR [1221].

1-(2-Hydroxy-5-nitrophenyl)-2-nitroethanone

[59507-91-4] $C_8H_6N_2O_6$ mol.wt. 226.15



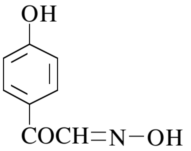
Synthesis

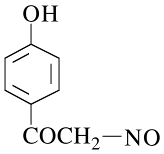
-Preparation by heating a solution of 3,6-dinitro-4-hydroxycoumarin (m.p. 188°) in 10% aqueous sodium hydroxide at 65° for 2 h, then cooling and acidification with hydrochloric acid (91%) [145].

m.p. 160° [145]; ^{1}H NMR [145].

1-(4-Hydroxyphenyl)-2-nitrosoethanone

[143527-88-2] $C_8H_7NO_3$ mol.wt. 165.15



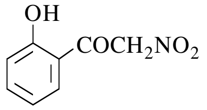


Synthesis

-Refer to: [1427].

1-(2-Hydroxyphenyl)-2-nitroethanone

[29378-60-7] $C_8H_7NO_4$ mol.wt. 181.15



Syntheses

-Preparation by alkaline degradation of 4-hydroxy-3-nitrocoumarin [1407] — m.p. 177° (d) — with 5% sodium hydroxide,
*for 1.5 h at 50-60° (95%) [145];
*for 24 h at 20°, (79%) [664], (75%) [1221].

-The same compound was isolated in reactions of either some *coumarins* or some *chromenes* with 5% sodium hydroxide for 1 h at r.t. or by heating at 90-95° (70-90%) [584]:

coumarins:

3-nitro-4-(pyridylamino)coumarin	m.p. 224-225°
3-nitro-4-(3-methyl-2-pyridylamino)coumarin	m.p. 227-229°
3-nitro-4-(4-methyl-2-pyridylamino)coumarin	m.p. 243-244°
3-nitro-4-(5-methyl-2-pyridylamino)coumarin	m.p. 225-226°
3-nitro-4-(6-methyl-2-pyridylamino)coumarin	m.p. 250-252°

chromenes:

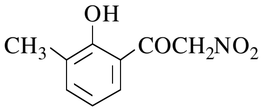
2-Hydroxy-3-nitro-4-(3-methyl-2-pyridylimino)-4*H*-chromene	m.p. 245-246°
2-Hydroxy-3-nitro-4-(4-methyl-2-pyridylimino)-4*H*-chromene	m.p. 250-252°
2-Hydroxy-3-nitro-4-(5-methyl-2-pyridylimino)-4*H*-chromene	m.p. 233-234°
2-Hydroxy-3-nitro-4-(6-methyl-2-pyridylimino)-4*H*-chromene	m.p. 274-275°

-Also refer to: [336] [552] [1045] [1134] [1135] [1220].

m.p. 106-107° [664], 106° [145], 105-106° [1221], 96-97° [584];
^{1}H NMR [145] [584] [1221], IR [145] [584] [1221].

1-(2-Hydroxy-3-methylphenyl)-2-nitroethanone

[60795-08-6] $C_9H_9NO_4$ mol.wt. 195.17



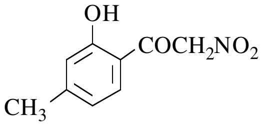
Synthesis

-Preparation by treatment of 4-hydroxy-8-methyl-3-nitrocoumarin with 4% potassium hydroxide solution at r.t. for 24 h (80%) [1221].

m.p. 126° [1221]; ^{1}H NMR [1221], IR [1221].

1-(2-Hydroxy-4-methylphenyl)-2-nitroethanone

[60795-10-0] $C_9H_9NO_4$ mol.wt. 195.17



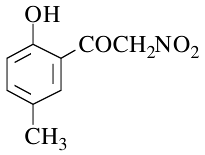
Synthesis

-Preparation by treatment of 4-hydroxy-7-methyl-3-nitrocoumarin with 4% potassium hydroxide solution at r.t. for 24 h (72%) [1221].

m.p. 114° [1221]; IR [1221].

1-(2-Hydroxy-5-methylphenyl)-2-nitroethanone

[60795-13-3] $C_9H_9NO_4$ mol.wt. 195.17



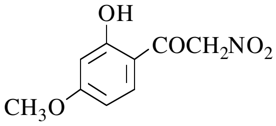
Syntheses

-Preparation by treatment of 4-hydroxy-6-methyl-3-nitrocoumarin with 4% potassium hydroxide solution at r.t. for 24 h (88%) [1221].
-Also refer to: [1134] [1135] [1136].

m.p. 134° [1221]; ^{1}H NMR [1221], IR [1221].

1-(2-Hydroxy-4-methoxyphenyl)-2-nitroethanone

[60795-12-2] $C_9H_9NO_5$ mol.wt. 211.17



Syntheses

-Preparation by treatment of 4-hydroxy-7-methoxy-3-nitrocoumarin with 4% potassium hydroxide solution at r.t. for 24 h (76%) [1221].
-Also refer to: [336] [1021].

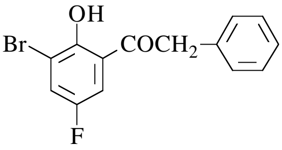
m.p. 140° [1221]; IR [1221].

Chapter 9. Compounds derived from arylacetic acids

9.1. *Compounds derived from phenylacetic acid*

1-(3-Bromo-5-fluoro-2-hydroxyphenyl)-2-phenylethanone

[4108-04-7] $C_{14}H_{10}BrFO_2$ mol.wt. 309.13



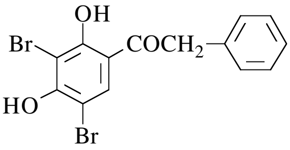
Syntheses

-Preparation by Fries rearrangement of 2-bromo-4-fluorophenyl phenylacetate with aluminium chloride, according to the methods [1313],
*without solvent at 130° for 2 h [742];
*in nitrobenzene at 25° for 6 h [742].
-Also refer to: [253].

m.p. 130° [253]; b.p.$_{1.5}$ 154-155° [742].

1-(3,5-Dibromo-2,4-dihydroxyphenyl)-2-phenylethanone

[19816-40-1] $C_{14}H_{10}Br_2O_3$ mol.wt. 386.04



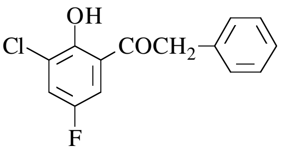
Syntheses

-Obtained by reaction of bromine (2 mol) with 4-phenylacetylresorcinol in acetic acid for 48 h [182].
-Also obtained by Friedel-Crafts acylation of 2,4-dibromoresorcinol with phenylacetyl chloride in nitrobenzene in the presence of aluminium chloride, first at r.t. overnight, then heating on a steam bath for 4 h (44%) [307].

m.p. 190° [307], 180° [182].

1-(3-Chloro-5-fluoro-2-hydroxyphenyl)-2-phenylethanone

[4108-05-8] $C_{14}H_{10}ClFO_2$ mol.wt. 264.68



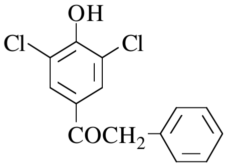
Syntheses

-Preparation by Fries rearrangement of 2-chloro-4-fluorophenyl phenylacetate with aluminium chloride, according to the methods [1313],
*without solvent at 130° for 2 h [742];
*in nitrobenzene at 25° for 6 h [742].
-Also obtained by Friedel-Crafts acylation of p-fluoroanisole, followed by demethylation and chlorination of the obtained ketone [253].

m.p. 122° [253]; b.p.$_{1\text{-}1.5}$ 209-210° [742].

1-(3,5-Dichloro-4-hydroxyphenyl)-2-phenylethanone

[73048-86-9] $C_{14}H_{10}Cl_2O_2$ mol.wt. 281.11



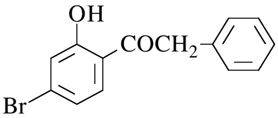
Synthesis

-Obtained by DDQ oxidation of 1-(3,5-dichloro-4-hydroxyphenyl)-2-phenylethanol in dioxane at r.t. for 16 h (82%) [144].

m.p. 132-135° [144]; ^{1}H NMR [144].

1-(4-Bromo-2-hydroxyphenyl)-2-phenylethanone

[54981-35-0] $C_{14}H_{11}BrO_2$ mol.wt. 291.14



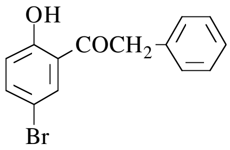
Synthesis

-Obtained by Fries rearrangement of 3-bromophenyl phenylacetate with aluminium chloride in carbon disulfide for 1 h at r.t. [1391].

m.p. 68° [1391].

1-(5-Bromo-2-hydroxyphenyl)-2-phenylethanone

[54981-34-9] $C_{14}H_{11}BrO_2$ mol.wt. 291.14



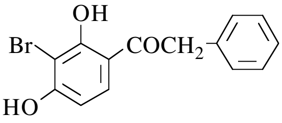
Synthesis

-Obtained by Fries rearrangement of 4-bromophenyl phenylacetate with aluminium chloride in carbon disulfide for 1 h at r.t. [1391].

m.p. 70° [1391].

1-(3-Bromo-2,4-dihydroxyphenyl)-2-phenylethanone

[19816-35-4] $C_{14}H_{11}BrO_3$ mol.wt. 307.14



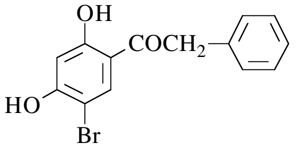
Synthesis

-Obtained by Friedel-Crafts acylation of 2-bromoresorcinol with phenylacetyl chloride in nitrobenzene in the presence of aluminium chloride, first at r.t. overnight, then heating on a steam bath for 4 h (50%) [307].

m.p. 195° [307].

1-(5-Bromo-2,4-dihydroxyphenyl)-2-phenylethanone

[92152-59-5] $C_{14}H_{11}BrO_3$ mol.wt. 307.14



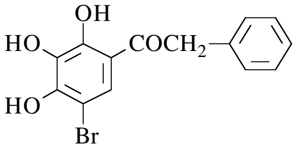
Syntheses

-Obtained by reaction of bromine (1 mol) with 4-phenylacetylresorcinol in acetic acid at r.t. for 24 h [182].
-Also obtained by Friedel-Crafts acylation [283] of 4-bromoresorcinol with phenylacetyl chloride in nitrobenzene in the presence of aluminium chloride [1259].
-Also refer to: [282].

m.p. 112° [283] [1259], 103° [182].

1-(5-Bromo-2,3,4-trihydroxyphenyl)-2-phenylethanone

$C_{14}H_{11}BrO_4$ mol.wt. 323.14



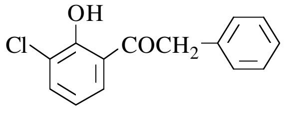
Synthesis

-Obtained by reaction of bromine with 4-phenylacetylpyrogallol in acetic acid [252], at r.t. for 24 h [182].

m.p. 164° [252], 155-156° [182].

1-(3-Chloro-2-hydroxyphenyl)-2-phenylethanone

[70331-83-8] $C_{14}H_{11}ClO_2$ mol.wt. 246.69



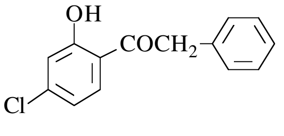
Syntheses

-Preparation by Friedel-Crafts reaction [876].
-Also refer to: [877].

protonation constants [725];
complexes with Cu (II), Ni (II) and Co (II) [725].

1-(4-Chloro-2-hydroxyphenyl)-2-phenylethanone

[107410-55-9] $C_{14}H_{11}ClO_2$ mol.wt. 246.69



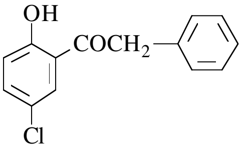
Synthesis

-Preparation by Fries rearrangement of m-chlorophenyl phenylacetate with aluminium chloride, first in carbon disulfide for 1 h, then, after elimination of the solvent, at 100° for 5 h (58%) [239].

m.p. 62-64° [239].

1-(5-Chloro-2-hydroxyphenyl)-2-phenylethanone

[126260-45-5] $C_{14}H_{11}ClO_2$ mol.wt. 246.69



Syntheses

-Obtained by Friedel-Crafts acylation of p-chlorophenol with phenylacetic acid in the presence of boron trifluoride at 160° for 4 h in a sealed tube (68%) [796].

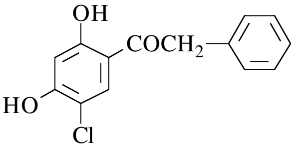
-Also obtained by Fries rearrangement of p-chlorophenyl phenylacetate with aluminium chloride in refluxing chlorobenzene for 4 h (25%) [1554].

-Also obtained by Friedel-Crafts acylation of p-chloroanisole with phenylacetyl chloride in the presence of aluminium chloride in refluxing carbon disulfide for 5 h (25%) [1541].

m.p. 69° [796], 66-67° [1541], 64-65° [1554];
b.p.$_{0.3}$ 153-154° [796], b.p.$_{30}$ 280-285° [1541].

1-(5-Chloro-2,4-dihydroxyphenyl)-2-phenylethanone

[92103-22-5] $C_{14}H_{11}ClO_3$ mol.wt. 262.69



Syntheses

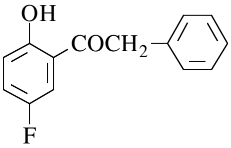
-Preparation by Friedel-Crafts acylation [283] of 4-chlororesorcinol with phenylacetyl chloride in nitrobenzene in the presence of aluminium chloride, first at 10°, then at r.t. for 36 h (73%) [1259].

-Also refer to: [282].

m.p. 121° [1259], 120° [283].

1-(5-Fluoro-2-hydroxyphenyl)-2-phenylethanone

[343-59-9] $C_{14}H_{11}FO_2$ mol.wt. 230.24



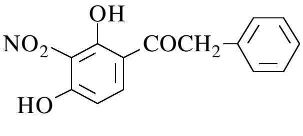
Syntheses

-Preparation by Fries rearrangement of p-fluorophenyl phenylacetate with aluminium chloride,
*at 150-180° for 20 min (85%) [838];
*at 130° for 2 h (77%) [1393], according to the method [249];
*at 130° for 2 h [742], according to the method [1313];
*in nitrobenzene at 25° for 6 h [742], according to the method [1313].

m.p. 85° [838]; b.p.$_{1.5}$ 175-179° [742], b.p.$_{1-2}$ 200-205° [1393].

1-(2,4-Dihydroxy-3-nitrophenyl)-2-phenylethanone

[19816-52-5] $C_{14}H_{11}NO_5$ mol.wt. 273.25



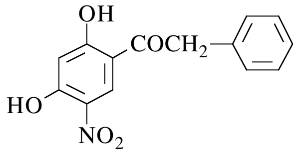
Synthesis

-Preparation by Fries rearrangement of 2,6-di(phenylacetoxy)nitrobenzene (m.p. 124°) with aluminium chloride in nitrobenzene, first at r.t. overnight, then at 70-80° for 30 min (72%) [307].

m.p. 109° [307].

1-(2,4-Dihydroxy-5-nitrophenyl)-2-phenylethanone

$C_{14}H_{11}NO_5$ mol.wt. 273.25



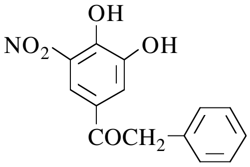
Synthesis

-Obtained by reaction of fuming nitric acid (d = 1.5) with 4-phenylacetylresorcinol in acetic acid in an ice bath for 48 h [182].

m.p. 156-157° [182].

1-(3,4-Dihydroxy-5-nitrophenyl)-2-phenylethanone

[274925-86-9] $C_{14}H_{11}NO_5$ mol.wt. 273.25



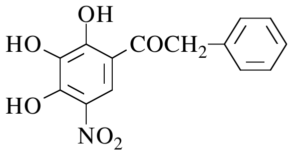
Synthesis

-Preparation by treatment of 1-(4-hydroxy-3-methoxy-5-nitrophenyl)-2-phenylethanone with aluminium chloride in refluxing ethyl acetate/pyridine mixture for 2 h (99%) [885] [887].

m.p. 178-179° [887], 177°6-178°8 [885]; ^{1}H NMR [885] [887], ^{13}C NMR [885] [887], IR [885] [887]; HPLC [885], IR [885] [887].

1-(2,3,4-Trihydroxy-5-nitrophenyl)-2-phenylethanone

$C_{14}H_{11}NO_6$ mol.wt. 289.24



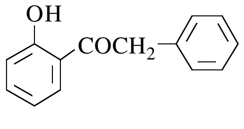
Synthesis

-Obtained by reaction of fuming nitric acid (d = 1.5) with 4-phenylacetylpyrogallol in acetic acid in an ice bath for 48 h [182].

m.p. 179-180° [182].

1-(2-Hydroxyphenyl)-2-phenylethanone

[2491-31-8] $C_{14}H_{12}O_2$ mol.wt. 212.25



Syntheses

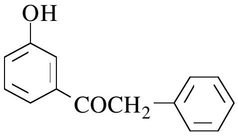
-Obtained by Fries rearrangement of phenyl phenylacetate,
*with aluminium chloride,
-without solvent, between 80 to 130° for 1 h (72%) [38], at 140° for 3 h (60%) [882] [883] [884], at 120° for 4 h [280] [475] or at 60° for 4 h (26%) [1553];
-in nitrobenzene at 60° for 4 h (14%) [1551], at r.t. for 24 h (4%) [882] [883];
-in nitroethane at r.t. for 24 h (< 13%) [1550];
-in chlorobenzene at 50° for 4 h (21%) [1553];
*with titanium tetrachloride in chlorobenzene at 50° for 4 h (< 5%) [1553];
*with polyphosphoric acid at 100° (1%) [1068];
*with or without 20% *Bleicherde* at 200° for 9 h (poor yields) [1369].

-Also obtained by stirring a mixture of S-[3-hydroxy-4-(phenylacetyl)phenyl] dimethylcarbamothioate, Raney nickel and ethanol at r.t. for 1 h (67%) [907].
-Also obtained by photo-Fries rearrangement of phenyl phenylacetate,
*in the presence of α- or β-cyclodextrin in organic solvents [1475];
*included in a Nafion membrane, at r.t. for 7 h (quantitative yield) [1476].
-Also obtained by acylation of phenol with phenylacetic acid,
*in the presence of boron trifluoride etherate under argon on a water bath for 1.5 h (23%) [1516];
*in the presence of zinc chloride and phosphorous oxychloride for 24 h at r.t. (21%) [391];
*in the presence of polyphosphoric acid at 100° (4%) [1068].
-Also obtained by degradation of 3-phenyl-4-hydroxycoumarin in refluxing 30% ethanolic hydrogen chloride for 1 h (56%) [387].
-Also obtained by demethylation of 2-methoxyphenyl benzyl ketone (oil, b.p.$_{0.001}$ 130-140°),
*with 47% hydrobromic acid (d = 1.5) in acetic acid for 5 h at reflux (87%) [475] or for 10 h on a steam bath (61%) [777];
*with aluminium chloride in nitrobenzene on a steam bath for 1 h (36%) [777].
-Also obtained by hydrolysis of (2-methoxybenzoyl)phenylacetonitrile (m.p. 108-109°) in acetic acid,
*with concentrated hydrochloric acid on a steam bath for 20 h (48%) [777];
*with 47% hydrobromic acid on a steam bath for 10 h (34%) [777].
-Also obtained from ethyl (2-methoxybenzoyl)phenylacetate (m.p. 67-68°),
*with boiling pyridinium chloride for 20 min (ca. 220°) (47%) [779];
*in acetic acid with concentrated hydrochloric acid for 15 h on a steam bath (35%) [777].
-Also obtained by heating under reflux flavone with 5% aqueous sodium hydroxide [335].
-Also refer to: [289] [412] [462] [585] [608] [609] [747] [844] [1271] [1334].
N.B.: Complexes with Mn (II) [1338], Ni (II) [1338], Hg (II) [1338] and Co (II) [1338] [1339].

m.p. 60-61° [907], 60° [280] [475], 59° [289], 58-60° [1553], 57-58° [779], 56-57° [777], 55° [387] [882] [883] [884] [1369].
b.p.$_{0.004}$ 150-155° [777], b.p.$_{23}$ 165° [1369];
^{1}H NMR [907], IR [882] [883] [884], UV [882] [883] [884],
MS [907]; GC [1476]; GC-MS [1476].

1-(3-Hydroxyphenyl)-2-phenylethanone

[332072-68-1] $C_{14}H_{12}O_2$ mol.wt. 212.25



Synthesis

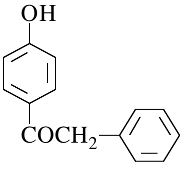
-Obtained by electrolysing in an undivided cell a DMF solution containing 3-iodophenol, chloromethylbenzene, iron pentacarbonyl and a catalytic amount of a nickel-2,2'-bipyridine complex (57%) [406].
-This compound seems to have not been described previously.

It is not mentioned in the ***Chemical Abstracts*** between 1907 (volume 1) and 2000 (volume 133) under the various denominations, namely: m-Hydroxy-α-phenylacetophenone, 3'-Hydroxy-2-phenyl-acetophenone and actually 1-(3-Hydroxyphenyl)-2-phenylethanone, neither in the ***Beilsteins Handbuch der Organischen Chemie*** under the denomination [3-Oxy-phenyl]-benzyl-keton. This ketone might very likely be prepared more simply by diazotization of the 1-(3-aminophenyl)-2-phenylethanone [55251-36-0], an amino ketone known for a long time [1029].

^{1}H NMR [406], ^{13}C NMR [406], IR [406], MS [406].

1-(4-Hydroxyphenyl)-2-phenylethanone

[2491-32-9] $C_{14}H_{12}O_2$ mol.wt. 212.25



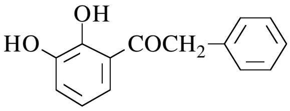
Syntheses

-Obtained by reaction of phenylacetic acid with phenol,
*in the presence of zinc chloride (Nencki reaction),
-at 170-200° (reflux) for 1.5 h (20%) [641] [1525];
-at 170-180° [1443], for 2 h (15%) [904];
*in the presence of zinc chloride and phosphorous oxychloride for 24 h at r.t. (75%) [391];
*in the presence of polyphosphoric acid in a boiling water bath for 15 min (28%) [1071] or at 100° (19%) [1068];
*in the presence of boron trifluoride at 80° for 2 h (87%) [798];
*in the presence of boron trifluoride etherate under argon on a water bath for 1.5 h (75%) [1516].
-Also obtained by Friedel-Crafts acylation of phenol with phenylacetyl chloride in nitrobenzene in the presence of aluminium chloride (60%) [904], at 80-90° for 1.5 h (61%) [987] or at ≤ 80° for 0.75 h (60-70%) [1525].
-Also obtained (by-product) by reaction of phenylacetyl chloride with anisole in benzene in the presence of stannic chloride between 55 to 75° for 1 h [641].
-Also obtained by Fries rearrangement of phenyl phenylacetate,
*with aluminium chloride,
-without solvent at 50° for 4 h (25%) [1553], at 80° for 4 h (72%) [1553], first in a water bath for 1 h, then at 120° for 4 h [280] [475] or at 140° for 3 h (10%) [882] [883] [884];
-in nitrobenzene at r.t. for 12 h (35%) [1550] or for 24 h (65%) [882] [883], at 50° for 4 h (64%) [1553], at 60° for 4 h (64%) [1551];
-in nitroethane at r.t. for 24 h (70%) [1550];
-in nitropropane at 70° for 6 h (30%) [1550];
*with polyphosphoric acid at 100° (8%) [1068];
*with titanium tetrachloride in chlorobenzene at 50° for 4 h (19%) [1553].
-Also obtained by diazotization of p-aminodeoxybenzoin [1084].
-Also obtained (poor yield) by heating phenyl phenylacetate with or without 20% of *Bleicherde* for 9 h at 200° [1369].
-Also obtained by photo-Fries rearrangement of phenyl phenylacetate in the presence of α- or β-cyclodextrin in organic solvents [1475].
-Also refer to: [166] [526] [539] [613] [617] [623] [790] [867] [1264] [1302] [1418] [1549].

m.p. 151° [280] [475], 149° [904], 148° [391], 146-147° [641], 145-147° [1553], 144° [1443] [1444], 143° [1071], 142° [798] [882] [883] [1525], 141° [1369], 139-142° [987], 129° [1084].
There is discrepancy between the different melting points.
b.p.$_1$ 220-230° [904]; IR [882] [883], UV [882] [883] [1443] [1444].

1-(2,3-Dihydroxyphenyl)-2-phenylethanone

[107410-01-5] $C_{14}H_{12}O_3$ mol.wt. 228.25



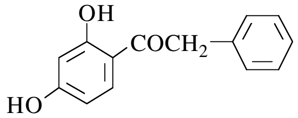
Syntheses

-Preparation by total demethylation of 2,3-dimethoxydesoxybenzoin (yellow oil, b.p.$_3$ 170-173°) with hydrobromic acid (d = 1.5) in refluxing acetic acid for 5 h (74%) [475].
-Also obtained by alkaline degradation of 8-hydroxyisoflavone (m.p. 222-224°) with sodium hydroxide in refluxing methanol for 1.5 h [475].

m.p. 79-81° [475]; paper chromatography [475].

1-(2,4-Dihydroxyphenyl)-2-phenylethanone

[3669-41-8] $C_{14}H_{12}O_3$ mol.wt. 228.25



Syntheses

-Preparation by Friedel-Crafts acylation of resorcinol with phenylacetyl chloride in the presence of aluminium chloride,

*in methylene chloride (85%) [877];

*in nitrobenzene at 70-80° for 15 min (< 80%) [496], at r.t. for 24 h (63%) [106] or for 2 days (60%) [182];

*in ethyl ether at r.t. for 24 h (43%) [601].

-Preparation by acylation of resorcinol with phenylacetyl chloride in boiling ethylene dichloride (84°), using a series of clay based catalysts (KSF, KSF/0, KP10, K10, K0, KS) (65-81%) [459], (60%) [152].

-Preparation by reaction of phenylacetic anhydride with resorcinol,

*in the presence of concentrated sulfuric acid as catalyst at 130° for some min (60%) [683];

*in the presence of boron trifluoride etherate for 2.5 h at 70-75° (48%) [1024].

-Preparation by reaction of phenylacetic acid with resorcinol,

*in the presence of boron trifluoride etherate under argon on a water bath for 1 h (89%) [1516];

*in the presence of boron trifluoride at 105-108° for 15 min, followed by hydrolysis of the obtained boron difluoride chelate (m.p. 154-155°) (78%) [1133] or at 90° for 1 h (66%) [1110];

*in the presence of boron trifluoride in chloroform (87%) [764];

*in the presence of zinc chloride (Nencki reaction) at 120° for 2.5 h (70%) [182], at 125-135° [404], at 140° for 15 min (10%) [496] or at 145-150° for 2 h [1443];

*in the presence of zinc chloride and phosphorous oxychloride for 24 h at r.t. (50%) [391];

*in the presence of 70% perchloric acid at 150° for 30 min (30%) [1003];

*in the presence of Amberlite IR-120, a cation exchange resin sulfonic acid type, at 160° for 2-3 h (41%) [1200]. **N.B.**: Zeokarb 225 was found to be as effective.

-Preparation by reaction of phenylacetonitrile with resorcinol (Hoesch reaction) [285] [873] [1019] [1145], (64%) [1345], (58%) [115], (40%) [992].

-Also obtained by heating 2-phenyl-4-benzylidene-7-hydroxy-[4*H*]-1-benzopyran (SM) with refluxing aqueous sodium hydroxide for 1 h. SM was obtained by condensation of 1,4-diphenyl-1,3-butanediol with resorcinol in acetic acid [245].

-Also obtained by degradation of 7-hydroxy-2-methyl-3-phenylchromone (m.p. 244-246°) with refluxing 5% aqueous sodium hydroxide for 3 h [182].

-Also obtained by treatment of ethyl (2,4-dimethoxybenzoyl)phenylacetate with boiling pyridinium chloride (ca. 220°) for 20 min (48%) [779].

-Also refer to: [282] [462] [463] [467] [585] [698] [701] [712] [718] [747] [839] [907] [1076] [1140] [1182] [1291] [1328] [1335] [1419] [1543].

N.B.: Complexes with Mn (II), Co (II), Ni (II) and Hg (II) [1338].

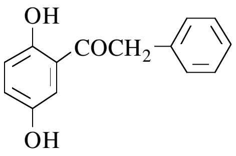
m.p. 116° [1443] [1444], 115-116° [182] [711],
115° [106] [245] [285] [764] [1003] [1110], 114-116° [1200],
114-115° [683] [718] [1019], 114° [496] [627], 113-115° [1133], 113-114° [601],
113° [391], 110-113° [779];

b.p.$_{10}$ 220-225° [404];

^{1}H NMR [992], IR [1133], UV [1019] [1133] [1443] [1444], MS [992].

1-(2,5-Dihydroxyphenyl)-2-phenylethanone

[52122-86-8] $C_{14}H_{12}O_3$ mol.wt. 228.25



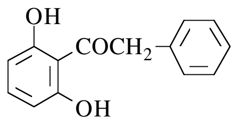
Syntheses

-Obtained by partial demethylation of 2,5-dimethoxyphenyl benzyl ketone,
*with hydriodic acid in acetic acid on a water bath for 2 h [110];
*with hydrobromic acid in acetic acid, first at 0°, then at reflux for 6 h [676].
-Also obtained by Friedel-Crafts acylation of hydroquinone with phenylacetyl chloride in the presence of aluminium chloride in nitrobenzene, keeping overnight, then on a water bath for 3 h [676] or at 70-80° for 15 min [496].
-Also obtained by acylation of hydroquinone with phenylacetic acid,
*in the presence of boron trifluoride etherate under argon on a water bath for 6 h (68%) [1516];
*in the presence of boron trifluoride (saturation) at 125° for 1.5 h (56%) [1110];
*in the presence of zinc chloride at 150° [496] (Nencki reaction).
-Also refer to: [206].

m.p. 170° [496], 113° [676], 112° [1110], 109°5 [110].
One of the reported melting points is obviously wrong.

1-(2,6-Dihydroxyphenyl)-2-phenylethanone

[13936-92-0] $C_{14}H_{12}O_3$ mol.wt. 228.25



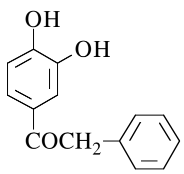
Syntheses

-Obtained by treatment of 3,5-dicarbomethoxy-2,6-dihydroxyphenyl benzyl ketone (m.p. 129-131°),
*with boiling 10% alcoholic caustic soda for 3 h. The obtained dicarboxylic acid was decarboxylated by boiling with water for 3 h (75%) [767];
*with refluxing 4% methanolic potassium hydroxide for 4 h, followed by refluxing 12 h in water (35%) [389].
-Also refer to: [585] [764].

m.p. 170° [767], 166-167° [389].

1-(3,4-Dihydroxyphenyl)-2-phenylethanone

[107410-02-6] $C_{14}H_{12}O_3$ mol.wt. 228.25



Syntheses

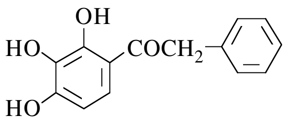
-Preparation by reaction of phenylacetic acid with pyrocatechol,
*in the presence of zinc chloride and phosphorous oxychloride for 24 h at r.t. (60%) [391];
*in the presence of phosphorous oxychloride for 2 h at 90-100° (59%) [987];
*in the presence of boron trifluoride in chloroform, first at 10°, then at r.t. overnight (36%) [474];
*in the presence of zinc chloride at 140-150° (Hoesch reaction) [496].

-Also obtained by total demethylation of 3,4-dimethoxydesoxybenzoin (m.p. 87-88°) with hydrobromic acid (d = 1.5) in refluxing acetic acid for 5 h [474].

m.p. 173-174° [474], 173° [391] [496], 168-170° [987].

2-Phenyl-1-(2,3,4-trihydroxyphenyl)ethanone

[22761-00-8] $C_{14}H_{12}O_4$ mol.wt. 244.25



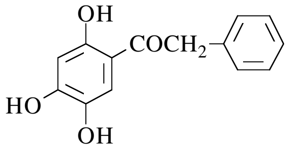
Syntheses

-Obtained by reaction of phenylacetic acid with pyrogallol,
*in the presence of zinc chloride at 150° for 30 min (Nencki reaction) [1443], (52%) [1095] or at 120° for 2.5 h (60%) [182];
*in the presence of Amberlite IR-120 cation exchange resin (sulfonic acid type) at 160° for 2-3 h (34%) [1200]. **N.B.**: Zeokarb 225 was found to be as effective;
*in the presence of 70% perchloric acid at 150° for 30 min (25%) [1003];
*in the presence of boron trifluoride in chloroform, first in ice cooling, then at r.t. overnight (96%) [764].
-Also obtained by Friedel-Crafts acylation of pyrogallol,
*with phenylacetyl chloride in nitrobenzene in the presence of aluminium chloride at r.t. for two days (50%) [182];
*with phenylacetic anhydride in the presence of boron trifluoride etherate for 2.5 h at 75-80° (26%) [1024].
-Also refer to: [698] [747] [1140].

m.p. 147° [1003], 144-145° [182], 141-142° [1095],
140-141° [764] [1443] [1444], 135-136° [1200].

2-Phenyl-1-(2,4,5-trihydroxyphenyl)ethanone

[787-06-4] $C_{14}H_{12}O_4$ mol.wt. 244.25



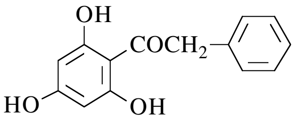
Syntheses

-Obtained by reaction of phenylacetonitrile with hydroxyhydroquinone (Hoesch reaction) (43%) [530].
-Also refer to: [1184].

m.p. 208-210° [530]; ^{13}C NMR [732].

2-Phenyl-1-(2,4,6-trihydroxyphenyl)ethanone

[727-71-9] $C_{14}H_{12}O_4$ mol.wt. 244.25



Syntheses

-Preparation by reaction of phenylacetonitrile with phloroglucinol (Hoesch reaction),
*in the presence of zinc chloride [141] [285] [1019] [1145], (44-45%) [106] [771], (39%) [1024];
*in the presence of boron trifluoride etherate (50%) [1024].
-Also obtained by reaction of phenylacetic acid with phloroglucinol in the presence of zinc chloride and phosphorous oxychloride for 24 h at r.t. (50%) [391].
-Also refer to: [559] [585] [698] [701] [747] [873] [988].

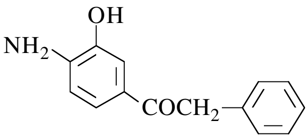
N.B.: Complexes with Mn (II), Co (II) Ni (II) and Hg (II) [1338].
The monohydrate of this ketone was at first obtained [106] [285]. The water of crystallisation is lost on heating the crystals at 90°.

m.p. 164-165° [1019], 163° [391], 162° [106] [285] [771];

IR [771], UV [771] [1019]; TLC [771].

1-(4-Amino-3-hydroxyphenyl)-2-phenylethanone

[54903-53-6] $C_{14}H_{13}NO_2$ mol.wt. 227.26



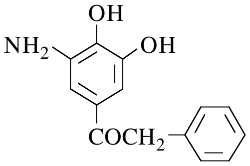
Syntheses

-Preparation from 6-phenylacetyl-benzoxazolinone by alkaline hydrolysis with boiling 10% aqueous sodium hydroxide solution for 4 h (90 to 100%) [204].
-Also refer to: [905].

m.p. 141-142° [204].

1-(3-Amino-4,5-dihydroxyphenyl)-2-phenylethanone

[473790-02-2] $C_{14}H_{13}NO_3$ mol.wt. 243.26



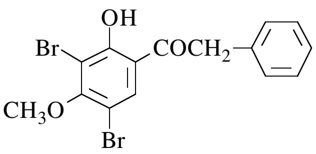
Synthesis

-Preparation by hydrogenation of 1-(3,4-dihydroxy-5-nitrophenyl)-2-phenylethanone in methanolic suspension in the presence of 10% Pd/C at r.t. for 2 h (91%) [886].

m.p. 234-237° [886];
^{1}H NMR [886], ^{13}C NMR [886], IR [886].

1-(3,5-Dibromo-2-hydroxy-4-methoxyphenyl)-2-phenylethanone

[19816-38-7] $C_{15}H_{12}Br_2O_3$ mol.wt. 400.07



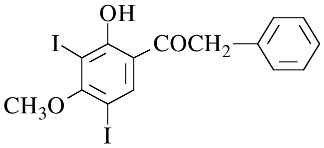
Syntheses

-Obtained by alkaline degradation of two substituted isoflavones with 10% sodium hydroxide in refluxing ethanol for 4 h,
*from 6,8-dibromo-7-methoxyisoflavone (m.p. 139°) (92%) [307];
*from 2,6,8-tribromo-7-methoxyisoflavone (m.p. 218°) [307].

m.p. 120° [307].

1-(2-Hydroxy-3,5-diiodo-4-methoxyphenyl)-2-phenylethanone

[19816-44-5] $C_{15}H_{12}I_2O_3$ mol.wt. 494.07



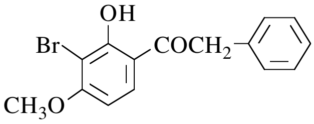
Syntheses

-Obtained by alkaline degradation of 6,8-diiodo-7-methoxyisoflavone (m.p. 210°) with 10% sodium hydroxide in refluxing ethanol for 4 h [307].
-Also obtained by iodination of benzyl 2-hydroxy-3-iodo-4-methoxyphenyl ketone with iodine and iodic acid in ethanol at 60-70° overnight [307].

m.p. 140° [307].

1-(3-Bromo-2-hydroxy-4-methoxyphenyl)-2-phenylethanone

[19816-33-2] $C_{15}H_{13}BrO_3$ mol.wt. 321.17



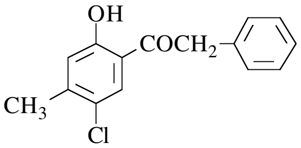
Synthesis

-Obtained by alkaline degradation of 8-bromo-7-methoxyisoflavone (m.p. 178°) wit 10% sodium hydroxide in refluxing ethanol for 4 h (83%) [307].

m.p. 198° [307].

1-(5-Chloro-2-hydroxy-4-methylphenyl)-2-phenylethanone

[92435-54-6] $C_{15}H_{13}ClO_2$ mol.wt. 260.72



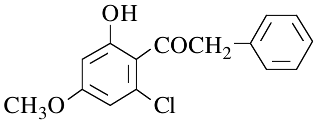
Synthesis

-Preparation by Friedel-Crafts acylation of 4-chloro-3-methylphenol with phenylacetyl chloride in nitrobenzene in the presence of aluminium chloride [1259].

m.p. 112° [1259].

1-(2-Chloro-6-hydroxy-4-methoxyphenyl)-2-phenylethanone

[116475-72-0] $C_{15}H_{13}ClO_3$ mol.wt. 276.72



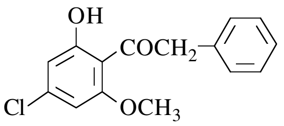
Syntheses

-Obtained by Friedel-Crafts reaction of 1-chloro-3,5-dimethoxybenzene with phenylacetyl chloride in the presence of aluminium chloride and zinc chloride in ethylene dichloride between -10 to -7°, then at r.t. for 1 h and subsequent demethylation at 70° for 1 h (47%) [813].
-Also refer to: [811] [812].

m.p. 123-125° [813]; ^1H NMR [813], IR [813].

1-(4-Chloro-2-hydroxy-6-methoxyphenyl)-2-phenylethanone

[137986-09-5] $C_{15}H_{13}ClO_3$ mol.wt. 276.72



Syntheses

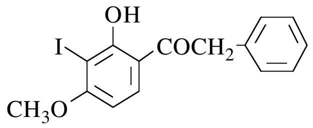
-Obtained by Friedel-Crafts reaction of phenylacetyl chloride with 1-chloro-3,5-dimethoxybenzene in the presence of aluminium chloride and zinc chloride in ethylene dichloride between 5 to 10°, then at r.t. for 1 h and subsequent demethylation at 65-70° for 3 h (54%) [813].

-Also refer to: [812].

m.p. 74-75° [813]; ^{1}H NMR [813], IR [813].

1-(2-Hydroxy-3-iodo-4-methoxyphenyl)-2-phenylethanone

$C_{15}H_{13}IO_3$ mol.wt. 368.17



Syntheses

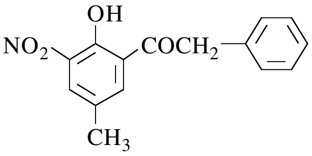
-Obtained by alkaline degradation of 8-iodo-7-methoxyisoflavone (m.p. 169°) with 10% sodium hydroxide in refluxing ethanol for 4 h (81%) [307].

-Also obtained by Friedel-Crafts acylation of 2-iodoresorcinol dimethyl ether with phenylacetyl chloride in nitrobenzene in the presence of aluminium chloride and heating for 2 h [307].

m.p. 217° [307].

1-(2-Hydroxy-5-methyl-3-nitrophenyl)-2-phenylethanone

[70978-50-6] $C_{15}H_{13}NO_4$ mol.wt. 271.27



Synthesis

-Obtained by nitration of 2-hydroxy-5-methylphenyl benzyl ketone,

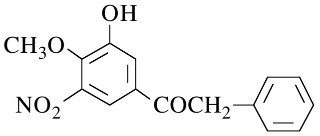
*using standard reagents at -20°(81%) [506];

*with fuming nitric acid in acetic acid/methylene chloride at r.t. [1215].

m.p. 80-82° [506] [1215].

1-(3-Hydroxy-4-methoxy-5-nitrophenyl)-2-phenylethanone

[473789-93-4] $C_{15}H_{13}NO_5$ mol.wt. 287.27



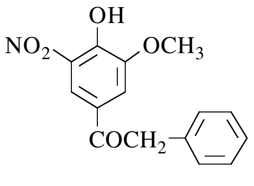
Synthesis

-Obtained by partial methylation of 1-(3,4-dihydroxy-5-nitrophenyl)-2-phenylethanone with dimethyl sulfate in the presence of potassium carbonate in DMF for 1 h at 80° (25%) [886].

m.p. 121-123° [886]; ^{1}H NMR [886], ^{13}C NMR [886], IR [886].

1-(4-Hydroxy-3-methoxy-5-nitrophenyl)-2-phenylethanone

[274925-97-2] $C_{15}H_{13}NO_5$ mol.wt. 287.27



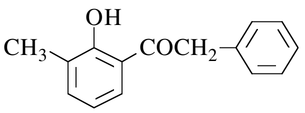
Synthesis

-Preparation by treatment of 1-(4-hydroxy-3-methoxyphenyl)-2-phenylethanone with 70% nitric acid in acetic acid at r.t. for 30 min (72%) [885], (71%) [887].

m.p. 129-130° [887];
^{1}H NMR [887], ^{13}C NMR [887].

1-(2-Hydroxy-3-methylphenyl)-2-phenylethanone

[7294-92-0] $C_{15}H_{14}O_2$ mol.wt. 226.27



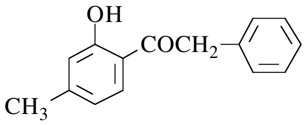
Syntheses

-Obtained by Fries rearrangement of o-cresyl phenylacetate,
*in the presence of aluminium chloride,
-without solvent at 160-180° for 30 min (53%) [776], at 140° for 3 h (45%) [881] [883] or at 130° for 4 h (12%) [1552];
-in nitrobenzene at 60° for 4 h (10%) [1551];
*with alumina in methanesulfonic acid at 160° for 10 min (15%) [1332].
-Also obtained by Friedel-Crafts acylation of o-cresol with phenylacetic acid in the presence of alumina in methanesulfonic acid at 140° for 5 min (12%) [1332].
-Also obtained by photo-Fries rearrangement of o-tolyl phenylacetate,
*in the presence of α- or β-cyclodextrin in organic solvents [1475];
*included in a Nafion membrane at r.t. for 7 h (quantitative yield) [1476].
-Also refer to: [972].

m.p. 44° [881] [883]; b.p.$_8$ 176-180° [776];
IR [881] [883], UV [881] [883]; GC [1476]; GC-MS [1476].

1-(2-Hydroxy-4-methylphenyl)-2-phenylethanone

[2491-34-1] $C_{15}H_{14}O_2$ mol.wt. 226.27



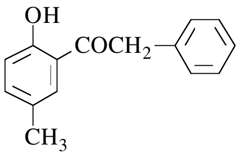
Syntheses

-Preparation by Fries rearrangement of m-cresyl phenylacetate,
*with aluminium chloride,
-without solvent, for 3 h at 140° (50%) [881] [884];
-starting in carbon disulfide and, after solvent elimination, for 1 h at 60-70°, then 24 h at r.t. (77%) [1010];
-in nitrobenzene for 4 h at 60° (65%) [1551] or in refluxing nitromethane for 3 h (49%) [1552];
*with alumina in methanesulfonic acid for 15 min at 160° (90%) [1332].
-Preparation by direct acylation of m-cresol with phenylacetic acid,
*with boron trifluoride for 2 h at 90° (93%) [798];
*with alumina in methanesulfonic acid for 5 min at 120° (83%) [1332].
-Also obtained by hydrolysis of 2-difluoroboryloxy-4-methylphenyl benzyl ketone (SM) (m.p. 125-126°) with refluxing dilute ethanol for 15-20 min. SM was prepared by action of phenylacetic acid with m-cresol in the presence of boron trifluoride etherate for 30 min at 125-130° (50%) [1189].

m.p. 52-53° [1189], 49° [1010], 32-33° [798].
One of the reported melting points is obviously wrong.
b.p.$_5$ 164° [881] [884], b.p.$_4$ 170-175° [798], b.p.$_{17}$ 218° [1010];
IR [1189], UV [1189].

1-(2-Hydroxy-5-methylphenyl)-2-phenylethanone

[24258-63-7] $C_{15}H_{14}O_2$ mol.wt. 226.27



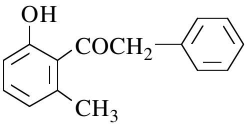
Syntheses

-Preparation by Fries rearrangement of p-cresyl phenylacetate with aluminium chloride (68%) [1355],
*without solvent at 120-140° for 20 min (82%) [776], at 130-135° for 30 min (80%) [281] or at 130-140° for 3 h (14%) [736];
*in nitrobenzene at r.t. for 48 h (80%) [882] [883] [884] or at 60° for 4 h (64%) [1551];
*in 1,2,4-trichlorobenzene at reflux for 30 min (78%) [1554];
*in chlorobenzene at reflux for 4 h (23%) [1552] or for 30 min (86%) [1554].
-Preparation by Friedel-Crafts acylation of p-cresol with phenylacetic acid,
*in the presence of boron trifluoride at 80° for 2 h (89%) [798];
*in the presence of zinc chloride [1502].
-Also obtained by Friedel-Crafts acylation of p-cresol methyl ether with phenylacetyl chloride in the presence of aluminium chloride, first in refluxing carbon disulfide for 5 h, then, after solvent elimination, at 120-130° for 5 h (54-61%) [99].
-Also obtained by photo-Fries rearrangement of p-tolyl phenylacetate,
*in the presence of α- or β-cyclodextrin in organic solvents [1475];
*included in a Nafion membrane, at r.t. for 7 h (quantitative yield) [1476].
-Also obtained by reaction of N-diethylaniline with α-bromo-2-hydroxy-5-methyldeoxybenzoin [99].
-Also refer to: [1544].

m.p. 65-66° [736] [1554], 65° [99] [882] [883] [884], 64° [798], 63°5-65° [1355], 63° [281] [1502], 54-58° [776];
b.p.$_7$ 169-174° [776], b.p.$_{0.6}$ 170° [798], b.p.$_6$ 195-199° [281], b.p.$_{13-14}$ 210-213° [99]; GC [1476]; GC-MS [1476];
IR [882] [883] [884], UV [882] [883] [884].

1-(2-Hydroxy-6-methylphenyl)-2-phenylethanone

[137937-39-4] $C_{15}H_{14}O_2$ mol.wt. 226.27



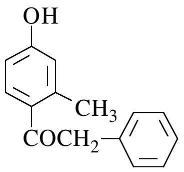
Synthesis

-Obtained (by-product) by Fries rearrangement of m-tolyl phenylacetate with aluminium chloride in chlorobenzene at 140° for 4 h (5%) [972].

m.p. 85° [972];
^{1}H NMR (Sadtler: standard n° 57893 M) [972],
IR (Sadtler: standard n° 84941 K) [972], UV [972], MS [972].

1-(4-Hydroxy-2-methylphenyl)-2-phenylethanone

[3669-50-9] $C_{15}H_{14}O_2$ mol.wt. 226.27



Syntheses

-Obtained by reaction of phenylacetyl chloride with m-cresol in the presence of aluminium chloride in nitrobenzene for 30 min in a boiling water bath (26%) [352].

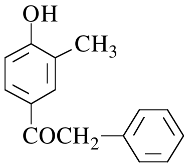
-Also obtained by reaction of phenylacetic acid with m-cresol,
*in the presence of boron trifluoride at 90° for 2 h (3%) [798];
*in the presence of zinc chloride at reflux (200°) for 1 h [189] [352].

-Also obtained by Fries rearrangement of m-cresyl phenylacetate with aluminium chloride,
*in refluxing chlorobenzene for 4 h (24%) [1552];
*in nitromethane or in nitroethane at r.t. for 12 h (18-21%) [1550];
*in nitrobenzene at 60° for 4 h (10%) [1550], (8%) [1551] or at r.t. for 10 h (10%) [1550];
*without solvent at 140° for 3 h (10%) [881] or first in carbon disulfide, then after elimination of the solvent, at 60-70° for 1 h and at r.t. for 24 h (2%) [1010].

m.p. 142° [352], 138-139° [798], 138° [881] [1010].

1-(4-Hydroxy-3-methylphenyl)-2-phenylethanone

[7354-81-6] $C_{15}H_{14}O_2$ mol.wt. 226.27



Syntheses

-Preparation by Fries rearrangement of o-cresyl phenylacetate with aluminium chloride,
*in nitroethane at r.t. for 12 h (73%) [1550];
*in nitrobenzene at 60° for 4 h (72%) [1551] or at 50° for 4 h (60%) [1552];
*in refluxing chlorobenzene for 4 h (58%) [1552];
*in refluxing nitromethane for 4 h (21%) [1552];
*without solvent at 130° for 4 h (49%) [1552] or at 140° for 3 h (30%) [881] [883].

-Preparation by Fries rearrangement of o-cresyl phenylacetate with alumina in methanesulfonic acid for 10 min at 160° (85%) [1332].

-Also obtained by photo-Fries rearrangement of o-cresyl phenylacetate in the presence of α- or β-cyclodextrin in organic solvents [1475].

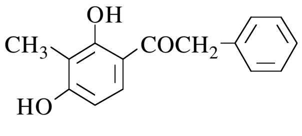
-Also obtained by reaction of phenylacetic acid with o-cresol,
*in the presence of alumina in methanesulfonic acid at 140° for 5 min (88%) [1332];
*in the presence of aluminium chloride in nitrobenzene in a water bath for 1 h-1.25 h (60-70%) [189];
*in the presence of zinc chloride at reflux (180-200°) [1422], (< 20%) [189] (Nencki reaction).

-Also refer to: [972].

m.p. 156° [881] [883], 152° [189];
IR [881] [883], UV [881] [883].

1-(2,4-Dihydroxy-3-methylphenyl)-2-phenylethanone

[39581-98-1] $C_{15}H_{14}O_3$ mol.wt. 242.27



Syntheses

-Preparation by demethylation of 2-hydroxy-4-methoxy-3-methylphenyl benzyl ketone with hydriodic acid in refluxing acetic anhydride (125-135°) for 2 h (64%) [1326].

-Also obtained by reaction of phenylacetic acid with 2-methylresorcinol in the presence of phosphorous oxychloride and zinc chloride, heating on a water bath for 3 h (45%) [1137].

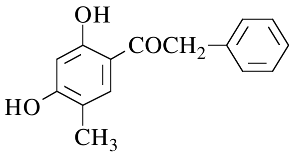
-Also obtained by reaction of phenylacetonitrile with 2-methylresorcinol (Hoesch reaction) [1325].

-Also refer to: [1138] [1328].

m.p. 178° [1137], 157-159° [1325] [1326].
One of the reported melting points is obviously wrong.

1-(2,4-Dihydroxy-5-methylphenyl)-2-phenylethanone

[106737-29-5] $C_{15}H_{14}O_3$ mol.wt. 242.27



Syntheses

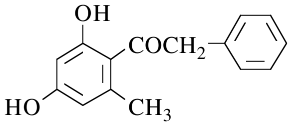
-Preparation by reaction of phenylacetonitrile with 4-methylresorcinol (Hoesch reaction) [1052].

-Also obtained by demethylation of 4-hydroxy-2-methoxy-5-methylphenyl benzyl ketone with aluminium chloride in refluxing benzene for 4 h (74%) [1572].

m.p. 98-99° [1052], 96° [1572].

1-(2,4-Dihydroxy-6-methylphenyl)-2-phenylethanone

[55338-29-9] $C_{15}H_{14}O_3$ mol.wt. 242.27



Syntheses

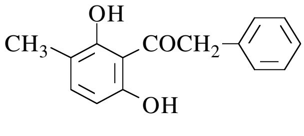
-Preparation by Friedel-Crafts acylation of orcinol with phenylacetyl chloride in nitrobenzene in the presence of aluminium chloride [1259].

-Also refer to: [483] [678].

m.p. 148° [1259].

1-(2,6-Dihydroxy-3-methylphenyl)-2-phenylethanone

[15578-06-0] $C_{15}H_{14}O_3$ mol.wt. 242.27



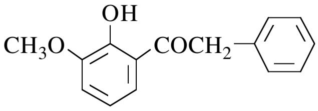
Synthesis

-Obtained by treatment of 5-carbomethoxy-2,6-dihydroxy-3-methyldeoxybenzoin (m.p. 168-170°) with potassium hydroxide in refluxing dilute ethanol for 4 h (38%) [964].

m.p. 135-136° [964].

1-(2-Hydroxy-3-methoxyphenyl)-2-phenylethanone

[93899-00-4] $C_{15}H_{14}O_3$ mol.wt. 242.27



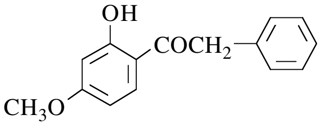
Syntheses

-Preparation from 2-acetoxy-3-methoxybenzonitrile and benzylmagnesium chloride (75-90%) [1161].
-Also obtained (by-product) by reaction of phenylacetic acid with guaiacol in the presence of zinc chloride and phosphorous oxychloride for 24 h at r.t. (5%) [391].

m.p. 165-168° [391], 78-79° [1161]. One of the reported melting points is obviously wrong.
UV [391].

1-(2-Hydroxy-4-methoxyphenyl)-2-phenylethanone

[18439-96-8] $C_{15}H_{14}O_3$ mol.wt. 242.27



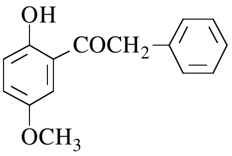
Syntheses

-Preparation by partial methylation of 2,4-dihydroxyphenyl benzyl ketone [1145],
*with methyl iodide in the presence of potassium carbonate in refluxing acetone for 3 h (85%) [106] or for 12 h (91%) [627];
*with methyl bromide in the presence of potassium carbonate in refluxing acetone for 20 h [148];
*with dimethyl sulfate,
-in the presence of potassium carbonate in boiling benzene for 90 min (51%) [117] or in boiling acetone [1076];
-in the presence of alkali in boiling ethanol [1439].
-Also obtained by Friedel-Crafts acylation of resorcinol dimethyl ether with phenylacetyl chloride in the presence of aluminium chloride in boiling carbon disulfide for 1 h (50%) [158] or in boiling ethyl ether (33%) [1122].
-Also obtained by acylation of resorcinol monomethyl ether with phenylacetic acid in the presence of polyphosphoric acid at 95° for 30 min (40%) [1503].
-Also obtained by degradation of 4-hydroxy-7-methoxy-3-phenylcoumarin with refluxing 30% ethanolic hydrogen chloride (45%) [387].
-Also obtained from 4,7-dimethoxy-3-phenylcoumarin on heating with 5% aqueous sodium hydroxide for 2 h on a water bath (71%) [14].
-Also obtained by hydrolysis of ethyl 2,4-dimethoxybenzoyl-phenylacetate (m.p. 76-77°) in acetic acid with concentrated hydrochloric acid on a steam bath for 15 h (68%) [777].
-Also obtained by hydrolysis of 2,4-dimethoxybenzoyl-phenylacetonitrile (m.p. 108-109°) in acetic acid with concentrated hydrochloric acid on a steam bath for 15 h (47%) [777].
-Also obtained by condensation of phenylacetonitrile with resorcinol monomethyl ether (Hoesch reaction) (23%) [112].
-Also refer to: [11] [412] [462] [463] [701] [724] [949] [1076] [1140] [1271] [1291] [1364].

m.p. 92° [158], 90° [112] [627] [1439], 88-89° [777],
88° [106] [117], 87-88° [14], 86-87° [148], 86° [387], 75° [1503].
One of the reported melting points is obviously wrong.
b.p.$_{0.001}$ 155-165° [777]; ^{1}H NMR [788] [1503].

1-(2-Hydroxy-5-methoxyphenyl)-2-phenylethanone

[80427-38-9] $C_{15}H_{14}O_3$ mol.wt. 242.27



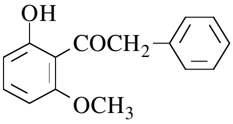
Syntheses

-Preparation by Fries rearrangement of p-methoxyphenyl phenylacetate with titanium tetrachloride at 120° for 1 h (60-74%) [969].
-Also obtained by Friedel-Crafts acylation of hydroquinone dimethyl ether with phenylacetyl chloride in the presence of aluminium chloride,
*in carbon disulfide at r.t. for 1 h (by-product) [772];
*in refluxing ethyl ether for 8 h [129], (43%) [585].
-Also obtained (poor yield) by partial degradation of 6-methoxy-3-phenyl-4-hydroxycoumarin with 30% ethanolic hydrogen chloride at reflux for 1 h [387].
-Also refer to: [149] [1413].

m.p. 45° [585], 44° [969]; IR [969], UV [969].

1-(2-Hydroxy-6-methoxyphenyl)-2-phenylethanone

[40584-06-3] $C_{15}H_{14}O_3$ mol.wt. 242.27



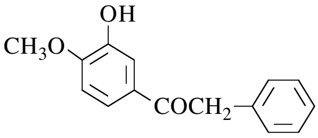
Syntheses

-Obtained by partial methylation of benzyl 2,6-dihydroxyphenyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone [585].
-Also obtained on heating 3-(6-methoxy-2-tosyloxyphenyl)-3-oxo-2-phenylpropanal (m.p. 137-138°) with ethanolic potassium hydroxide (2N) at reflux for 2 h (88%) [574].

m.p. 71° [574], 66° [585]; IR [574].

1-(3-Hydroxy-4-methoxyphenyl)-2-phenylethanone

[58451-99-3] $C_{15}H_{14}O_3$ mol.wt. 242.27



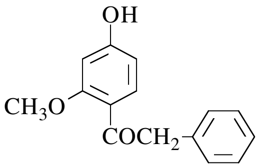
Syntheses

-Preparation from 2-methoxy-5-(phenylacetyl)phenyl phenylacetate (SM) with refluxing methanolic potassium hydroxide (91%) [966]. SM was obtained by acylation of 2-methoxyphenyl phenylacetate with phenylacetyl chloride in the presence of stannic chloride in nitromethane for 1 h at 20° (76%, m.p. 95°).
-Preparation from 3-benzyloxy-4-methoxybenzonitrile and benzylmagnesium chloride (75-90%) [1161].
-Preparation by treatment of 3-benzyloxy-4-methoxyphenyl benzyl ketone (SM) with a mixture of concentrated hydrochloric acid and acetic acid (1:2 v/v) and heating at 70° for 1 h (69%) [1557]. SM was obtained by oxidation of 1-(3-benzyloxy-4-methoxyphenyl)-2-phenylethanol (m.p. 79-82°) with potassium dichromate in dilute sulfuric acid at 50° for 1 h (80%, m.p. 105-106°).

m.p. 106-107° [1161] [1557], 101° [966];
^{1}H NMR (Sadtler: standard n° 28214 M) [1557],
IR (Sadtler: standard n° 55286) [966], UV [966], MS [1557].

1-(4-Hydroxy-2-methoxyphenyl)-2-phenylethanone

[85288-47-7] $C_{15}H_{14}O_3$ mol.wt. 242.27



Syntheses

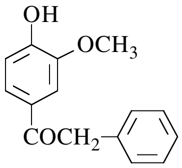
-Obtained by acylation of resorcinol monomethyl ether with phenylacetic acid in the presence of polyphosphoric acid at 95° for 30 min (30%) [1503].

-Also obtained (by-product) by condensation of phenylacetonitrile with resorcinol monomethyl ether (Hoesch reaction) (7%) [112].

m.p. 113° [112], 86° [1503].
One of the reported melting points is obviously wrong.
b.p.$_{13}$ 260-265° [112]; ^{1}H NMR [788] [1503].

1-(4-Hydroxy-3-methoxyphenyl)-2-phenylethanone

[66476-02-6] $C_{15}H_{14}O_3$ mol.wt. 242.27



Syntheses

-Preparation by oxidation of 1-(4-hydroxy-3-methoxyphenyl)-2-phenylethanol with DDQ in dioxane at r.t. for 16 h (89%) [144].

-Preparation by reaction of benzylmagnesium chloride with 4-acetoxy-3-methoxybenzonitrile (72%) [1160].

-Preparation by reaction of phenylacetic acid with guaiacol in the presence of zinc chloride and phosphorous oxychloride for 24 h at r.t. (60%) [391].

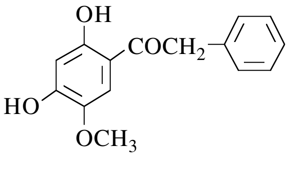
-Preparation from 1-(4-benzyloxy-3-methoxyphenyl)-2-phenylethanone (m.p. 136-138°) by catalytic hydrogen transfer using ammonium formate as hydrogen donor and 10% Pd/C catalysis in refluxing methanol for 30 min (94%) [887].

N.B.: Na salt [1160].

m.p. 110-111° [1160], 108-110° [144], 108° [391], 106-108° [887];
^{1}H NMR [144] [887], ^{13}C NMR [887], UV [391].

1-(2,4-Dihydroxy-5-methoxyphenyl)-2-phenylethanone

[79744-57-3] $C_{15}H_{14}O_4$ mol.wt. 258.27



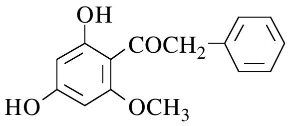
Syntheses

-Refer to: [246] [732].

^{13}C NMR [732].

1-(2,4-Dihydroxy-6-methoxyphenyl)-2-phenylethanone

[55607-18-6] $C_{15}H_{14}O_4$ mol.wt. 258.27



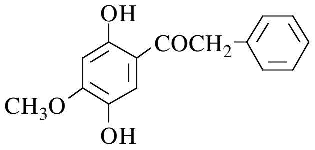
Syntheses

-Obtained by reaction of phenylacetonitrile with phloroglucinol monomethyl ether (Hoesch reaction) (38%) [559].
-Preparation by tosylation of 2,4,6-trihydroxyphenyl benzyl ketone with p-toluenesulfonyl chloride in the presence of potassium carbonate in refluxing acetone for 4 h, followed by methylation with dimethyl sulfate (reflux 30 h) and final detosylation with refluxing ethanolic sodium hydroxide for 45 min (19%) [14].
-Also refer to: [715].

m.p. 146° [14], 145-146° [559].

1-(2,5-Dihydroxy-4-methoxyphenyl)-2-phenylethanone

[789-80-0] $C_{15}H_{14}O_4$ mol.wt. 258.27



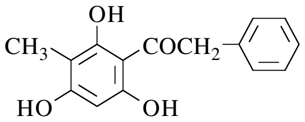
Syntheses

-Obtained by partial methylation of 2,4,5-trihydroxyphenyl benzyl ketone with excess diazomethane in ethyl ether at r.t. overnight (47%) [530].
-Also obtained by alkaline oxidation of 2-hydroxy-4-methoxyphenyl benzyl ketone with potassium persulfate in aqueous potassium hydroxide/pyridine mixture (Elbs reaction) [129].
-Also refer to: [585].

m.p. 153-154° [129], 150-152° [530]; ^{13}C NMR [732].

2-Phenyl-1-(2,4,6-trihydroxy-3-methylphenyl)ethanone

[3136-47-8] $C_{15}H_{14}O_4$ mol.wt. 258.27



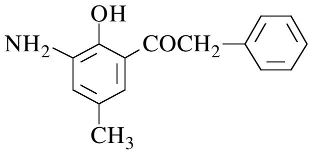
Syntheses

-Obtained by reaction of phenylacetonitrile with 2-methylphloroglucinol (Hoesch reaction) [672].
-Also obtained by reduction of 2,4,6-trihydroxy-3-formylphenyl benzyl ketone with hydrogen in acetic acid using 5% Pd/C as catalyst [594].
-Also refer to: [988] [1208] [1209].

m.p. 200° [672], 198-199° [594].

1-(3-Amino-2-hydroxy-5-methylphenyl)-2-phenylethanone

[70977-87-6] $C_{15}H_{15}NO_2$ mol.wt. 241.29



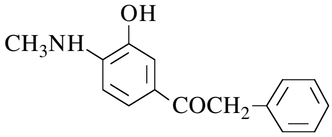
Synthesis

-Preparation by hydrogenation of 2-hydroxy-5-methyl-3-nitrophenyl benzyl ketone in ethanol using 5% Pd/C as catalyst at atmospheric pressure [1215], (74%) [506].

m.p. 74-76° [506] [1215].

1-[3-Hydroxy-4-(methylamino)phenyl]-2-phenylethanone

[54943-18-9] $C_{15}H_{15}NO_2$ mol.wt. 241.29



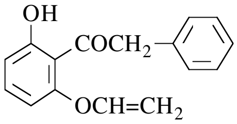
Synthesis

-Preparation from 3-methyl-6-phenylacetyl-benzoxazolinone by alkaline hydrolysis with boiling 10% aqueous sodium hydroxide for 4 h (90-100%) [204].

m.p. 164-165° [204].

1-[2-(Ethenyloxy)-6-hydroxyphenyl]-2-phenylethanone

$C_{16}H_{14}O_3$ mol.wt. 254.29



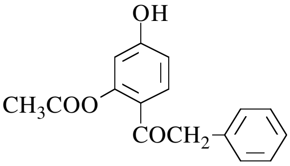
Synthesis

-Obtained (by-product) by reaction of diethylaminochloroethane with 2,6-dihydroxydesoxybenzoin in the presence of sodium ethoxide in refluxing ethanol for 4 h (6%) [914].

m.p. 85° [914].

1-[2-(Acetyloxy)-4-hydroxyphenyl]-2-phenylethanone

[145747-27-9] $C_{16}H_{14}O_4$ mol.wt. 270.28



Syntheses

-Obtained by selective deacetylation catalyzed by porcine pancreas lipase in THF at 42-45° of,

*1-acetoxy-1-(2,4-diacetoxyphenyl)-2-phenylethene during 72 h (20%) [1145];

*2,4-diacetoxyphenyl benzyl ketone during 48 h (65%) [1145] or [1144] [1146] (in the table below):

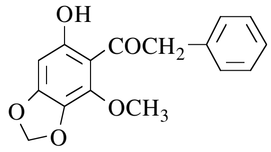
lipase	solvent	time (h)	yields (%)
PPL	acetone/n-BuOH	40	35
PPL	CH_3CN/n-BuOH	50	35
PPL	THF/n-BuOH	42	65
CCL	DIPE/n-BuOH	45	60

PPL = porcine pancreas lipase; CCL = candida cylindracea lipase; DIPE = diisopropyl ether

m.p. 140° [1145]; TLC [1145];
^{1}H NMR [1145], ^{13}C NMR [1145], IR [1145], UV [1145], MS [1145].

1-(6-Hydroxy-4-methoxy-1,3-benzodioxol-5-yl)-2-phenylethanone

[2652-17-7] $C_{16}H_{14}O_5$ mol.wt. 286.28



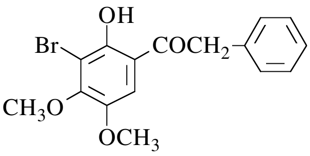
Synthesis

Obtained by reaction of phenylacetonitrile with 3-methoxy-4,5-methylenedioxyphenol (Hoesch reaction) (24%) [533].

m.p. 162-164° [533]; UV [533].

1-(3-Bromo-2-hydroxy-4,5-dimethoxyphenyl)-2-phenylethanone

[54921-24-3] $C_{16}H_{15}BrO_4$ mol.wt. 351.20



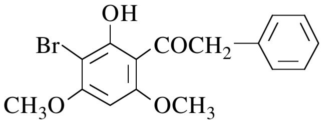
Synthesis

-Obtained by alkaline degradation of 6,7-dimethoxy-8-bromoisoflavone with 3% alcoholic potassium hydroxide at reflux for 30 min (41%) [960].

m.p. 146° [960].

1-(3-Bromo-2-hydroxy-4,6-dimethoxyphenyl)-2-phenylethanone

[28750-55-2] $C_{16}H_{15}BrO_4$ mol.wt. 351.20



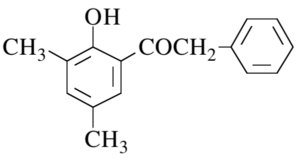
Syntheses

-Preparation by bromination of 2-acetoxy-4,6-dimethoxyphenyl benzyl ketone with bromine in acetic acid for 1 h at r.t. (69%) [412].
-Also obtained by bromination of 2-hydroxy-4,6-dimethoxyphenyl benzyl ketone with bromine in chloroform under UV light at r.t. overnight (55%) [771].

m.p. 205-206° [412], 200-202° [771]; TLC [771];
^{1}H NMR [412] [771], IR [771], UV [771].

1-(2-Hydroxy-3,5-dimethylphenyl)-2-phenylethanone

[93433-76-2] $C_{16}H_{16}O_2$ mol.wt. 240.30



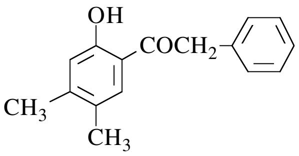
Syntheses

-Preparation by Fries rearrangement of 2,4-dimethylphenyl phenylacetate with aluminium chloride,
*without solvent for 15 min at 140-145° (85%) [1569] or for 1 h at 120° (56%) [1502];
*in refluxing chlorobenzene for 4 h (18%) [1552].

b.p.$_{0.01}$ 180-190° [1569], b.p.$_{10}$ 201-203° [1502].

1-(2-Hydroxy-4,5-dimethylphenyl)-2-phenylethanone

[18439-99-1] $C_{16}H_{16}O_2$ mol.wt. 240.30



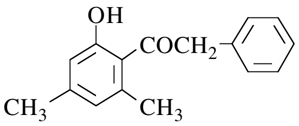
Syntheses

-Preparation by Fries rearrangement of 3,4-dimethylphenyl phenylacetate with aluminium chloride at 130° for 25 min (72%) [974].
-Also obtained (poor yield) by treatment of 6,7-dimethyl-3-phenyl-4-hydroxycoumarin with refluxing 30% ethanolic hydrogen chloride for 1 h [387].

m.p. 69-70° [974], 68° [387]; ^{1}H NMR [974], IR [974].

1-(2-Hydroxy-4,6-dimethylphenyl)-2-phenylethanone

[38319-83-4] $C_{16}H_{16}O_2$ mol.wt. 240.30



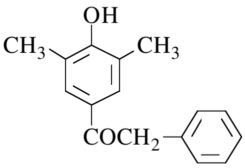
Syntheses

-Preparation by Friedel-Crafts acylation of 3,5-dimethylanisole with phenylacetyl chloride in the presence of aluminium chloride, first for 1 h at r.t., then for 1 h at reflux (43%) [1065].
-Also obtained by Fries rearrangement of 3,5-dimethylphenyl phenylacetate with aluminium chloride for 30 min on a water bath (10%) [1502].

b.p.$_1$ 168-173° [1065], b.p.$_{20}$ 220-225° [1502];
^{1}H NMR [1065], IR [1065]; $n_D^{23.2}$ = 1.5921 [1065].

1-(4-Hydroxy-3,5-dimethylphenyl)-2-phenylethanone

[73049-13-5] $C_{16}H_{16}O_2$ mol.wt. 240.30



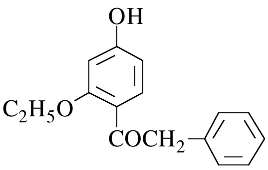
Syntheses

-Preparation by oxidation of 1-(4-hydroxy-3,5-dimethylphenyl)-2-phenylethanol with DDQ in dioxane at r.t. for 16 h (83%) [144].
-Preparation by Fries rearrangement of 2,6-dimethylphenyl phenylacetate with aluminium chloride in refluxing chlorobenzene for 4 h (74%) [1552].

m.p. 117-118° [144]; ^{1}H NMR [144].

1-(2-Ethoxy-4-hydroxyphenyl)-2-phenylethanone

[50775-90-1] $C_{16}H_{16}O_3$ mol.wt. 256.30

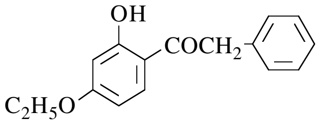


Syntheses

-Refer to: [481] [482].

1-(4-Ethoxy-2-hydroxyphenyl)-2-phenylethanone

$C_{16}H_{16}O_3$ mol.wt. 256.30



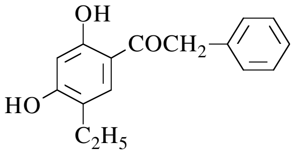
Syntheses

-Obtained by partial ethylation of 2,4-dihydroxydeoxybenzoin with ethyl iodide in the presence of potassium carbonate in boiling acetone during 3 h (68%) [106].
-Also refer to: [914].

m.p. 86° [106].

1-(5-Ethyl-2,4-dihydroxyphenyl)-2-phenylethanone

[96643-95-7] $C_{16}H_{16}O_3$ mol.wt. 256.30



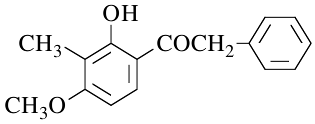
Syntheses

-Preparation by reaction of phenylacetonitrile with 4-ethylresorcinol,
*in the presence of boron trifluoride etherate (96%) [786] [936];
*in the presence of zinc chloride (Hoesch reaction) [1052].

m.p. 105-105°5 [1052], 100-102° [786] [936]; ^1H NMR [786].

1-(2-Hydroxy-4-methoxy-3-methylphenyl)-2-phenylethanone

[87538-40-7] $C_{16}H_{16}O_3$ mol.wt. 256.30



Synthesis

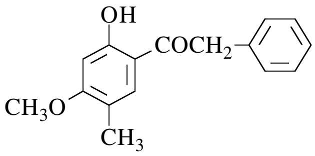
-Obtained by reaction of methyl iodide with benzyl 2,4-dihydroxyphenyl ketone in methanol in the presence of potassium hydroxide, first at 0°, then standing overnight and refluxing for 6 h (45%) [1326].

-Also refer to: [724] [1291].

m.p. 110-111° [1326].

1-(2-Hydroxy-4-methoxy-5-methylphenyl)-2-phenylethanone

[87538-41-8] $C_{16}H_{16}O_3$ mol.wt. 256.30

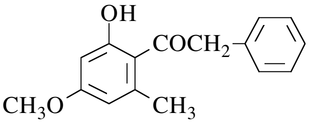


Syntheses

-Refer to: [724] [1291].

1-(2-Hydroxy-4-methoxy-6-methylphenyl)-2-phenylethanone

$C_{16}H_{16}O_3$ mol.wt. 256.30



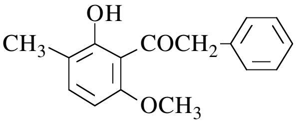
Syntheses

- Obtained by condensation of phenylacetonitrile with orcinol monomethyl ether (1%) (Hoesch reaction) [112].
- Also obtained by reaction of phenylacetyl chloride with orcinol dimethyl ether in the presence of aluminium chloride [814].

m.p. 110° [112].

1-(2-Hydroxy-6-methoxy-3-methylphenyl)-2-phenylethanone

[15578-05-9] $C_{16}H_{16}O_3$ mol.wt. 256.30



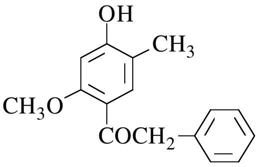
Synthesis

- Obtained by partial methylation of 2,6-dihydroxy-3-methyldeoxybenzoin with dimethyl sulfate in the presence of potassium carbonate in boiling acetone (74%) [964].

m.p. 80-82° [964].

1-(4-Hydroxy-2-methoxy-5-methylphenyl)-2-phenylethanone

[101169-10-2] $C_{16}H_{16}O_3$ mol.wt. 256.30



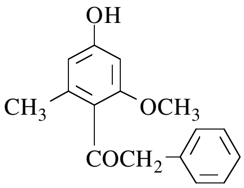
Synthesis

- Obtained by reaction of phenylacetonitrile with 4-methylresorcinol dimethyl ether (Hoesch reaction) [1572].

m.p. 129° [1572].

1-(4-Hydroxy-2-methoxy-6-methylphenyl)-2-phenylethanone

$C_{16}H_{16}O_3$ mol.wt. 256.30



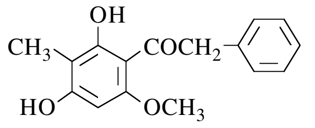
Synthesis

- Obtained (poor yield) by condensation of phenylacetonitrile with orcinol monomethyl ether (7%) (Hoesch reaction) [112].

m.p. 93° [112].

1-(2,4-Dihydroxy-6-methoxy-3-methylphenyl)-2-phenylethanone

$C_{16}H_{16}O_4$ mol.wt. 272.30



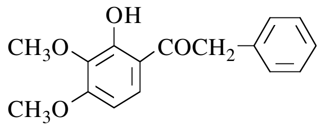
Synthesis

-Obtained by reaction of phenylacetonitrile with 2,6-dihydroxy-4-methoxytoluene (Hoesch reaction) (52%) [672].

m.p. 141-143° [672].

1-(2-Hydroxy-3,4-dimethoxyphenyl)-2-phenylethanone

[24852-33-3] $C_{16}H_{16}O_4$ mol.wt. 272.30



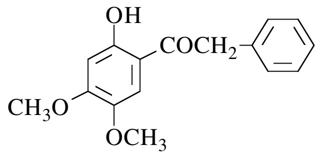
Syntheses

-Obtained by Friedel-Crafts acylation of pyrogallol trimethyl ether with phenylacetyl chloride in the presence of aluminium chloride,
*in boiling carbon disulfide for 30 min (39%) [758] or for 12 h [129];
*in ice-cold ethyl ether, then at r.t. overnight (57%) [681].
-Also refer to: [246] [704] [705] [706] [720] [722] [732] [1140].

m.p. 113-114° [129], 112-113° [758], 106-107° [681]; ^{13}C NMR [732].

1-(2-Hydroxy-4,5-dimethoxyphenyl)-2-phenylethanone

[24195-31-1] $C_{16}H_{16}O_4$ mol.wt. 272.30



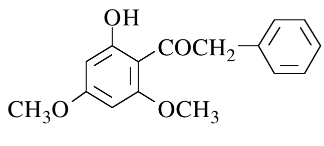
Syntheses

-Obtained by partial methylation of benzyl 2,5-dihydroxy-4-methoxyphenyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone [585].
-Also obtained (by-product) by reaction of phenylacetyl chloride with hydroxyhydroquinone trimethyl ether in the presence of aluminium chloride [129] [135] [136].
-Also obtained by reaction of phenylacetonitrile with 3,4-dimethoxyphenol (Hoesch reaction) (56%) [262].
-Also obtained (compound 7c) [699] according to the procedure [530].

m.p. 94-95° [262], 94° [135] [136], 93° [585];
^{13}C NMR [732], IR [262], UV [262], MS [262].

1-(2-Hydroxy-4,6-dimethoxyphenyl)-2-phenylethanone

[39604-66-5] $C_{16}H_{16}O_4$ mol.wt. 272.30



Syntheses

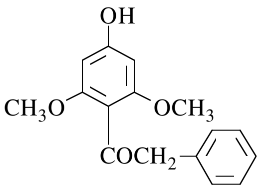
-Obtained by partial methylation of benzyl 2,4,6-trihydroxyphenyl ketone [1145],
*with dimethyl sulfate in the presence of potassium carbonate in boiling acetone [771], for 1 h [12], (69%) [106] or for 14 h (68%) [686];

*with methyl iodide in the presence of potassium carbonate in refluxing acetone for 6 h [672].
-Also obtained by condensation of phenylacetonitrile with phloroglucinol dimethyl ether (Hoesch reaction) (28%) [1239], (19%) [1573].
-Also obtained by Friedel-Crafts acylation of phloroglucinol trimethyl ether with phenylacetyl chloride in ethyl ether in the presence of aluminium chloride, first in an ice bath for 30 min and then at r.t. for 24 h [13].
-Also obtained from 4,5,7-trimethoxy-3-phenylcoumarin on heating with 5% aqueous sodium hydroxide [14].
-Also refer to: [11] [412] [559] [614] [699] [701] [720] [724] [747] [949] [1076] [1291] [1364].

m.p. 118° [1573], 117-118° [13], 117° [106] [771] [1239], 116° [672] [686], 115-116° [14]; ^{1}H NMR [788], IR [771], UV [771]; TLC [771].

1-(4-Hydroxy-2,6-dimethoxyphenyl)-2-phenylethanone

[131196-74-2] $C_{16}H_{16}O_4$ mol.wt. 272.30



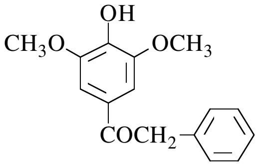
Syntheses

-Obtained (by-product) by condensation of phenylacetonitrile with phloroglucinol dimethyl ether (Hoesch reaction) [1239], (26%) [1573].
-Also obtained by saponification of (4-acetoxy-2,6-dimethoxyphenyl) benzyl ketone (m.p. 108-110°) in ethanol with 3% aqueous sodium hydroxide on a water bath (77%) [1573].

m.p. 77° [1573].

1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-phenylethanone

[73049-12-4] $C_{16}H_{16}O_4$ mol.wt. 272.30



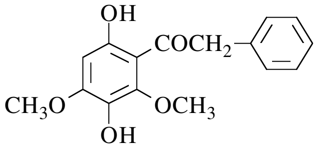
Synthesis

-Preparation by oxidation of 1-(3,5-dimethoxy-4-hydroxyphenyl)-2-phenylethanol with DDQ in dioxane at r.t. for 16 h (92%) [144].

m.p. 117-118° [144]; ^{1}H NMR [144].

1-(3,6-Dihydroxy-2,4-dimethoxyphenyl)-2-phenylethanone

$C_{16}H_{16}O_5$ mol.wt. 288.30



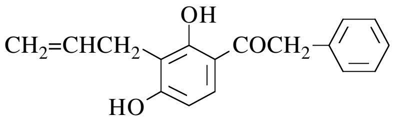
Syntheses

-Preparation by condensation of 2,6-dimethoxyhydroquinone with the complex phenylacetic acid and boron trifluoride (83%) [766], (quantitative yield) [765].
-Also obtained by saponification of 6-hydroxy-2,4-dimethoxy-3-(phenylacetoxy)phenyl benzyl ketone with 10% alcoholic potassium hydroxide for 2 h on a water bath [766].
-Also obtained (poor yield) by persulfate oxidation of 2-hydroxy-4,6-dimethoxyphenyl benzyl ketone (Elbs reaction) (8%) [766].

yellow oil [765]; m.p. 108° [766]; b.p.$_1$ 220-240° [766], b.p.$_1$ 230-250° [765].

1-[2,4-Dihydroxy-3-(2-propenyl)phenyl]-2-phenylethanone

[38987-02-9] $C_{17}H_{16}O_3$ mol.wt. 268.31



Syntheses

-Obtained by Claisen rearrangement of 4-allyloxy-2-hydroxyphenyl benzyl ketone either using boiling dimethylaniline or heating up to 185-190° under reduced pressure [839].

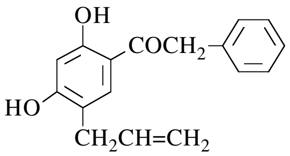
-Also obtained by reaction of allyl bromide with 2,4-dihydroxydesoxybenzoin in the presence of methanolic potassium hydroxide (22%) [711].

-Also refer to: [1140].

m.p. 162-163° [711], 126° [839]. One of the reported melting points is obviously wrong. ^{1}H NMR [711], IR [711], UV [711] [839].

1-[2,4-Dihydroxy-5-(2-propenyl)phenyl]-2-phenylethanone

[38987-03-0] $C_{17}H_{16}O_3$ mol.wt. 268.31



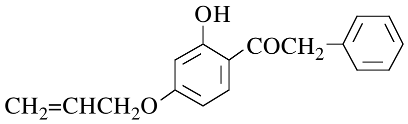
Synthesis

-Obtained by demethylation of 5-allyl-4-hydroxy-2-methoxyphenyl benzyl ketone with aluminium chloride in ethyl ether or acetonitrile [839].

m.p. 99-100° [839]; UV [839].

1-[2-Hydroxy-4-(2-propenyloxy)phenyl]-2-phenylethanone

[78660-73-8] $C_{17}H_{16}O_3$ mol.wt. 268.31

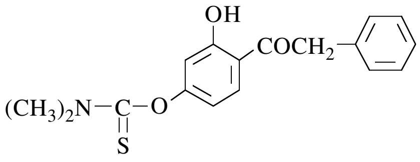


Syntheses

-Refer to: [839] [1328].

O-[3-Hydroxy-4-(phenylacetyl)phenyl] dimethylcarbamothioate

[142751-36-8] $C_{17}H_{17}NO_3S$ mol.wt. 315.39



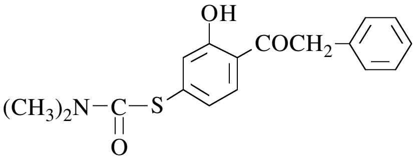
Synthesis

-Obtained by stirring a mixture of 2,4-dihydroxyphenyl benzyl ketone (1 mol), dimethylthiocarbamoyl chloride (2 mol), 1,4-diazabicyclo[2,2,2]octane (2 mol) and DMF at r.t. for 2 h (95%) [907].

m.p. 94-95° [907]; ^{1}H NMR [907], MS [907].

S-[3-Hydroxy-4-(phenylacetyl)phenyl] dimethylcarbamothioate

[142751-40-4] $C_{17}H_{17}NO_3S$ mol.wt. 315.39



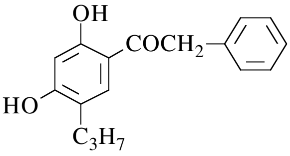
Synthesis

-Obtained by refluxing a solution of O-[3-hydroxy-4-(phenylacetyl)phenyl] dimethylcarbamothioate [142751-36-8] in N,N-dimethylaniline for 1 h (87%) (Newman-Kwart rearrangement) [907].

m.p. 100-101° [907]; ^{1}H NMR [907], MS [907].

1-(2,4-Dihydroxy-5-propylphenyl)-2-phenylethanone

[96661-12-0] $C_{17}H_{18}O_3$ mol.wt. 270.33



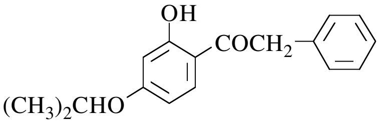
Syntheses

-Preparation by reaction of phenylacetonitrile with 4-propylresorcinol,
*in the presence of boron trifluoride etherate (88%) [786] [936];
*in the presence of zinc chloride (Hoesch reaction) [1052].

m.p. 95-96° [1052], 92-93° [786] [936]; ^{1}H NMR [786].

1-[2-Hydroxy-4-(1-methylethoxy)phenyl]-2-phenylethanone

[50561-04-1] $C_{17}H_{18}O_3$ mol.wt. 270.33



Syntheses

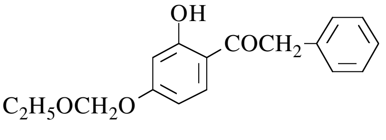
-Obtained by partial alkylation of benzyl 2,4-dihydroxyphenyl ketone with isopropyl bromide in DMF in the presence of potassium carbonate (79%) [1345].

-Also obtained by alkali degradation of *ipriflavone* (7-(1-methylethoxy)-3-phenyl-[4*H*]-1-benzopyran-4-one) (m.p. 115-117°) at high pH (pH > 9) (main degradation product) [1509].

-Also refer to: [481] [482] [484] [485] [486].

1-[4-(Ethoxymethoxy)-2-hydroxyphenyl]-2-phenylethanone

[97714-79-9] $C_{17}H_{18}O_4$ mol.wt. 286.33



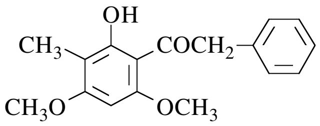
Syntheses

-Obtained by reaction of chloromethyl ethyl ether with benzyl 2,4-dihydroxyphenyl ketone in acetone in the presence of potassium carbonate at r.t. for 15-45 min [710].

-Also refer to: [701].

1-(2-Hydroxy-4,6-dimethoxy-3-methylphenyl)-2-phenylethanone

[39604-67-6] $C_{17}H_{18}O_4$ mol.wt. 286.33



Syntheses

-Preparation by partial methylation of 2,4-dihydroxy-3-methyl-6-methoxyphenyl benzyl ketone with methyl iodide in the presence of potassium carbonate in boiling acetone for 4 h (82%) [672].

-Also obtained by O and nuclear methylations of 2,4,6-trihydroxyphenyl benzyl ketone with methyl iodide in the presence of potassium carbonate in refluxing acetone for 6 h (11%) [672].

-Also obtained by partial methylation of 2,4,6-trihydroxy-3-methylphenyl benzyl ketone with dimethyl sulfate or with an excess methyl iodide in the presence of potassium carbonate in refluxing acetone for 3 h [672].

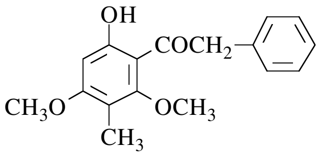
-Also obtained by reduction of 2-hydroxy-3-formyl-4,6-dimethoxyphenyl benzyl ketone with hydrogen in acetic acid using 5% Pd/C as catalyst (90%) [594].

-Also refer to: [12].

m.p. 153-155° [672], 153-154° [594].

1-(6-Hydroxy-2,4-dimethoxy-3-methylphenyl)-2-phenylethanone

[22080-99-5] $C_{17}H_{18}O_4$ mol.wt. 286.33



Syntheses

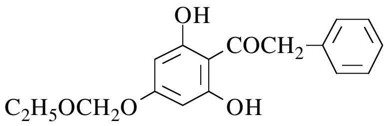
-Obtained (poor yield) by reaction of phenylacetyl chloride with 4-hydroxy-2,6-dimethoxytoluene in ethyl ether in the presence of aluminium chloride for 3 days at r.t. (8%) [717].

-Also refer to: [12].

m.p. 47-48° [717]; IR [717].

1-[4-(Ethoxymethoxy)-2,6-dihydroxyphenyl]-2-phenylethanone

[97714-81-3] $C_{17}H_{18}O_5$ mol.wt. 302.33

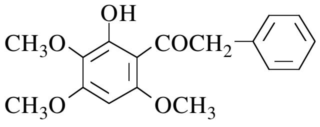


Synthesis

-Obtained by reaction of chloromethyl ethyl ether with benzyl 2,4,6-trihydroxyphenyl ketone in acetone in the presence of potassium carbonate at r.t. for 15-45 min [710].

1-(2-Hydroxy-3,4,6-trimethoxyphenyl)-2-phenylethanone

[55742-64-8] $C_{17}H_{18}O_5$ mol.wt. 302.33



Syntheses

-Obtained by reaction of phenylacetyl chloride with 1,2,3,5-tetramethoxybenzene in the presence of aluminium chloride,

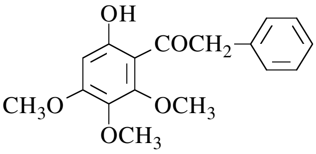
*in nitrobenzene on a water bath for 6 h (13%) [1329].

*in ethyl ether for 8 h on a water bath [129].

m.p. 89° [1329], 85-86° [129].

1-(6-Hydroxy-2,3,4-trimethoxyphenyl)-2-phenylethanone

[22137-59-3] $C_{17}H_{18}O_5$ mol.wt. 302.33



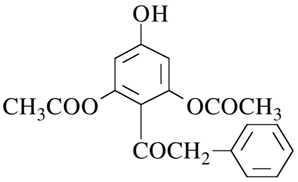
Synthesis

-Preparation by Friedel-Crafts acylation of antiarol with phenylacetyl chloride in ethyl ether in the presence of aluminium chloride at r.t. for 12 h (45%) [842] or for 24 h (59%) [601].

m.p. 64° [842], 63° [601].

1-[2,6-Bis(acetyloxy)-4-hydroxyphenyl]-2-phenylethanone

[145747-29-1] $C_{18}H_{16}O_6$ mol.wt. 328.32



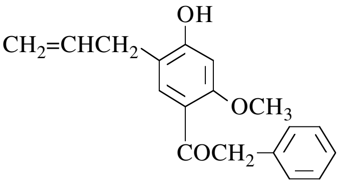
Syntheses

-Obtained by regioselective enzyme-catalyzed deacetylation of benzyl 2,4,6-triacetoxyphenyl ketone in various solvents containing n-butanol with two different lipases at 42-45° for 40 h,
*using porcine pancreas lipase in acetone or in acetonitrile (40%), in THF (70%) [1144] [1146], in diisopropyl ether (65%) [1144];
*using candida cylindracea lipase in diisopropyl ether (40%) [1146].

-Also obtained (small amount) by selective deacetylation of 1-acetoxy-1-(2,4,6-triacetoxyphenyl)-2-phenylethene (m.p. 67°) using porcine pancreas lipase in THF at 42-45° for 72 h [1145].

1-[4-Hydroxy-2-methoxy-5-(2-propenyl)phenyl]-2-phenylethanone

[39022-25-8] $C_{18}H_{18}O_3$ mol.wt. 282.34



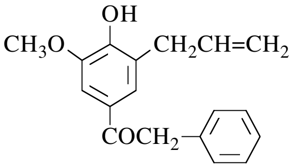
Synthesis

-Obtained by Claisen rearrangement of 4-allyloxy-2-methoxyphenyl benzyl ketone (m.p. 126-127°) either using boiling dimethylaniline or heating up to 185-190° under reduced pressure [839].

m.p. 127-128° [839]; UV [839].

1-[4-Hydroxy-3-methoxy-5-(2-propenyl)phenyl]-2-phenylethanone

$C_{18}H_{18}O_3$ mol.wt. 282.34



Synthesis

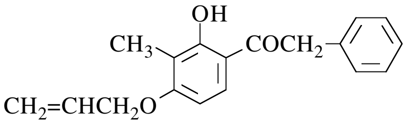
-Obtained by DDQ oxidation of 1-(3-allyl-4-hydroxy-5-methoxyphenyl)-2-phenylethanol in dioxane at r.t. for 16 h (88%) [144].

m.p. 140-142° [144]; ^{1}H NMR [144].

N.B.: In the original paper -page 1600- [144], the authors point out a registry N° [73049-14-6] for the title compound (**4e**) (benzyl 3-allyl-4-hydroxy-5-methoxyphenyl ketone) $C_{18}H_{18}O_3$. Nevertheless, the same registry number was assigned, undoubtedly by mistake, to 1-[4-hydroxy-3-methoxy-5-(2-propenyloxy)phenyl]-2-phenylethanone $C_{18}H_{18}O_4$, Chem. Abstr., Formula Index **92**, 215017w (1980). Actually, this ketone is not represented in [144]. The assigning of this registry number for the ketone $C_{18}H_{18}O_4$ by Chem. Abstr. is definitive.

1-[2-Hydroxy-3-methyl-4-(2-propenyloxy)phenyl]-2-phenylethanone

[57097-17-3] $C_{18}H_{18}O_3$ mol.wt. 282.34

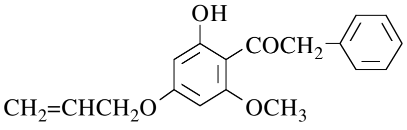


Syntheses

-Refer to: [1138] [1328].

1-[2-Hydroxy-6-methoxy-4-(2-propenyloxy)phenyl]-2-phenylethanone

[66541-26-2] $C_{18}H_{18}O_4$ mol.wt. 298.34



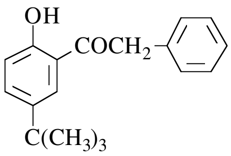
Synthesis

-Obtained by treatment of 2,4-dihydroxy-6-methoxyphenyl benzyl ketone with allyl bromide in the presence of potassium carbonate in refluxing acetone for 4 h [14].

m.p. 81-82° [14].

1-[5-(1,1-Dimethylethyl)-2-hydroxyphenyl]-2-phenylethanone

[75060-51-4] $C_{18}H_{20}O_2$ mol.wt. 268.36

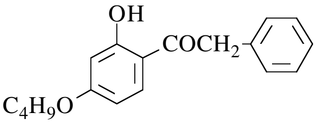


Synthesis

-Obtained by demethylation of 2-phenylacetyl-4-tert-butyl-anisole with a 47% hydrobromic acid/57% hydriodic acid mixture in refluxing acetic acid (63%) [685].

1-(4-Butoxy-2-hydroxyphenyl)-2-phenylethanone

[50775-75-2] $C_{18}H_{20}O_3$ mol.wt. 284.36



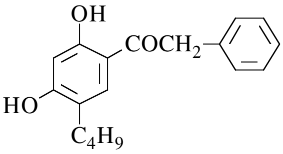
Syntheses

-Preparation by partial alkylation of 2,4-dihydroxyphenyl benzyl ketone with butyl bromide in the presence of potassium carbonate in refluxing acetone for 20 h [148].
-Also refer to: [481] [482] [484] [486].

m.p. 72-75° [148].

1-(5-Butyl-2,4-dihydroxyphenyl)-2-phenylethanone

[96643-96-8] $C_{18}H_{20}O_3$ mol.wt. 284.36



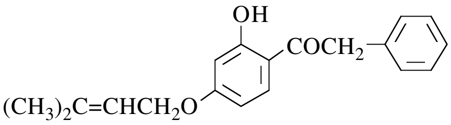
Syntheses

-Preparation by reaction of phenylacetonitrile with 4-butylresorcinol,
*in the presence of boron trifluoride etherate (92%) [786] [936];
*in the presence of zinc chloride (Hoesch reaction) [1052].

m.p. 91° [1052], 79-80° [786] [936]; ^{1}H NMR [786].

1-[2-Hydroxy-4-[(3-methyl-2-butenyl)oxy]phenyl]-2-phenylethanone

[35486-77-2] $C_{19}H_{20}O_3$ mol.wt. 296.37



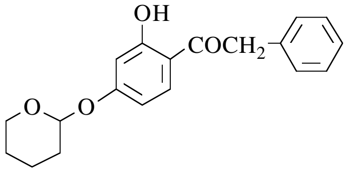
Synthesis

-Refer to: [393].

paper chromatography [393].

1-[2-Hydroxy-4-[(tetrahydro-2*H*-pyran-2-yl)oxy]phenyl]-2-phenylethanone

[130064-20-9] $C_{19}H_{20}O_4$ mol.wt. 312.37



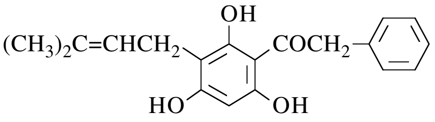
Synthesis

-Preparation by reaction of 3,4-dihydro-2*H*-pyran with 1-(2,4-dihydroxyphenyl)-2-phenylethanone in dioxane in the presence of PTSA (p-toluenesulfonic acid) at r.t. for 4 h (80%) [1335].

m.p. 89° [1335];
^{1}H NMR [1335], IR [1335], MS [1335].

2-Phenyl-1-[2,4,6-trihydroxy-3-(3-methyl-2-butenyl)phenyl]ethanone

[85602-17-1] $C_{19}H_{20}O_4$ mol.wt. 312.37

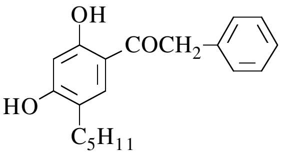


Synthesis

-Refer to: [1491].

1-(2,4-Dihydroxy-5-pentylphenyl)-2-phenylethanone

[96643-97-9] $C_{19}H_{22}O_3$ mol.wt. 298.38



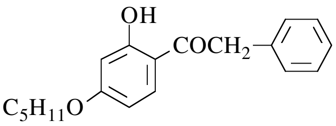
Syntheses

-Preparation by reaction of phenylacetonitrile with 4-pentylresorcinol,
*in the presence of boron trifluoride etherate (81%) [786] [936];
*in the presence of zinc chloride (Hoesch reaction) [1052].

m.p. 94-95° [786] [936], 89-90° [1052]; ^{1}H NMR [786].

1-[2-Hydroxy-4-(pentyloxy)phenyl]-2-phenylethanone

[50775-76-3] $C_{19}H_{22}O_3$ mol.wt. 298.38



Synthesis

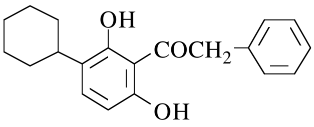
-Preparation by partial alkylation of benzyl 2,4-dihydroxyphenyl ketone with pentyl bromide in the presence of potassium carbonate in refluxing acetone for 20 h [148].

-Also refer to: [481] [482] [484] [486].

m.p. 70-73° [148].

1-(3-Cyclohexyl-2,6-dihydroxyphenyl)-2-phenylethanone

$C_{20}H_{22}O_3$ mol.wt. 310.39



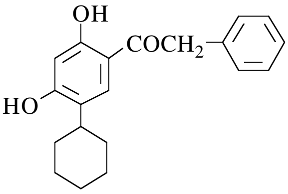
Synthesis

-Obtained by reaction of phenylacetonitrile with 4-cyclohexylresorcinol (Hoesch reaction) [914].

m.p. 221° [914].

1-(5-Cyclohexyl-2,4-dihydroxyphenyl)-2-phenylethanone

[159977-40-9] $C_{20}H_{22}O_3$ mol.wt. 310.39



Syntheses

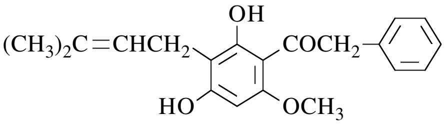
-Preparation by reaction of phenylacetic acid with 4-cyclohexylresorcinol in the presence of boron trifluoride etherate at 125° for 30 min, followed by hydrolysis of the complex obtained (m.p. 165-166°) with boiling dilute ethanol for 15-20 min (39%) [1133].

-Also obtained by reaction of phenylacetonitrile with 4-cyclohexylresorcinol (Hoesch reaction) [914].

m.p. 133° [914], 132-133° [1133]; IR [1133], UV [1133].

1-[2,4-Dihydroxy-6-methoxy-3-(3-methyl-2-butenyl)phenyl]-2-phenylethanone

[55607-21-1] $C_{20}H_{22}O_4$ mol.wt. 326.39



Syntheses

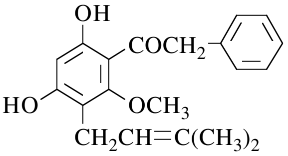
-Obtained by reaction of 2-hydroxy-2-methyl-3-butene with 2,4-dihydroxy-6-methoxyphenyl benzyl ketone in dioxane in the presence of boron trifluoride etherate for 1 h at r.t. (14%) [715].

-Also obtained by reaction of prenyl bromide with 2,4-dihydroxy-6-methoxyphenyl benzyl ketone in methanolic potassium hydroxide for 20 h at r.t. (20%) [715].

m.p. 133-134° [715]; ^{1}H NMR [715]; TLC [715].

1-[4,6-Dihydroxy-2-methoxy-3-(3-methyl-2-butenyl)phenyl]-2-phenylethanone

[55607-22-2] $C_{20}H_{22}O_4$ mol.wt. 326.39



Syntheses

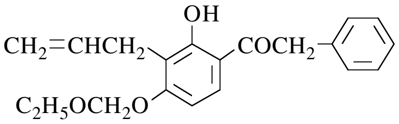
-Obtained by reaction of 2-hydroxy-2-methyl-3-butene with 2,4-dihydroxy-6-methoxyphenyl benzyl ketone in dioxane in the presence of boron trifluoride etherate for 1 h at r.t. (19%) [715].

-Also obtained by reaction of prenyl bromide with 2,4-dihydroxy-6-methoxyphenyl benzyl ketone in methanolic potassium hydroxide for 20 h at r.t. (13%) [715].

m.p. 93-94° [715]; ^{1}H NMR [715]; TLC [715].

1-[4-(Ethoxymethoxy)-2-hydroxy-3-(2-propenyl)phenyl]-2-phenylethanone

[117951-95-8] $C_{20}H_{22}O_4$ mol.wt. 326.39



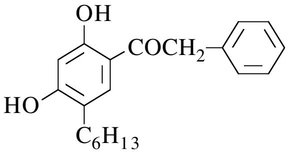
Synthesis

-Obtained (poor yield) by reaction of ethoxymethyl chloride with 3-allyl-2,4-dihydroxydesoxybenzoin in the presence of potassium carbonate in acetone (9%) [711].

light brown oil [711]; ^1H NMR [711], IR [711], UV [711].

1-(5-Hexyl-2,4-dihydroxyphenyl)-2-phenylethanone

[96643-98-0] $C_{20}H_{24}O_3$ mol.wt. 312.41



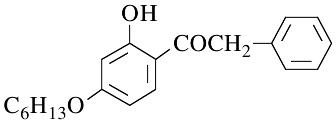
Syntheses

-Preparation by reaction of phenylacetonitrile with 4-hexylresorcinol,
*in the presence of boron trifluoride etherate under hydrogen chloride atmosphere (8-10 h) and at r.t. overnight (83%) [786] [936];
*in the presence of zinc chloride (Hoesch reaction) [1052].
-Also obtained (poor yield) by Friedel-Crafts acylation of 4-hexylresorcinol with phenylacetyl chloride in the presence of aluminium chloride in nitrobenzene at 80° for 2 days [913].

m.p. 90° [913], 86-87° [1052], 83-84° [786] [936]; ^1H NMR [786].

1-[4-(Hexyloxy)-2-hydroxyphenyl]-2-phenylethanone

[50776-01-7] $C_{20}H_{24}O_3$ mol.wt. 312.41



Syntheses

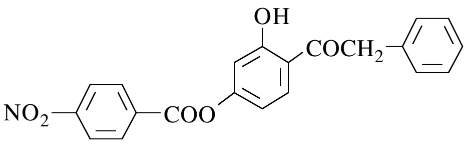
-Preparation by partial alkylation of benzyl 2,4-dihydroxyphenyl ketone with hexyl bromide in the presence of potassium carbonate in refluxing acetone for 20 h [148].

-Also refer to: [481] [482].

m.p. 60-62° [148].

1-[2-Hydroxy-4-(4-nitrobenzoyloxy)phenyl]-2-phenylethanone

$C_{21}H_{15}NO_6$ mol.wt. 377.35



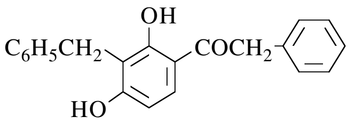
Synthesis

-Obtained by partial esterification of benzyl 2,4-dihydroxyphenyl ketone [106] with p-nitrobenzoyl chloride in the presence of pyridine [585].

m.p. 178-180° [585].

1-[2,4-Dihydroxy-3-(phenylmethyl)phenyl]-2-phenylethanone

[95832-51-2] $C_{21}H_{18}O_3$ mol.wt. 318.37



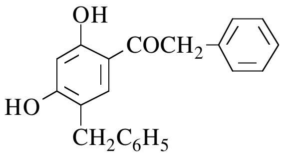
Syntheses

-Obtained by reaction of benzyl alcohol with 2,4-dihydroxydesoxybenzoin in dioxane in the presence of boron trifluoride etherate at 60-70° for 7 h (21%) [713].
-Also obtained by rearrangement of 2-hydroxy-4-(benzyloxy)desoxybenzoin in TFA at r.t. for 70 h (16%) [713].
-Obtained by reaction of benzyl bromide with 2,4-dihydroxydesoxybenzoin in methanol in the presence of potassium hydroxide at r.t. for 24 h (11%) [718].

m.p. 122-124° [718], 121-122° [713];
column chromatography [713]; TLC [713];
^{1}H NMR [713], IR [713], UV [713].

1-[2,4-Dihydroxy-5-(phenylmethyl)phenyl]-2-phenylethanone

[95832-52-3] $C_{21}H_{18}O_3$ mol.wt. 318.37



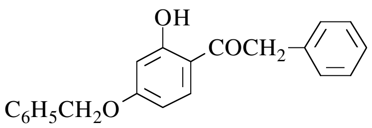
Syntheses

-Obtained by reaction of benzyl alcohol with 2,4-dihydroxydesoxybenzoin in dioxane in the presence of boron trifluoride etherate at 60-70° for 7 h (31%) [713].
-Also obtained by rearrangement of 2-hydroxy-4-(benzyloxy)desoxybenzoin in TFA at r.t. for 70 h (31%) [713].
-Also obtained by reaction of benzyl bromide with 2,4-dihydroxydesoxybenzoin in methanol in the presence of potassium hydroxide at r.t. for 24 h (< 3%) [718].

m.p. 128-129° [713], 126-128° [718];
column chromatography [713]; TLC [713];
^{1}H NMR [713], IR [713], UV [713].

1-[2-Hydroxy-4-(phenylmethoxy)phenyl]-2-phenylethanone

[39604-80-3] $C_{21}H_{18}O_3$ mol.wt. 318.37



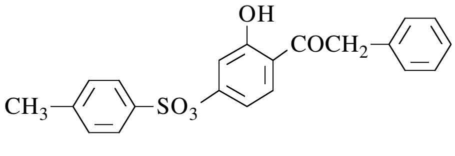
Syntheses

-Preparation by partial benzylation of 2,4-dihydroxyphenyl benzyl ketone,
*with benzyl chloride in the presence of potassium carbonate in refluxing acetone [1145], (72%) [12];
*with benzyl bromide in the presence of potassium carbonate in refluxing acetone [148] or in the presence of potassium hydroxide at r.t. for 24 h (29%) [718].
-Also refer to: [11] [953].

m.p. 105-106° [718], 104-108° [148], 104-105° [12].

1-[2-Hydroxy-4-[[(4-methylphenyl)sulfonyl]oxy]phenyl]-2-phenylethanone

[102478-26-2] $C_{21}H_{18}O_5S$ mol.wt. 382.44



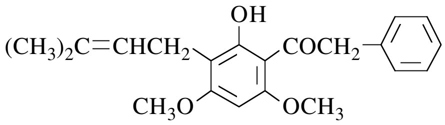
Synthesis

-Obtained by partial esterification of benzyl 2,4-dihydroxyphenyl ketone with p-toluenesulfonyl chloride in acetone in the presence of potassium carbonate [585].

m.p. 117° [585].

1-[2-Hydroxy-4,6-dimethoxy-3-(3-methyl-2-butenyl)phenyl]-2-phenylethanone

[55607-23-3] $C_{21}H_{24}O_4$ mol.wt. 340.42



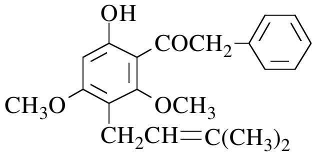
Synthesis

-Obtained by partial methylation of 2,4-dihydroxy-6-methoxy-3-prenylphenyl benzyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 3.5 h (96%) [715].

m.p. 113-114° [715]; ^1H NMR [715]; TLC [715].

1-[6-Hydroxy-2,4-dimethoxy-3-(3-methyl-2-butenyl)phenyl]-2-phenylethanone

[55607-25-5] $C_{21}H_{24}O_4$ mol.wt. 340.42



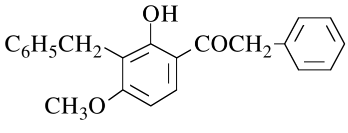
Synthesis

-Obtained by partial methylation of 2,4-dihydroxy-6-methoxy-5-prenylphenyl benzyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 4 h [715].

m.p. 80-81° [715]; ^1H NMR [715]; TLC [715].

1-[2-Hydroxy-4-methoxy-3-(phenylmethyl)phenyl]-2-phenylethanone

[95832-54-5] $C_{22}H_{20}O_3$ mol.wt. 332.40



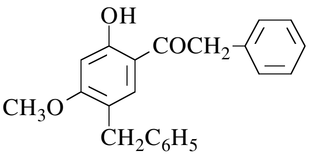
Synthesis

-Preparation by reaction of dimethyl sulfate with 3-benzyl-2,4-dihydroxydeoxybenzoin in the presence of potassium carbonate in refluxing acetone for 3 h [713].

oil [713]; TLC [713]; ^1H NMR [713].

1-[2-Hydroxy-4-methoxy-5-(phenylmethyl)phenyl]-2-phenylethanone

[95832-53-4] $C_{22}H_{20}O_3$ mol.wt. 332.40



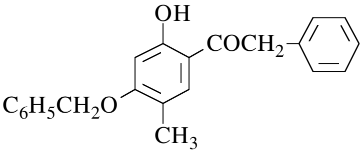
Synthesis

-Preparation by reaction of dimethyl sulfate with 5-benzyl-2,4-dihydroxydeoxybenzoin in the presence of potassium carbonate in refluxing acetone for 3 h (84%) [713].

m.p. 80-81° [713]; TLC [713]; ^{1}H NMR [713].

1-[2-Hydroxy-5-methyl-4-(phenylmethoxy)phenyl]-2-phenylethanone

[112198-28-4] $C_{22}H_{20}O_3$ mol.wt. 332.40



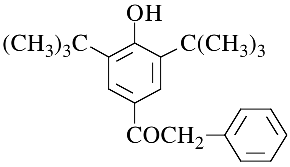
Synthesis

-Preparation by reaction of benzyl chloride with 2,4-dihydroxy-5-methylphenyl benzyl ketone in the presence of potassium carbonate in refluxing acetone for 7 h (73%) [1572].

m.p. 108° [1572].

1-[3,5-Bis(1,1-dimethylethyl)-4-hydroxyphenyl]-2-phenylethanone

[14035-39-3] $C_{22}H_{28}O_2$ mol.wt. 324.46



Syntheses

-Preparation by Friedel-Crafts acylation of 2,6-di-tert-butylphenol with phenylacetyl chloride in the presence of aluminium chloride for 15 min at -10° (84%) [1192], (75%) [1316].

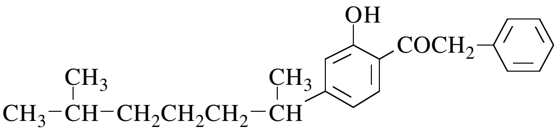
-Preparation by oxidation of 1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenylethanol with DDQ in dioxane at r.t. for 16 h (90%) [144].

-Also refer to: [380] [1469].

m.p. 129-130° [144], 120-122° [1192] [1316]; ^{1}H NMR [144].

1-[4-(1,5-Dimethylhexyl)-2-hydroxyphenyl]-2-phenylethanone

[146935-09-3] $C_{22}H_{28}O_2$ mol.wt. 324.46

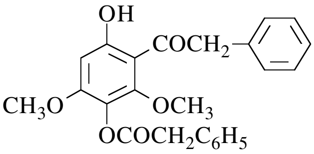


Synthesis

-Refer to: [1546] (Japanese patent).

1-[6-Hydroxy-2,4-dimethoxy-3-[(phenylacetyl)oxy]phenyl]-2-phenylethanone

$C_{24}H_{22}O_6$ mol.wt. 406.44



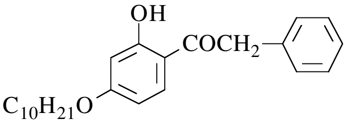
Synthesis

-Obtained (by-product) by condensation of 2,6-dimethoxyhydroquinone with the complex phenylacetic acid and boron trifluoride [766].

m.p. 105° [766].

1-[4-(Decyloxy)-2-hydroxyphenyl]-2-phenylethanone

[143287-02-9] $C_{24}H_{32}O_3$ mol.wt. 368.52



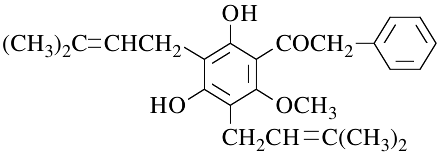
Synthesis

-Preparation by partial alkylation of benzyl 2,4-dihydroxyphenyl ketone with decyl bromide in the presence of potassium carbonate in refluxing acetone for 20 h [148].

m.p. 66-69° [148].

1-[2,4-Dihydroxy-6-methoxy-3,5-bis(3-methyl-2-butenyl)phenyl]-2-phenylethanone

[55607-20-0] $C_{25}H_{30}O_4$ mol.wt. 394.51



Syntheses

-Obtained (poor yield) by reaction of 2-hydroxy-2-methyl-3-butene with 2,4-dihydroxy-6-methoxyphenyl benzyl ketone in dioxane in the presence of boron trifluoride etherate for 1 h at r.t. (4%) [715].

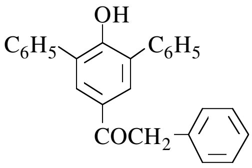
-Also obtained (poor yield) by reaction of prenyl bromide with 2,4-dihydroxy-6-methoxyphenyl benzyl ketone in methanolic potassium hydroxide for 20 h at r.t. (5%) [715].

oil [715]; TLC [715].

1-[(4-Hydroxy-3,5-diphenyl)phenyl]-2-phenylethanone

1-(2′-Hydroxy[1,1′:3′,1″-terphenyl]-5′-yl)-2-phenylethanone

[73048-87-0] $C_{26}H_{20}O_2$ mol.wt. 364.45



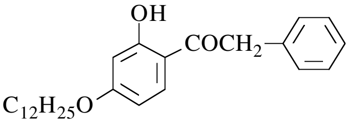
Synthesis

-Obtained by DDQ oxidation of 1-[4-hydroxy-3,5-(diphenyl)phenyl]-2-phenylethanol in dioxane at r.t. for 76 h (89%) [144].

m.p. 155-156° [144]; ^{1}H NMR [144].

1-[4-(Dodecyloxy)-2-hydroxyphenyl]-2-phenylethanone

[143287-03-0] $C_{26}H_{36}O_3$ mol.wt. 396.57



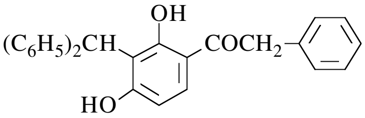
Synthesis

-Preparation by partial alkylation of 2,4-dihydroxyphenyl benzyl ketone with dodecyl bromide in the presence of potassium carbonate in refluxing acetone for 20 h [148].

m.p. 68-71° [148].

1-[3-(Diphenylmethyl)-2,4-dihydroxyphenyl]-2-phenylethanone

[98497-96-2] $C_{27}H_{22}O_3$ mol.wt. 394.47



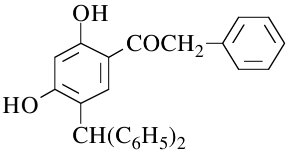
Synthesis

-Obtained by reaction of 2,4-dihydroxydesoxybenzoin with diphenylcarbinol in dioxane in the presence of boron trifluoride etherate at 60-70° for 3 h (17%) [712].

m.p. 133-134° [712]; column chromatography [712]; TLC [712];
^{1}H NMR [712], IR [712], UV [712].

1-[5-(Diphenylmethyl)-2,4-dihydroxyphenyl]-2-phenylethanone

[98497-97-3] $C_{27}H_{22}O_3$ mol.wt. 394.47



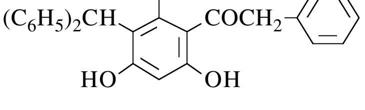
Synthesis

-Obtained by reaction of 2,4-dihydroxydesoxybenzoin with diphenylcarbinol in dioxane in the presence of boron trifluoride etherate at 60-70° for 3 h (24%) [712].

m.p. 142-143° [712];
column chromatography [712]; TLC [712];
^{1}H NMR [712], IR [712], UV [712].

1-[3-(Diphenylmethyl)-2,4,6-trihydroxyphenyl]-2-phenylethanone

[104310-95-4] $C_{27}H_{22}O_4$ mol.wt. 410.47



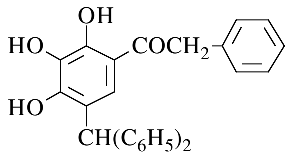
Synthesis

-Obtained by reaction of diphenylcarbinol with 2,4,6-trihydroxyphenyl benzyl ketone in dioxane in the presence of boron trifluoride etherate at 60-70° for 3.5 h (24%) [719].

m.p. 160-162° [719]; TLC [719];
^{1}H NMR [719], IR [719], UV [719].

1-[5-(Diphenylmethyl)-2,3,4-trihydroxyphenyl]-2-phenylethanone

[106556-47-2] $C_{27}H_{22}O_4$ mol.wt. 410.47



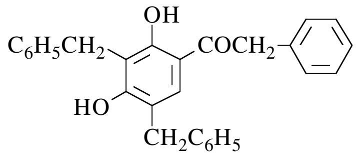
Synthesis

-Obtained by reaction of diphenylcarbinol with 2,3,4-trihydroxyphenyl benzyl ketone in dioxane in the presence of boron trifluoride etherate for 4 h at r.t. (39%) [698].

m.p. 177-178° [698]; TLC [698];
^{1}H NMR [698], IR [698], UV [698].

1-[2,4-Dihydroxy-3,5-bis(phenylmethyl)phenyl]-2-phenylethanone

[95832-50-1] $C_{28}H_{24}O_3$ mol.wt. 408.50



Syntheses

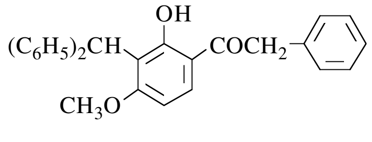
-Obtained by reaction of benzyl alcohol with 2,4-dihydroxydesoxybenzoin in dioxane in the presence of boron trifluoride etherate at 60-70° for 7 h (10%) [713].

-Also obtained (trace) by reaction of benzyl bromide with 2,4-dihydroxydesoxybenzoin in methanol in the presence of potassium hydroxide at r.t. for 24 h (< 2%) [718].

m.p. 111-112° [713], 110-112° [718]; column chromatography [713];
^{1}H NMR [713], ^{13}C NMR [718], IR [713], UV [713].

1-[3-(Diphenylmethyl)-2-hydroxy-4-methoxyphenyl]-2-phenylethanone

[98498-01-2] $C_{28}H_{24}O_3$ mol.wt. 408.50



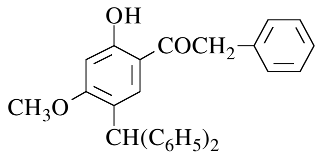
Synthesis

-Preparation by reaction of dimethyl sulfate with 2,4-dihydroxy-3-(diphenylmethyl)desoxybenzoin in the presence of potassium carbonate in refluxing acetone for 3 h (93%) [712].

m.p. 126-127° [712]; TLC [712]; ^{1}H NMR [712].

1-[5-(Diphenylmethyl)-2-hydroxy-4-methoxyphenyl]-2-phenylethanone

[98498-02-3] $C_{28}H_{24}O_3$ mol.wt. 408.50



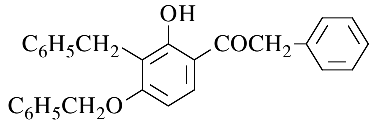
Synthesis

-Preparation by reaction of dimethyl sulfate with 2,4-dihydroxy-5-(diphenylmethyl)desoxybenzoin in the presence of potassium carbonate in refluxing acetone for 3 h (93%) [712].

m.p. 110-111° [712]; TLC [712]; ^{1}H NMR [712].

1-[2-Hydroxy-4-(phenylmethoxy)-3-(phenylmethyl)phenyl]-2-phenylethanone

[107044-42-8] $C_{28}H_{24}O_3$ mol.wt. 408.50



Syntheses

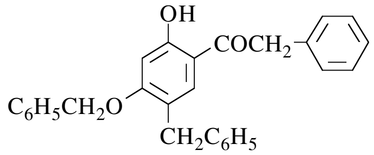
-Obtained by reaction of benzyl chloride (1 mol) with 3-benzyl-2,4-dihydroxydesoxybenzoin in the presence of potassium carbonate (4 mol) in boiling acetone for 1.5 h [718].

-Also obtained (trace) by reaction of benzyl bromide with 2,4-dihydroxydesoxybenzoin in methanol in the presence of potassium hydroxide at r.t. for 24 h (< 1%) [718].

m.p. 97-98° [718]; column chromatography [718];
^{1}H NMR [718], IR [718], UV [718].

1-[2-Hydroxy-4-(phenylmethoxy)-5-(phenylmethyl)phenyl]-2-phenylethanone

[107044-44-0] $C_{28}H_{24}O_3$ mol.wt. 408.50



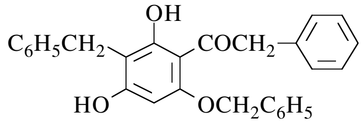
Synthesis

-Obtained by reaction of benzyl bromide (1 mol) with 5-benzyl-2,4-dihydroxydesoxybenzoin in the presence of potassium carbonate (4 mol) in boiling acetone for 1.5 h (19%) [718].

m.p. 90-92° [718]; column chromatography [718];
^{1}H NMR [718], IR [718].

1-[2,4-Dihydroxy-6-(phenylmethoxy)-3-(phenylmethyl)phenyl]-2-phenylethanone

[39548-97-5] $C_{28}H_{24}O_4$ mol.wt. 424.50



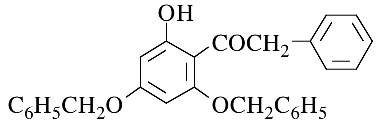
Synthesis

-Obtained (by-product) by benzylation of 2,4,6-trihydroxyphenyl benzyl ketone with benzyl chloride in the presence of potassium carbonate in refluxing acetone for 7 h (9%) [714].

m.p. 170-171° [714]; ^{1}H NMR [714], UV [714].

1-[2-Hydroxy-4,6-bis(phenylmethoxy)phenyl]-2-phenylethanone

[39548-96-4] $C_{28}H_{24}O_4$ mol.wt. 424.50



Syntheses

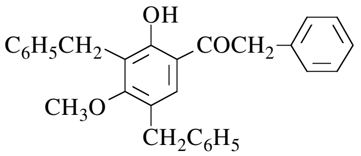
-Obtained by reaction of benzyl chloride with 2,4,6-trihydroxyphenyl benzyl ketone in the presence of potassium carbonate in refluxing acetone for 5 h (34%) [12] or for 7 h (21%) [714].

-Also refer to: [953].

m.p. 99-100° [12], 95-96° [714]; ^{1}H NMR [714], UV [714].

1-[2-Hydroxy-4-methoxy-3,5-bis(phenylmethyl)phenyl]-2-phenylethanone

[95832-55-6] $C_{29}H_{26}O_3$ mol.wt. 422.52



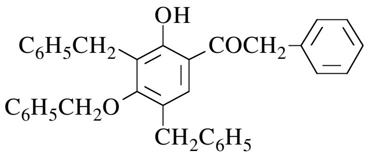
Synthesis

-Obtained by reaction of dimethyl sulfate with 3,5-dibenzyl-2,4-dihydroxyphenyl benzyl ketone in the presence of potassium carbonate in refluxing acetone for 3 h (23%) [713].

oil [713]; TLC [713]; ^{1}H NMR [713].

1-[2-Hydroxy-4-(phenylmethoxy)-3,5-bis(phenylmethyl)phenyl]-2-phenylethanone

[107044-43-9] $C_{35}H_{30}O_3$ mol.wt. 498.62



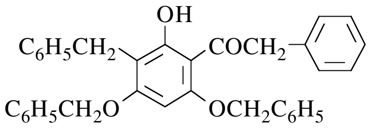
Synthesis

-Obtained by reaction of benzyl chloride (1 mol) with 3,5-dibenzyl-2,4-dihydroxydesoxybenzoin in the presence of potassium carbonate (4 mol) in boiling acetone for 1.5 h (33%) [718].

m.p. 51-52° [718]; TLC [718];
^{1}H NMR [718], IR [718], UV [718].

1-[2-Hydroxy-4,6-bis(phenylmethoxy)-3-(phenylmethyl)phenyl]-2-phenylethanone

[39548-95-3] $C_{35}H_{30}O_4$ mol.wt. 514.62



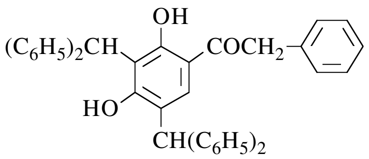
Synthesis

-Obtained (by-product) by benzylation of 2,4,6-trihydroxyphenyl benzyl ketone with benzyl chloride in the presence of potassium carbonate in refluxing acetone for 7 h (6%) [714].

m.p. 131-132° [714]; ^{1}H NMR [714], UV [714].

1-[3,5-Bis(diphenylmethyl)-2,4-dihydroxyphenyl]-2-phenylethanone

[98497-95-1] $C_{40}H_{32}O_3$ mol.wt. 560.69



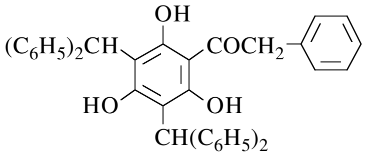
Synthesis

-Obtained by reaction of 2,4-dihydroxydesoxybenzoin with diphenylcarbinol in dioxane in the presence of boron trifluoride etherate at 60-70° for 3 h (15%) [712].

m.p. 136-137° [712]; column chromatography [712]; TLC [712];
^{1}H NMR [712], IR [712], UV [712].

1-[3,5-Bis(diphenylmethyl)-2,4,6-trihydroxyphenyl]-2-phenylethanone

[104310-93-2] $C_{40}H_{32}O_4$ mol.wt. 576.69



Synthesis

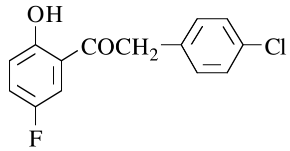
-Obtained by reaction of diphenylcarbinol with 2,4,6-trihydroxyphenyl benzyl ketone in dioxane in the presence of boron trifluoride etherate at 60-70° for 3.5 h (21%) [719].

m.p. 122-124° [719]; TLC [719];
^{1}H NMR [719], IR [719], UV [719].

9.2. *Compounds derived from substituted phenylacetic acids*

2-(4-Chlorophenyl)-1-(5-fluoro-2-hydroxyphenyl)ethanone

$C_{14}H_{10}ClFO_2$ mol.wt. 264.68



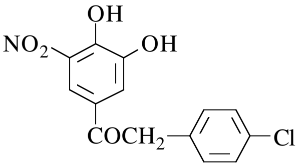
Synthesis

-Preparation by Fries rearrangement of p-fluorophenyl p-chlorophenylacetate with aluminium chloride at 150-180° for 20 min (32%) [838].

m.p. 124-126° [838]; ^{1}H NMR [838], MS [838].

2-(4-Chlorophenyl)-1-(3,4-dihydroxy-5-nitrophenyl)ethanone

[274925-89-2] $C_{14}H_{10}ClNO_5$ mol.wt. 307.69



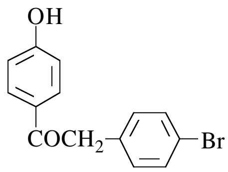
Synthesis

-Preparation by treatment of 2-(4-chlorophenyl)-1-(4-hydroxy-3-methoxy-5-nitrophenyl)ethanone with aluminium chloride in refluxing ethyl acetate/pyridine mixture for 2 h (94%) [885], (90-96%) [887].

m.p. 162-164° [885] [887]; HPLC [885];
^{1}H NMR [885] [887], ^{13}C NMR [885] [887], IR [885] [887].

2-(4-Bromophenyl)-1-(4-hydroxyphenyl)ethanone

[63186-92-5] $C_{14}H_{11}BrO_2$ mol.wt. 291.14



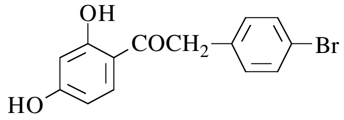
Synthesis

-Preparation by demethylation of 2-(4-bromophenyl)-1-(4-methoxyphenyl)ethanone with 48% hydrobromic acid in refluxing acetic acid for 7 h (89%) [505], (82%) [420].

m.p. 186° [420] [505];
^{1}H NMR [505], IR [505].

2-(4-Bromophenyl)-1-(2,4-dihydroxyphenyl)ethanone

[92152-60-8] $C_{14}H_{11}BrO_3$ mol.wt. 307.14



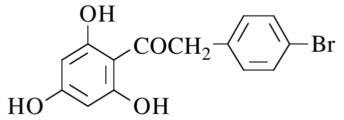
Syntheses

-Preparation by reaction of p-bromophenylacetonitrile with resorcinol,
*in the presence of boron trifluoride etherate under hydrogen chloride atmosphere (8-10 h) and at r.t. overnight (90%) [786] [936];
*in the presence of zinc chloride and hydrogen chloride (Hoesch reaction) [282].
-Preparation by Friedel-Crafts acylation of resorcinol with p-bromophenylacetyl chloride in nitrobenzene in the presence of aluminium chloride at 50° (54%) [914].
-Also refer to: [1182] [1449].

m.p. 176-177° [786] [936], 176° [914], 100-101° [282]. One of the reported melting points is obviously wrong. ¹H NMR [786].

2-(4-Bromophenyl)-1-(2,4,6-trihydroxyphenyl)ethanone

[147220-80-2] $C_{14}H_{11}BrO_4$ mol.wt. 323.15



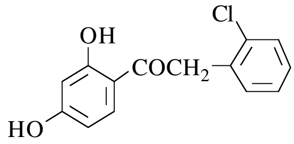
Synthesis

-Refer to: [1182] (compound IIg), preparation according to reported procedures [5] [1420].

m.p. 231° [1182]; ¹H NMR [1182], IR [1182].

2-(2-Chlorophenyl)-1-(2,4-dihydroxyphenyl)ethanone

$C_{14}H_{11}ClO_3$ mol.wt. 262.69



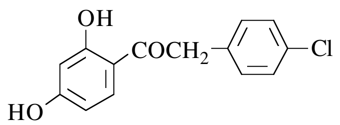
Synthesis

-Obtained by reaction of o-chlorophenylacetonitrile with resorcinol (Hoesch reaction) (20%) [1125].

m.p. 142° [1125].

2-(4-Chlorophenyl)-1-(2,4-dihydroxyphenyl)ethanone

[15485-64-0] $C_{14}H_{11}ClO_3$ mol.wt. 262.69



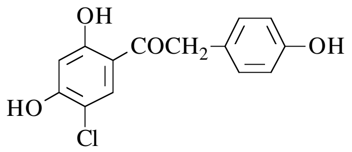
Syntheses

-Preparation by Friedel-Crafts acylation of resorcinol with p-chlorophenylacetyl chloride in nitrobenzene in the presence of aluminium chloride for some hours at 40-50° (64%) [914].
-Obtained by reaction of p-chlorophenylacetonitrile with resorcinol (Hoesch reaction) [285] [1019].
-Also refer to: [467] [1182] [1183] [1449].

m.p. 159°5-160° [1019], 156° [914], 153-154° [285]; UV [1019].

1-(5-Chloro-2,4-dihydroxyphenyl)-2-(4-hydroxyphenyl)ethanone

[139256-02-3] $C_{14}H_{11}ClO_4$ mol.wt. 278.69



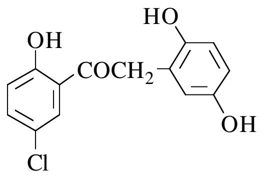
Synthesis

-Obtained by reaction of p-hydroxyphenylacetic acid with 4-chlororesorcinol in the presence of boron trifluoride etherate under argon, on a water bath for 1 h (67%) [1516].

m.p. 196-197° [1516]; ^{1}H NMR [1516], ^{13}C NMR [1516], MS [1516].

1-(5-Chloro-2-hydroxyphenyl)-2-(2,5-dihydroxyphenyl)ethanone

[115781-55-0] $C_{14}H_{11}ClO_4$ mol.wt. 278.69



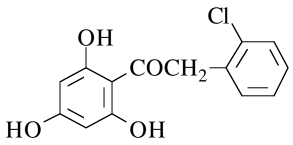
Synthesis

-Obtained by alkali cleavage of 6-chloro-3-(2',5'-dihydroxyphenyl)-4-hydroxycoumarin with refluxing 2% methanolic potassium hydroxide for 4 h (73%) [1218].

m.p. 219° [1218]; IR [1218], UV [1218].

2-(2-Chlorophenyl)-1-(2,4,6-trihydroxyphenyl)ethanone

$C_{14}H_{11}ClO_4$ mol.wt. 278.69



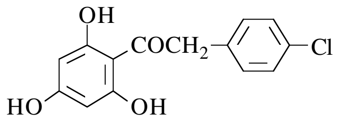
Synthesis

-Obtained by reaction of o-chlorophenylacetonitrile with phloroglucinol (20%) (Hoesch reaction) [1125].

m.p. 172-172°5 [1125].

2-(4-Chlorophenyl)-1-(2,4,6-trihydroxyphenyl)ethanone

[15485-68-4] $C_{14}H_{11}ClO_4$ mol.wt. 278.69



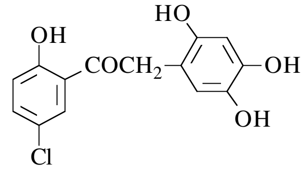
Syntheses

-Obtained by reaction of p-chlorophenylacetonitrile with phloroglucinol (Hoesch reaction) [285] [1019].
-Also refer to: [1182] [1183] [1188].

m.p. 224-225° [1019], 221-222° [285]; UV [1019].

1-(5-Chloro-2-hydroxyphenyl)-2-(2,4,5-trihydroxyphenyl)ethanone

[115781-51-6] $C_{14}H_{11}ClO_5$ mol.wt. 294.69



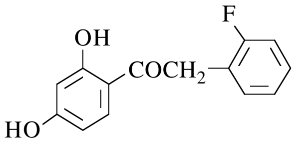
Synthesis

-Obtained from 6-chloro-4-hydroxy-3-(2',4',5'-trihydroxyphenyl)coumarin with refluxing 2% methanolic potassium hydroxide for 4 h (72%) [1218].

m.p. 189° [1218]; IR [1218], UV [1218].

1-(2,4-Dihydroxyphenyl)-2-(2-fluorophenyl)ethanone

[121060-02-4] $C_{14}H_{11}FO_3$ mol.wt. 246.24



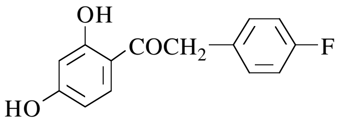
Syntheses

-Refer to: [1182] (compound Id), preparation according to reported procedures [5] [1420].
-Also refer to: [1185] [1186] [1497].

m.p. 138° [1182]; ^{1}H NMR [1182], IR [1182].

1-(2,4-Dihydroxyphenyl)-2-(4-fluorophenyl)ethanone

[15485-70-8] $C_{14}H_{11}FO_3$ mol.wt. 246.24



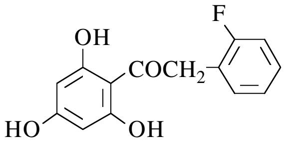
Syntheses

-Preparation by reaction of p-fluorophenylacetonitrile with resorcinol (Hoesch reaction) [1019], (70%) [1490], (45%) [1448].
-Also refer to: [1182] [1183] [1185] [1186] [1497].

m.p. 149-150° [1019], 144-145° [1448], 143-144° [1490];
^{1}H NMR [1448] [1490], UV [1019], MS [1448].

2-(2-Fluorophenyl)-1-(2,4,6-trihydroxyphenyl)ethanone

[101068-28-4] $C_{14}H_{11}FO_4$ mol.wt. 262.24



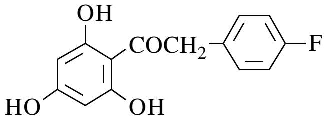
Synthesis

-Refer to: [1182] (compound IId), preparation according to reported procedures [5] [1420].

m.p. 182° [1182]; ^{1}H NMR [1182], IR [1182].

2-(4-Fluorophenyl)-1-(2,4,6-trihydroxyphenyl)ethanone

[15485-69-5] $C_{14}H_{11}FO_4$ mol.wt. 262.24



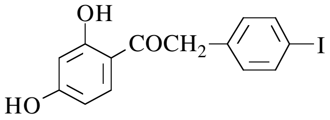
Syntheses

-Obtained by reaction of p-fluorophenylacetonitrile with phloroglucinol (Hoesch reaction) [141] [1019].
-Also refer to: [1182] [1183].

m.p. 199-200° [1019]; UV [1019].

1-(2,4-Dihydroxyphenyl)-2-(4-iodophenyl)ethanone

$C_{14}H_{11}IO_3$ mol.wt. 354.14



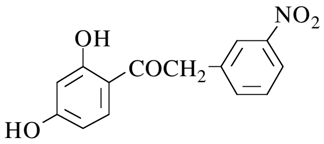
Syntheses

-Obtained by reaction of resorcinol with p-iodophenylacetyl chloride in nitrobenzene in the presence of aluminium chloride at 50-60° (27%) [914].
-Also refer to: [915].

m.p. 186° [914] [915].

1-(2,4-Dihydroxyphenyl)-2-(3-nitrophenyl)ethanone

$C_{14}H_{11}NO_5$ mol.wt. 273.25



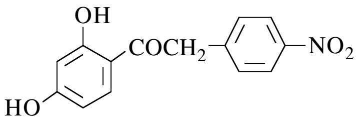
Synthesis

-Preparation by reaction of m-nitrophenylacetonitrile with resorcinol (Hoesch reaction) (46%) [1556].

m.p. 156°5 [1556].

1-(2,4-Dihydroxyphenyl)-2-(4-nitrophenyl)ethanone

[15485-63-9] $C_{14}H_{11}NO_5$ mol.wt. 273.25



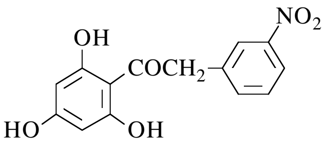
Syntheses

-Obtained by reaction of p-nitrophenylacetonitrile with resorcinol (Hoesch reaction) [1019], (65%) [913], (60%) [992], (40%) [430], (35%) [743], (27%) [1556].
-Also obtained by reaction of p-nitrophenylacetic acid with resorcinol in the presence of boron trifluoride in chloroform, first cooling in ice, then at r.t. overnight (12%) [764].
-Also refer to: [467] [585] [1182].

m.p. 295-297° [1019], 210° [743] [764], 205° [913], 204° [430], 202° [1556]. One of the reported melting points is obviously wrong. ^{1}H NMR [992], UV [1019], MS [992].

2-(3-Nitrophenyl)-1-(2,4,6-trihydroxyphenyl)ethanone

$C_{14}H_{11}NO_6$ mol.wt. 289.25



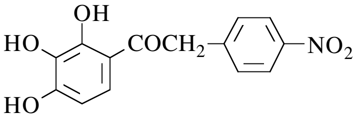
Synthesis

-Preparation by reaction of m-nitrophenylacetonitrile with phloroglucinol (Hoesch reaction) (63%) [1556].

m.p. 211-212° [1556].

2-(4-Nitrophenyl)-1-(2,3,4-trihydroxyphenyl)ethanone

$C_{14}H_{11}NO_6$ mol.wt. 289.25



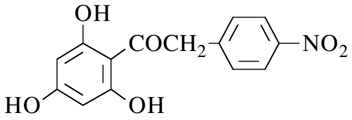
Synthesis

-Obtained by reaction of p-nitrophenylacetic acid with pyrogallol in the presence of boron trifluoride in chloroform, first cooling in ice, then at r.t. overnight (93%) [764].

m.p. 227-228° [764].

2-(4-Nitrophenyl)-1-(2,4,6-trihydroxyphenyl)ethanone

[15485-67-3] $C_{14}H_{11}NO_6$ mol.wt. 289.25



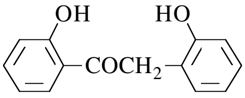
Syntheses

-Obtained by reaction of p-nitrophenylacetonitrile with phloroglucinol (Hoesch reaction) [1019], (quantitative yield) [430], (56%) [1556].
-Also refer to: [585] [764] [1418].

m.p. 249-250° [1019], 247° [1556], 245° [430]; UV [1019].

1,2-Bis(2-hydroxyphenyl)ethanone

[7622-42-6] $C_{14}H_{12}O_3$ mol.wt. 228.25



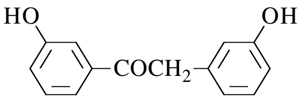
Syntheses

-Preparation by reduction of 2,2'-dihydroxybenzoin with zinc dust and 15% potassium hydroxide in boiling ethanol for 8 h [344], (70-75%) [868].
-Also refer to: [1459].

m.p. 104° [868].

1,2-Bis(3-hydroxyphenyl)ethanone

[63192-59-6] $C_{14}H_{12}O_3$ mol.wt. 228.25



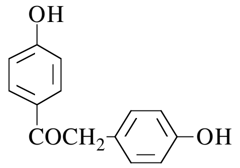
Syntheses

-Obtained by reductive coupling of methyl m-hydroxybenzoate using $TiCl_3/LiAlH_4$ in refluxing tetrahydrofuran for 3 h under nitrogen (20%) [359].
-Also refer to: [659].

GC [359]; GC-MS [359];
^{1}H NMR [359], ^{13}C NMR [359], IR [359], MS [359].

1,2-Bis(4-hydroxyphenyl)ethanone

[3669-47-4] $C_{14}H_{12}O_3$ mol.wt. 228.25



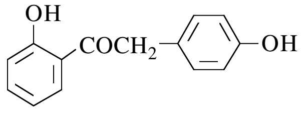
Syntheses

-Preparation by total demethylation of 4-methoxyphenyl 4-methoxybenzyl ketone (4,4'-dimethoxydeoxybenzoin),
*with refluxing pyridinium chloride (4 equiv) for 1 h (80-85%) [250];
*with boiling a mixture of 50% aqueous hydriodic acid and phenol for 30 min (94%) [1351];
*with hydriodic acid (d = 1.7) in acetic acid at 135-140° for 10 min (quantitative yield) [1351];
*with aluminium chloride in refluxing benzene for 1.5 h (25%) [889].
-Also obtained by diazotization of 4,4'-diaminodeoxybenzoin, followed by hydrolysis of the diazonium salt formed [1582].
-Also obtained (by-product) by Fries rearrangement of phenyl p-methoxyphenylacetate with aluminium chloride for 1.5 h at 145° (31%) [1335].
-Also refer to: [866].

m.p. 217° [1351], 215-219° [889], 215° [250], 214-215° [1582], 212° [1335].

1-(2-Hydroxyphenyl)-2-(4-hydroxyphenyl)ethanone

[109561-92-4] $C_{14}H_{12}O_3$ mol.wt. 228.25



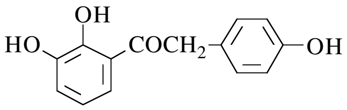
Syntheses

-Obtained by treatment of ethyl [(2-methoxybenzoyl)-(4-methoxyphenyl)]acetate with boiling pyridinium chloride for 20 min (ca. 220°) (48%) [779].
-Also obtained (by-product) by Fries rearrangement of phenyl p-methoxyphenylacetate with aluminium chloride for 1.5 h at 145° (12%) [1335].
-Also obtained by demethylation of 2-hydroxyphenyl 4-methoxybenzyl ketone with pyridinium chloride at 220° for 1 h (79%) [1335].
-Also refer to: [762] [763].

m.p. 140° [1335], 106-107° [779]. One of the reported melting points is obviously wrong.

1-(2,3-Dihydroxyphenyl)-2-(4-hydroxyphenyl)ethanone

[139256-01-2] $C_{14}H_{12}O_4$ mol.wt. 244.25

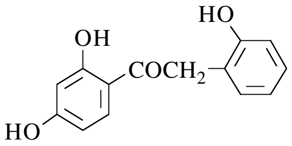


Synthesis

-Refer to: [1516].

1-(2,4-Dihydroxyphenyl)-2-(2-hydroxyphenyl)ethanone

$C_{14}H_{12}O_4$ mol.wt. 244.25

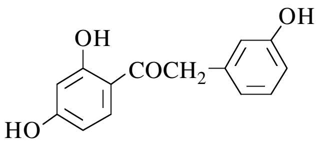


Synthesis not yet described

N.B.: This ketone (XIII) cannot be prepared by condensation of o-hydroxyphenylacetonitrile with resorcinol (Hoesch reaction) [1321].

1-(2,4-Dihydroxyphenyl)-2-(3-hydroxyphenyl)ethanone

[89019-84-1] $C_{14}H_{12}O_4$ mol.wt. 244.25



Syntheses

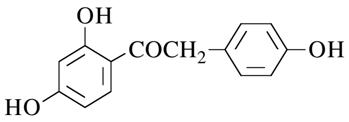
-Preparation by reaction of m-hydroxyphenylacetic acid with resorcinol in the presence of boron trifluoride etherate under argon on a water bath for 1 h (93%) [1516].

-Also obtained by demethylation of 1-(2,4-dihydroxyphenyl)-2-(3-methoxyphenyl)ethanone with concentrated hydrobromic acid in refluxing acetic acid for 4 h under an argon atmosphere (89%) [937].

m.p. 214-216° [937]; ^{1}H NMR [937], IR [937], UV [937], MS [937].

1-(2,4-Dihydroxyphenyl)-2-(4-hydroxyphenyl)ethanone

[17720-60-4] $C_{14}H_{12}O_4$ mol.wt. 244.25



Syntheses

-Preparation by reaction of p-hydroxyphenylacetic acid with resorcinol [871] in the presence of boron trifluoride etherate under argon on a water bath for 1 h (98%) [1516], at 100° for 1 h (70%) [549] or for 15 min (40%) [992].

-Preparation by demethylation of 2,4-dihydroxy-4'-methoxydesoxybenzoin with pyridinium bromide, kept at the melting stage for 1 min (quantitative yield) [703].

-Preparation by catalytic hydrogenation of 2,4-dihydroxy-4'-(benzyloxy)desoxybenzoin [1564].

-Also obtained by treatment of ethyl 2,4-dimethoxybenzoyl-4-methoxyphenylacetate with boiling pyridinium chloride for 20 min (ca. 220°) (49%) [779].

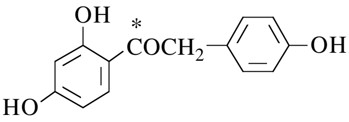
-Also obtained by alkaline degradation of *daidzein* (m.p. 315-320°) (7,4'-dihydroxyisoflavone) with refluxing 30% potassium hydroxide for 5 min (99%) [1520].

-Also obtained by reaction of p-hydroxyphenylacetonitrile with resorcinol (Hoesch reaction) (26%) [1520].
-Also refer to: [9] [461] [462] [463] [762] [870] [1165] [1182] [1184] [1335] [1527].

m.p. 192° [1520] [1564], 190-191° [703], 183-184° [779];
^{1}H NMR [992], ^{13}C NMR [732] [1167], MS [992].

1-(2,4-Dihydroxyphenyl)-2-(4-hydroxyphenyl)ethanone-*1*-^{13}C

[215653-80-8] $C_{14}H_{12}O_4$ mol.wt. 245.25

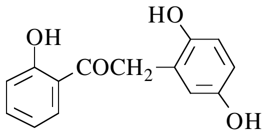


Synthesis

-Preparation by reaction of 4-benzyloxyphenylacetonitrile [1-^{13}C] with resorcinol (Hoesch reaction) (96%) [159].

2-(2,5-Dihydroxyphenyl)-1-(2-hydroxyphenyl)ethanone

[115781-54-9] $C_{14}H_{12}O_4$ mol.wt. 244.25



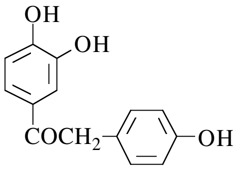
Synthesis

-Obtained by alkali cleavage of 3-(2',5'-dihydroxyphenyl)-4-hydroxycoumarin with refluxing 2% methanolic potassium hydroxide for 4 h (62%) [1218].

m.p. 203° [1218]; IR [1218], UV [1218].

1-(3,4-Dihydroxyphenyl)-2-(4-hydroxyphenyl)ethanone

[150295-88-8] $C_{14}H_{12}O_4$ mol.wt. 244.25



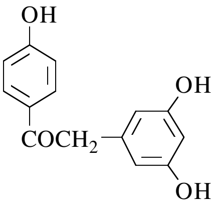
Synthesis

-Obtained by reaction of p-hydroxyphenylacetic acid with pyrocatechol in the presence of boron trifluoride etherate under argon on a water bath for 2 h (78%) [1516].

m.p. 211° [1516];
^{1}H NMR [1516], ^{13}C NMR [1516], MS [1516].

2-(3,5-Dihydroxyphenyl)-1-(4-hydroxyphenyl)ethanone

[402490-73-7] $C_{14}H_{12}O_4$ mol.wt. 244.25



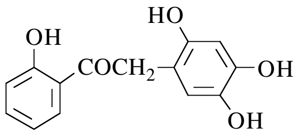
Synthesis

-Obtained by treatment of fluororesveratrol blocked by three MOM groups using trifluoroacetic acid in methylene chloride at r.t. [441].

MS [441].

1-(2-Hydroxyphenyl)-2-(2,4,5-trihydroxyphenyl)ethanone

[115781-50-5] $C_{14}H_{12}O_5$ mol.wt. 260.25



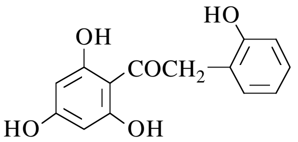
Synthesis

-Obtained from 4-hydroxy-3-(2',4',5'-trihydroxyphenyl)-coumarin with refluxing 2% methanolic potassium hydroxide for 4 h (75%) [1218].

m.p. 185° [1218]; IR [1218], UV [1218].

2-(2-Hydroxyphenyl)-1-(2,4,6-trihydroxyphenyl)ethanone

$C_{14}H_{12}O_5$ mol.wt. 260.25



Syntheses

-Obtained by alkaline degradation of *isogenistein* (5,7,2'-trihydroxyisoflavone) (SM) (m.p. 302°) [1118] with potassium hydroxide [119] [1117] [1118] [1319]. SM was obtained by hydrolysis of *isogenistin*, its glycoside, (m.p. 265°) [1117], isolated from soya bean [119] [1117] [1118].

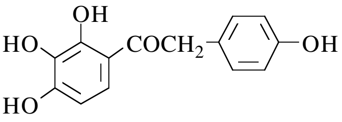
-Also obtained by partial demethylation of 2-hydroxy-4,6-dimethoxyphenyl 2-methoxybenzyl ketone (m.p. 116-118°) with aluminium chloride in refluxing benzene for 2 h (35%) [1319].

-Also refer to: [118].

m.p. 217-220° [1319], 182-183° [1118].
One of the reported melting points is obviously wrong.

2-(4-Hydroxyphenyl)-1-(2,3,4-trihydroxyphenyl)ethanone

[77316-95-1] $C_{14}H_{12}O_5$ mol.wt. 260.25



Syntheses

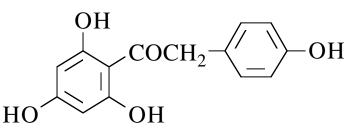
-Obtained by reaction of p-hydroxyphenylacetic acid with pyrogallol in the presence of boron trifluoride etherate under argon on a water bath for 1 h (92%) [1516] or at 100° for 15 min (40%) [992].

-Also refer to: [1331] (Chinese paper).

m.p. 208-209° [1516]; ^1H NMR [992] [1516], ^{13}C NMR [1516], MS [992] [1516].

2-(4-Hydroxyphenyl)-1-(2,4,6-trihydroxyphenyl)ethanone

[15485-65-1] $C_{14}H_{12}O_5$ mol.wt. 260.25



Syntheses

-Preparation by reaction of p-hydroxyphenyl-acetonitrile with phloroglucinol (Hoesch reaction) (58%) [113].

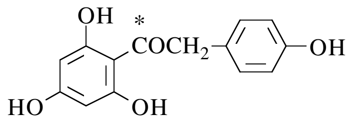
-Also obtained by alkaline degradation of *genistein* (5,7,4'-trihydroxyisoflavone) (m.p. 296-298°) with refluxing 5% potassium hydroxide for 30 min [1520].

-Also obtained by reaction of p-hydroxyphenylacetic with phloroglucinol in the presence of boron trifluoride etherate under argon for 5 h at 0° (83%) [1516].
-Also refer to: [559] [1140] [1166] [1168] [1169].

monohydrate [113];
m.p. 259° (d) [113], 253-257° [1520]; ^{13}C NMR [732].

2-(4-Hydroxyphenyl)-1-(2,4,6-trihydroxyphenyl)ethanone-*1*-^{13}C

[262591-28-6] $C_{14}H_{12}O_5$ mol.wt. 261.25

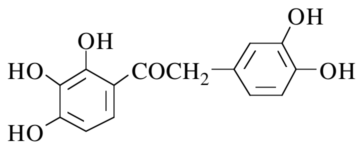


Synthesis

-Preparation by reaction of 4-benzyloxyphenylacetonitrile [1-^{13}C] with phloroglucinol (Hoesch reaction) (75%) [159].

2-(3,4-Dihydroxyphenyl)-1-(2,3,4-trihydroxyphenyl)ethanone

[57165-58-9] $C_{14}H_{12}O_6$ mol.wt. 276.25



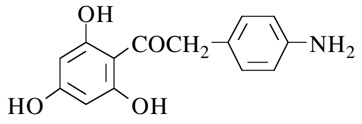
Synthesis

-Preparation in two steps: First, reaction of 3,4-dimethoxyphenylacetyl chloride with 1,2,3-trimethoxybenzene in the presence of aluminium chloride at 30-40° for 16 h. Then, the formed 2,3,4,3',4'-pentamethoxydeoxybenzoin was demethylated by heating at reflux with pyridinium chloride [551].

m.p. 155-156° [551].

2-(4-Aminophenyl)-1-(2,4,6-trihydroxyphenyl)ethanone

[64225-20-3] $C_{14}H_{13}NO_4$ mol.wt. 259.26



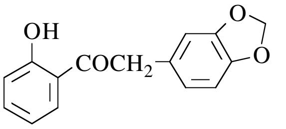
Syntheses

-Preparation by reaction of p-acetamidophenylacetonitrile with phloroglucinol in ethyl ether in the presence of zinc chloride under hydrogen chloride atmosphere for 4 h. Then, hydrolysis of the obtained ketimine hydrochloride in boiling water for 2 h (Hoesch reaction) [686].
-Preparation by hydrogenation of 2,4,6-trihydroxyphenyl 4-nitrobenzyl ketone in ethanol in the presence of Raney nickel as catalyst with hydrogen at 40 lb pressure for 6 h (67%) [686].
-Also refer to: [394].

m.p. 240-242° [394], 197° [686]. One of the reported melting points is obviously wrong. IR [394].

2-(1,3-Benzodioxol-5-yl)-1-(2-hydroxyphenyl)ethanone

[142751-44-8] $C_{15}H_{12}O_4$ mol.wt. 256.26



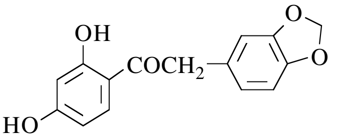
Synthesis

-Preparation by stirring a mixture of S-[4-(1,3-benzodioxol-5-ylacetyl)-3-hydroxyphenyl] dimethylcarbamothioate [142751-43-7], Raney nickel and ethanol at r.t. for 1 h (71%) [907].

m.p. 62-63° [907]; ^{1}H NMR [907], MS [907].

2-(1,3-Benzodioxol-5-yl)-1-(2,4-dihydroxyphenyl)ethanone *(Pseudo-baptigenetin)*

[5653-25-8] $C_{15}H_{12}O_5$ mol.wt. 272.26



Syntheses

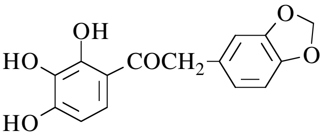
-Preparation by reaction of (3,4-methylenedioxy)-phenylacetyl chloride with resorcinol in nitromethane in the presence of aluminium chloride, under nitrogen, first at 0° for 3 h and at r.t. for 20 h (59%) [1301].

-Also obtained by reaction of (3,4-methylenedioxy)phenylacetonitrile with resorcinol (Hoesch reaction) [1383].
-Also obtained by alkaline degradation of *pseudo-baptigenin* (7-hydroxy-3',4'-methylenedioxy-isoflavone) (SM) (m.p. 298-299° [1383], 298° [575], 296-298° [1385], 293-295° [1217]) with 12% sodium hydroxide in refluxing dilute ethanol for 15 min [1217] or with refluxing 5% potassium hydroxide for 2 h (78%) [1385]. SM was obtained from *pseudo-baptisin* (isolated from *Baptisia tinctoria* RBr) whether by heating at 280° or by hydrolysis with various acids or emulsin [575].
-Also refer to: [467] [699] [848] [907] [1140].

m.p. 151° [1385], 148-149° [711], 146-148° [1217], 87-89° [1301]. One of the reported melting points is obviously wrong.
b.p.$_{0.03}$ 210-220° [1385]; TLC [1301];
^{1}H NMR [1301], IR [1301].

2-(1,3-Benzodioxol-5-yl)-1-(2,3,4-trihydroxyphenyl)ethanone

[84018-72-4] $C_{15}H_{12}O_6$ mol.wt. 288.26



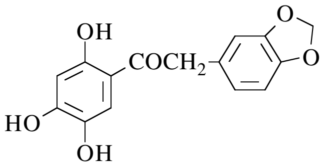
Synthesis

-Obtained by reaction of 3,4-(methylenedioxy)phenyl-acetonitrile with pyrogallol (Hoesch reaction) (21%) [848].

m.p. 185° [848].

2-(1,3-Benzodioxol-5-yl)-1-(2,4,5-trihydroxyphenyl)ethanone

[2828-14-0] $C_{15}H_{12}O_6$ mol.wt. 288.26



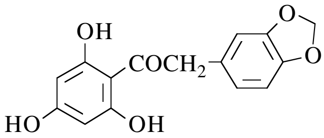
Synthesis

-Obtained by reaction of 3,4-(methylenedioxy)phenylacetonitrile with hydroxyhydroquinone (Hoesch reaction) (73%) [707], (42%) [528].

m.p. 206-208° [528], 202-203° [707]; ^1H NMR [707]. ^{13}C NMR [732], UV [528]; TLC [707].

2-(1,3-Benzodioxol-5-yl)-1-(2,4,6-trihydroxyphenyl)ethanone

[39548-98-6] $C_{15}H_{12}O_6$ mol.wt. 288.26



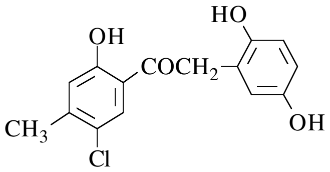
Syntheses

-Preparation by reaction of 3,4-(methylenedioxy)phenylacetonitrile with phloroglucinol (Hoesch reaction) (65-66%) [117] [687].
-Also refer to: [559].

m.p. 202° [117] [687].

1-(5-Chloro-2-hydroxy-4-methylphenyl)-2-(2,5-dihydroxyphenyl)ethanone

[115781-56-1] $C_{15}H_{13}ClO_4$ mol.wt. 292.74



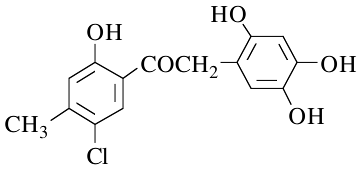
Synthesis

-Obtained by alkali cleavage of 6-chloro-3-(2',5'-dihydroxyphenyl)-4-hydroxy-7-methylcoumarin with refluxing 2% methanolic potassium hydroxide for 4 h (65%) [1218].

m.p. 222° [1218]; IR [1218], UV [1218].

1-(5-Chloro-2-hydroxy-4-methylphenyl)-2-(2,4,5-trihydroxyphenyl)ethanone

[115781-52-7] $C_{15}H_{13}ClO_5$ mol.wt. 308.72



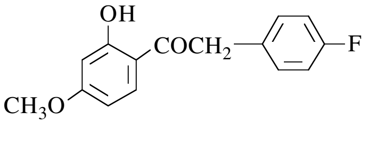
Synthesis

-Obtained from 6-chloro-4-hydroxy-7-methyl-3-(2',4',5'-trihydroxyphenyl)coumarin with refluxing 2% methanolic potassium hydroxide for 4 h (78%) [1218].

m.p. 201° [1218]; IR [1218], UV [1218].

1-(2-Hydroxy-4-methoxyphenyl)-2-(4-fluorophenyl)ethanone

[128040-46-0] $C_{15}H_{13}FO_3$ mol.wt. 260.26



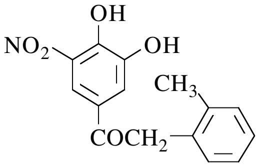
Synthesis

-Preparation by partial methylation of 4'-fluoro-2,4-dihydroxydeoxybenzoin with dimethyl sulfate in refluxing acetone for 6 h (90%) [1490] or in the presence of potassium carbonate in refluxing acetone for 4 h (60%) [1448].

m.p. 90-92° [1448], 78-80° [1490]; ^{1}H NMR [1448] [1490], MS [1448].

1-(3,4-Dihydroxy-5-nitrophenyl)-2-(2-methylphenyl)ethanone

[274925-87-0] $C_{15}H_{13}NO_5$ mol.wt. 287.27



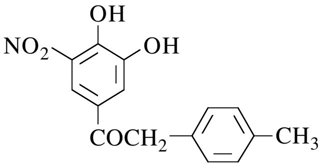
Synthesis

-Preparation by treatment of 1-(4-hydroxy-3-methoxy-5-nitrophenyl)-2-(2-methylphenyl)ethanone with aluminium chloride in refluxing ethyl acetate/pyridine mixture for 2 h (90-96%) [887].

m.p. 163-165° [887];
^{1}H NMR [887], ^{13}C NMR [887], IR [887].

1-(3,4-Dihydroxy-5-nitrophenyl)-2-(4-methylphenyl)ethanone

[400871-10-5] $C_{15}H_{13}NO_5$ mol.wt. 287.27



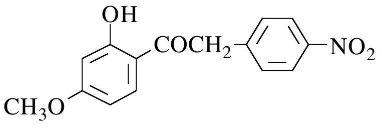
Synthesis

-Preparation by treatment of 1-(4-hydroxy-3-methoxy-5-nitrophenyl)-2-(4-methylphenyl)ethanone with aluminium chloride in refluxing ethyl acetate/pyridine mixture for 2 h (90-96%) [887].

m.p. 189-190° [887];
^{1}H NMR [887], ^{13}C NMR [887], IR [887].

1-(2-Hydroxy-4-methoxyphenyl)-2-(4-nitrophenyl)ethanone

[57272-98-7] $C_{15}H_{13}NO_5$ mol.wt. 287.27



Syntheses

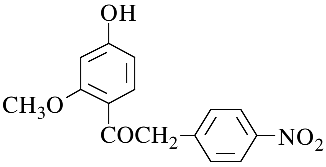
-Obtained (poor yield) by reaction of p-nitrophenylacetonitrile with resorcinol monomethyl ether (9%) (Hoesch reaction) [743].

-Also obtained by partial methylation of 2,4-dihydroxyphenyl 4-nitrobenzyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone [585].

m.p. 136° [743], 134-136° [585].

1-(4-Hydroxy-2-methoxyphenyl)-2-(4-nitrophenyl)ethanone

$C_{15}H_{13}NO_5$ mol.wt. 287.27



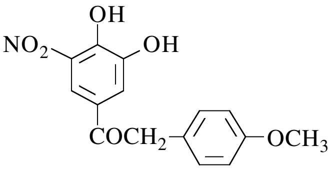
Synthesis

-Obtained by reaction of p-nitrophenylacetonitrile with resorcinol monomethyl ether (Hoesch reaction) [743].

m.p. 149-150° [743].

1-(3,4-Dihydroxy-5-nitrophenyl)-2-(4-methoxyphenyl)ethanone

[440362-23-2] $C_{15}H_{13}NO_6$ mol.wt. 303.27



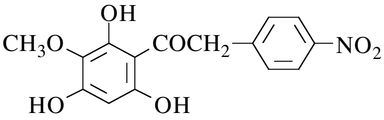
Synthesis

-Preparation by partial demethylation of 1-(4-hydroxy-3-methoxy-5-nitrophenyl)-2-(4-methoxyphenyl)-ethanone using aluminium chloride and pyridine in ethyl acetate at reflux for 2 h (91%) [885].

diacetate m.p. 88-89° [885].

2-(4-Nitrophenyl)-1-(2,4,6-trihydroxy-3-methoxyphenyl)ethanone

$C_{15}H_{13}NO_7$ mol.wt. 319.27



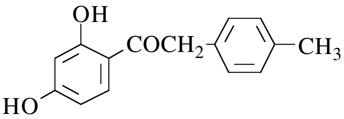
Synthesis

-Obtained by reaction of p-nitrophenylacetonitrile with iretol (Hoesch reaction) (50%) [746].

m.p. 220° [746].

1-(2,4-Dihydroxyphenyl)-2-(4-methylphenyl)ethanone

[59208-55-8] $C_{15}H_{14}O_3$ mol.wt. 242.27



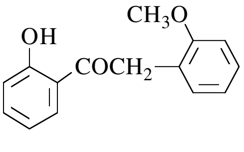
Synthesis

-Obtained by reaction of p-tolylacetonitrile with resorcinol (Hoesch reaction) [285].

m.p. 114° [285].

1-(2-Hydroxyphenyl)-2-(2-methoxyphenyl)ethanone

[92549-19-4] $C_{15}H_{14}O_3$ mol.wt. 242.27



Syntheses

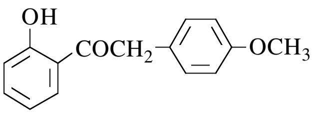
-Preparation by stirring a mixture of S-[3-hydroxy-4-[(2-methoxyphenyl)acetyl]phenyl] dimethylcarbamothioate [142751-41-5], Raney nickel and ethanol at r.t. for 1 h (71%) [907].
-Also obtained by heating 2-methoxybenzoyl-2-methoxy-

phenylacetonitrile (m.p. 107-108°) in acetic acid with concentrated hydrochloric acid on a steam bath for 15 h (47%) [780].
-Also obtained by alkaline degradation of 2'-methoxyisoflavone (m.p. 184°) with potassium hydroxide in boiling aqueous methanol for 1.5 h (almost quantitative yield) [1530].
-Also obtained by heating ethyl 2-methoxybenzoyl-2-methoxyphenylacetate (m.p. 76-77°) in acetic acid with concentrated hydrochloric acid on a steam bath for 15 h (54%) [780].
-Also refer to: [388].

colourless oil [780]; b.p.$_{0.004}$ 140-150° [780];
m.p. 64° [1530], 59-60° [907]; ^{1}H NMR [907], MS [907].

1-(2-Hydroxyphenyl)-2-(4-methoxyphenyl)ethanone

[79744-47-1] $C_{15}H_{14}O_3$ mol.wt. 242.27



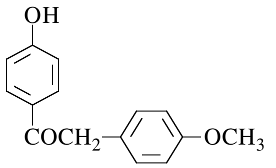
Syntheses

-Preparation by addition of p-methoxybenzylmagnesium chloride to a solution of 2-hydroxybenzonitrile in THF at r.t. overnight, then refluxing with aqueous hydrochloric acid for 4 h (90%) [1489].
-Also obtained by heating a solution of 2-methoxybenzoyl-4-methoxyphenylacetonitrile (m.p. 109-110°5) in acetic acid containing hydrochloric acid on a steam bath for 15 h (47%) [778].
-Also obtained by stirring a mixture of S-[3-hydroxy-4-[(4-methoxyphenyl)acetyl]phenyl] dimethylcarbamothioate [142751-42-6], Raney nickel and ethanol at r.t. for 1 h (73%) [907].
-Also obtained by heating a solution of ethyl 2-methoxybenzoyl-4-methoxyphenylacetate (b.p.$_{0.004}$ 180-200°) in acetic acid containing hydrochloric acid on a steam bath for 15 h (54%) [778].
-Also obtained by Fries rearrangement of phenyl p-methoxyphenylacetate with aluminium chloride for 1.5 h at 145° (13%) [1335].

m.p. 86° [1335], 85-86° [907], 79-81° [1489]; b.p.$_{0.003}$ 160-180° [778];
^{1}H NMR [907] [1335], ^{13}C NMR [732], IR [1335], MS [907] [1335] [1489];
TLC [1489].

1-(4-Hydroxyphenyl)-2-(4-methoxyphenyl)ethanone

[3669-46-3] $C_{15}H_{14}O_3$ mol.wt. 242.27



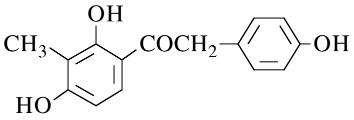
Syntheses

-Obtained by Fries rearrangement of phenyl p-methoxyphenylacetate in nitromethane,
*in the presence of aluminium chloride for 25 h at 20° (48%) [971] or for 1.5 h at 145° (12%) [1335];
*in the presence of titanium tetrachloride for 6 h at 20° (26%) [971].
-Also obtained by partial demethylation of 4,4'-dimethoxydeoxybenzoin,
*with aluminium chloride in refluxing benzene for 1.5 h (33%) [889];
*with sodium in refluxing ethylene glycol for 3 h (12%) [1424].

m.p. 175-178° [889], 175° [1335] [1424], 171° [971];
^{1}H NMR (Sadtler: standard n° 44611 M),
IR (Sadtler: standard n° 71639 K) [971], UV [971], MS [971].

1-(2,4-Dihydroxy-3-methylphenyl)-2-(4-hydroxyphenyl)ethanone

[139256-03-4] $C_{15}H_{14}O_4$ mol.wt. 258.27



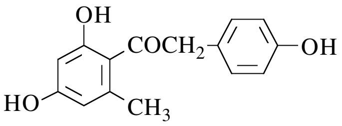
Synthesis

-Obtained by reaction of p-hydroxyphenylacetic acid with 2-methylresorcinol in the presence of boron trifluoride etherate under argon, on a water bath for 5 h (97%) [1516].

m.p. 187-188° [1516]; ^{1}H NMR [1516], ^{13}C NMR [1516], MS [1516].

1-(2,4-Dihydroxy-6-methylphenyl)-2-(4-hydroxyphenyl)ethanone

[139256-04-5] $C_{15}H_{14}O_4$ mol.wt. 258.27



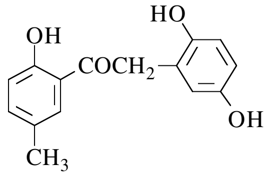
Synthesis

-Obtained by reaction of p-hydroxyphenylacetic acid with orcinol in the presence of boron trifluoride etherate under argon on a water bath for 2 h (86%) [1516].

m.p. 186-187° [1516]; ^{1}H NMR [1516], ^{13}C NMR [1516], MS [1516].

2-(2,5-Dihydroxyphenyl)-1-(2-hydroxy-5-methylphenyl)ethanone

[115781-53-8] $C_{15}H_{14}O_4$ mol.wt. 258.27



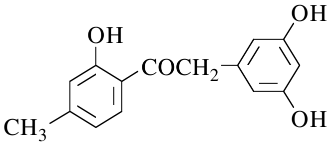
Synthesis

-Obtained by alkali cleavage of 3-(2',5'-dihydroxyphenyl)-4-hydroxy-6-methylcoumarin with refluxing 2% methanolic potassium hydroxide for 4 h (79%) [1218].

m.p. 223° [1218]; IR [1218], UV [1218].

2-(3,5-Dihydroxyphenyl)-1-(2-hydroxy-4-methylphenyl)ethanone

[111192-02-0] $C_{15}H_{14}O_4$ mol.wt. 258.27



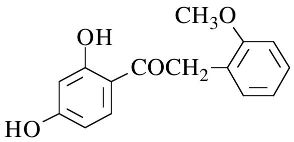
Synthesis

-Obtained by decarboxylation of 6,8-dihydroxy-3-(2-hydroxy-4-methylphenyl)isocoumarin (m.p. 201-202°) with refluxing 10% aqueous potassium hydroxide solution for 6 h (90%) [495].

m.p. 89° [495]; ^{1}H NMR [495], IR [495], MS [495].

1-(2,4-Dihydroxyphenyl)-2-(2-methoxyphenyl)ethanone

[92549-46-7] $C_{15}H_{14}O_4$ mol.wt. 258.27



Syntheses

-Preparation by reaction of o-methoxyphenylacetic acid with resorcinol in the presence of boron trifluoride etherate under argon on a water bath for 1 h (98%) [1516].

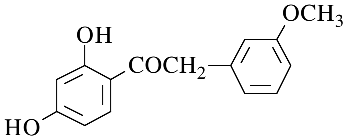
-Also obtained by reaction of o-methoxyphenylacetonitrile with resorcinol (Hoesch reaction) (25%) [1321], (23%) [1536].

-Also refer to: [873] [1530].

m.p. 164° [1536], 159-160° [1321].

1-(2,4-Dihydroxyphenyl)-2-(3-methoxyphenyl)ethanone

[89019-83-0] $C_{15}H_{14}O_4$ mol.wt. 258.27



Syntheses

-Preparation by reaction of m-methoxyphenylacetic acid with resorcinol under argon atmosphere,

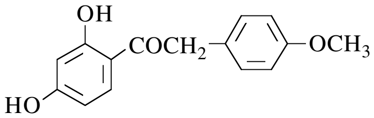
*in the presence of boron trifluoride etherate on a water bath for 1 h (96%) [1516];

*in ethylene dichloride in the presence of boron trifluoride, first at r.t., then at 60° for 2 h (63%) [937].

m.p. 109-110° [937]; ^{1}H NMR [937], IR [937], UV [937], MS [937].

1-(2,4-Dihydroxyphenyl)-2-(4-methoxyphenyl)ethanone *(Ononetin)*

[487-49-0] $C_{15}H_{14}O_4$ mol.wt. 258.27



Syntheses

-Preparation by condensation of p-methoxyphenylacetonitrile with resorcinol (Hoesch reaction) [13] [110] [1019] [1145], (64%) [1526], (50%) [992], (48%) [1520].

-Preparation by Friedel-Crafts acylation of resorcinol with p-methoxyphenylacetyl chloride in the presence of aluminium chloride for 24 h at r.t., in nitrobenzene (50%) [106] or in ethyl ether (36%) [601].

-Also obtained by reaction of p-methoxyphenylacetic anhydride with resorcinol in the presence of boron trifluoride etherate for 3.5 h at 75° (67%) [1024].

-Also obtained by reaction of p-methoxyphenylacetic acid with resorcinol,

*in the presence of boron trifluoride etherate under argon on a water bath for 1.5 h (98%) [1516] or at 100° for 1 h (77%) [937];

*in the presence of boron trifluoride in chloroform (51%) [764].

-Also obtained by alkaline degradation of *formononetin* (7-hydroxy-4'-methoxyisoflavone) (SM) (m.p. 265°) [121] [1520] [1526] [1528], (95%) [221], (51%) [1526].

SM was prepared by hydrolysis of *ononin* with 4% sulfuric acid [1526].

-Also obtained by degradation of *onospin* (m.p. 172°) (SM1) by heating with dilute sulfuric acid or by treatment with emulsin. SM1 was prepared from *ononin* by heating with 10% sodium hydroxide for 2 min [1526] [1528].

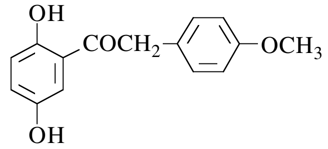
-Also obtained by decarboxylation of 5-carboxy-2,4-dihydroxy-4'-methoxydeoxybenzoin

(m.p. 200°) in boiling quinoline containing copper bronze during 5 min (26%) [1534].
-Also refer to: [282] [467] [585] [701] [703] [747] [769] [873] [907] [1140] [1165] [1182] [1183] [1188] [1328] [1419] [1527].

m.p. 161°5-162°5 [1019], 159°5 [1526], 159° [110] [764], 158-159° [601], 158° [106] [221] [1520] [1534], 156-157° [711], 153-155° [937];
^{1}H NMR [937] [992], ^{13}C NMR [732] [1167], IR [937],
UV [937] [1019], MS [937] [992].

1-(2,5-Dihydroxyphenyl)-2-(4-methoxyphenyl)ethanone

[56308-07-7] $C_{15}H_{14}O_4$ mol.wt. 258.27

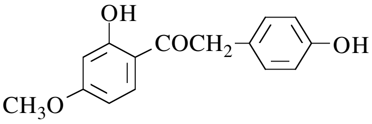


Synthesis

-Refer to: [1419] (Hungarian paper).

1-(2-Hydroxy-4-methoxyphenyl)-2-(4-hydroxyphenyl)ethanone

[60278-33-3] $C_{15}H_{14}O_4$ mol.wt. 258.27



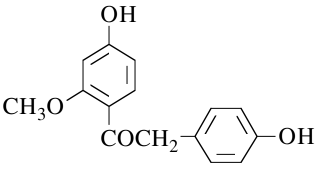
Syntheses

-Obtained by reaction of p-hydroxyphenylacetic acid with m-methoxyphenol,
*in the presence of boron trifluoride in ethylene dichloride at 80° for 2 h under an argon atmosphere (47%) [937];
*in the presence of polyphosphoric acid at 95° for 30 min (57%) [1503].
-Also refer to: [463] [735] [1165].

gum [1503]; m.p. 151-154° [937];
^{1}H NMR [937], ^{13}C NMR [732], IR [937], UV [937], MS [937].

1-(4-Hydroxy-2-methoxyphenyl)-2-(4-hydroxyphenyl)ethanone

[89019-88-5] $C_{15}H_{14}O_4$ mol.wt. 258.27



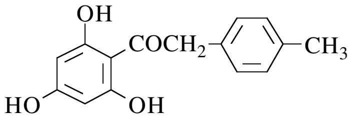
Synthesis

-Obtained by reaction of p-hydroxyphenylacetic acid with m-methoxyphenol in ethylene dichloride in the presence of boron trifluoride at 80° for 2 h under an argon atmosphere (23%) [937].

m.p. 147-151° [937]; ^{1}H NMR [937],
IR [937], UV [937], MS [937].

2-(4-Methylphenyl)-1-(2,4,6-trihydroxyphenyl)ethanone

[59108-68-8] $C_{15}H_{14}O_4$ mol.wt. 258.27



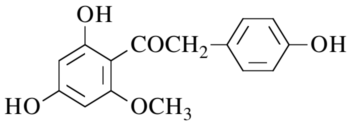
Synthesis

-Preparation by reaction of p-tolylacetonitrile with phloroglucinol (Hoesch reaction) [141] [285].

m.p. 205-206° (anhydrous) [285];
sesquihydrate [285].

1-(2,4-Dihydroxy-6-methoxyphenyl)-2-(4-hydroxyphenyl)ethanone

[56308-11-3] $C_{15}H_{14}O_5$ mol.wt. 274.27



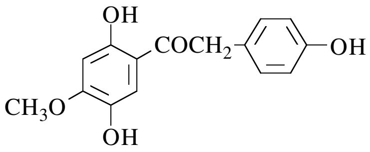
Syntheses

-Preparation by reaction of p-hydroxyphenylacetonitrile with phloroglucinol monomethyl ether (57%) (Hoesch reaction) [117].
-Also refer to: [559] [1419].

m.p. 186-188° [117].

1-(2,5-Dihydroxy-4-methoxyphenyl)-2-(4-hydroxyphenyl)ethanone

[79744-54-0] $C_{15}H_{14}O_5$ mol.wt. 274.27



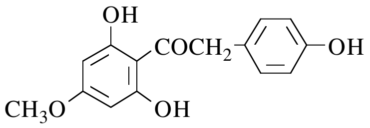
Synthesis

-Obtained by reaction of p-hydroxyphenylacetonitrile with 2-methoxyhydroquinone (Hoesch reaction) [246] [732].

^{13}C NMR [732].

1-(2,6-Dihydroxy-4-methoxyphenyl)-2-(4-hydroxyphenyl)ethanone

[101094-12-6] $C_{15}H_{14}O_5$ mol.wt. 274.27



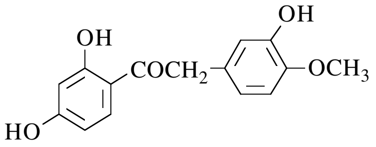
Synthesis

-Obtained by heating a mixture of 5,4'-dihydroxy-7-methoxyisoflavone and tribasic sodium phosphate in water at reflux for 1 h (83%) [559].

m.p. 247-249° [559].

1-(2,4-Dihydroxyphenyl)-2-(3-hydroxy-4-methoxyphenyl)ethanone

[36754-72-0] $C_{15}H_{14}O_5$ mol.wt. 274.27



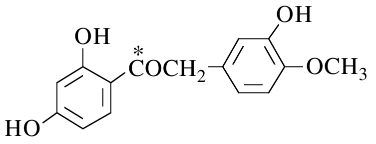
Syntheses

-Obtained by reaction of (3-hydroxy-4-methoxyphenyl)acetonitrile with resorcinol (Hoesch reaction) (41%) [471] [472].
-Also refer to: [174] [699].

m.p. 161-162° [471] [472].

1-(2,4-Dihydroxyphenyl)-2-(3-hydroxy-4-methoxyphenyl)ethanone-*1*-^{14}*C*

[142050-40-6] $C_{15}H_{14}O_5$ mol.wt. 274.27



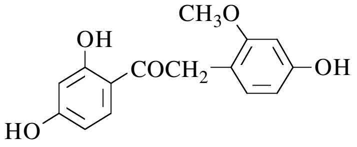
Synthesis

-Obtained by hydrolysis of 2,4-dihydroxyphenyl 3-benzoyloxy-4-methoxybenzyl [^{14}C] ketone (SM) with sodium hydroxide in dilute methanol (31-35%). SM was obtained by reaction of 3-benzoyloxy-4-methoxybenzyl [^{14}C] nitrile with resorcinol (Hoesch reaction) [174].

m.p. 166-168° [174].

1-(2,4-Dihydroxyphenyl)-2-(4-hydroxy-2-methoxyphenyl)ethanone

[175546-62-0] $C_{15}H_{14}O_5$ mol.wt. 274.27

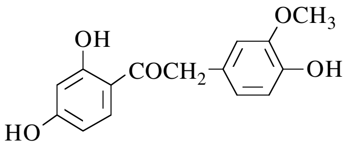


Synthesis

-Refer to: [1140].

1-(2,4-Dihydroxyphenyl)-2-(4-hydroxy-3-methoxyphenyl)ethanone

[40456-49-3] $C_{15}H_{14}O_5$ mol.wt. 274.27



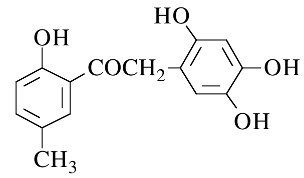
Syntheses

-Preparation by reaction of 4-hydroxy-3-methoxyphenylacetic acid with resorcinol in the presence of boron trifluoride etherate under argon on a water bath for 1 h (99%) [1516].
-Also obtained by reaction of (4-acetoxy-3-methoxyphenyl)acetonitrile with resorcinol (Hoesch reaction) [1430].

colourless granules [1430]; ^{1}H NMR [1430], IR [1430].

1-(2-Hydroxy-5-methylphenyl)-2-(2,4,5-trihydroxyphenyl)ethanone

[115781-49-2] $C_{15}H_{14}O_5$ mol.wt. 274.27



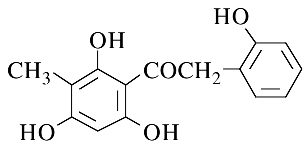
Synthesis

-Obtained from 4-hydroxy-6-methyl-3-(2',4',5'-trihydroxyphenyl)coumarin with refluxing 2% methanolic potassium hydroxide for 4 h (67%) [1218].

m.p. 193° [1218]; IR [1218], UV [1218].

2-(2-Hydroxyphenyl)-1-(2,4,6-trihydroxy-3-methylphenyl)ethanone

$C_{15}H_{14}O_5$ mol.wt. 274.27



Synthesis

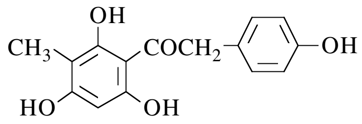
-Obtained by alkaline degradation of *methylisogenistein* (8-methyl-5,7,2'-trihydroxyisoflavone) (SM) (m.p. 255°) with potassium hydroxide [1117] [1118]. SM was obtained by hydrolysis of *methylisogenistin*, its glycoside, (m.p. 301-302°) [1117], isolated from soya bean [1117] [1118].

N.B.: This ketone cannot be prepared by condensation of o-hydroxyphenylacetonitrile with 2-methylphloroglucinol (Hoesch reaction) [1321].

m.p. 186° [1117].

2-(4-Hydroxyphenyl)-1-(2,4,6-trihydroxy-3-methylphenyl)ethanone

$C_{15}H_{14}O_5$ mol.wt. 274.27



Syntheses

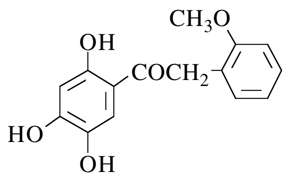
-Obtained by partial demethylation of 2-hydroxy-4,6-dimethoxy-3-methylphenyl 4-methoxybenzyl ketone with aluminium chloride in refluxing benzene for 2 h (58%) [1318].

-Also obtained by alkaline degradation of *methylgenistein* (8-methyl-5,7,4'-trihydroxyisoflavone) (m.p. 298°) with potash [1117] [1118].

m.p. 235-237° [1318], 190° [1117]. One of the reported melting points is obviously wrong.

2-(2-Methoxyphenyl)-1-(2,4,5-trihydroxyphenyl)ethanone

[79744-49-3] $C_{15}H_{14}O_5$ mol.wt. 274.27



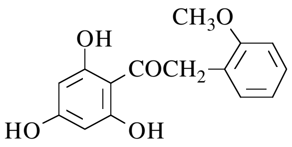
Synthesis

-Obtained by reaction of 2-methoxyphenylacetonitrile with hydroxyhydroquinone (Hoesch reaction) [246] [732].

^{13}C NMR [732].

2-(2-Methoxyphenyl)-1-(2,4,6-trihydroxyphenyl)ethanone

[116854-95-6] $C_{15}H_{14}O_5$ mol.wt. 274.27



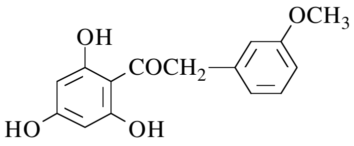
Syntheses

-Preparation by reaction of 2-methoxyphenylacetonitrile with phloroglucinol (Hoesch reaction),
*in the presence of zinc chloride [118] [767], (74%) [119], (48%) [1319], (42%) [1024], (37%) [1531];
*in the presence of boron trifluoride etherate (45%) [1024].
-Also refer to: [208] [559] [989] [1320].

monohydrate [1319] [1531]; sublimation at 120°/0.04 mm [1531];
m.p. 170° [767], 169° [1531], 168-170° [1319], 167-169° [118] [119].

2-(3-Methoxyphenyl)-1-(2,4,6-trihydroxyphenyl)ethanone

[111474-27-2] $C_{15}H_{14}O_5$ mol.wt. 274.27



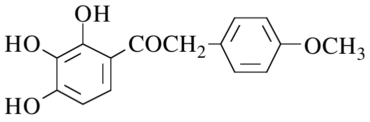
Synthesis

-Preparation by reaction of 3-methoxyphenylacetonitrile with phloroglucinol (Hoesch reaction) (75%) [208], (30%) [559].

m.p. 168-169° [559], 165-166° [208]; ^{1}H NMR [208], IR [208].

2-(4-Methoxyphenyl)-1-(2,3,4-trihydroxyphenyl)ethanone

[38412-59-8] $C_{15}H_{14}O_5$ mol.wt. 274.27



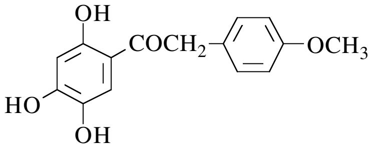
Syntheses

-Obtained by acid hydrolysis of 4-methoxybenzyl 2-hydroxy-3,4-diphenylmethylenedioxyphenyl ketone (m.p. 146°) in acetic acid in the presence of 2 drops of concentrated hydrochloric acid at 100° for 5 min (48%) [744].
-Also obtained by reaction of 4-methoxyphenylacetic acid with pyrogallol in chloroform in the presence of excess boron trifluoride, first at 0°, then at r.t. overnight (77%) [764] or for 2 days (54%) [744].
-Also refer to: [246] [732] [1148].

m.p. 157° [744], 145-146° [764];
^{1}H NMR [744], ^{13}C NMR [732]; TLC [744].

2-(4-Methoxyphenyl)-1-(2,4,5-trihydroxyphenyl)ethanone

[76095-38-0] $C_{15}H_{14}O_5$ mol.wt. 274.27



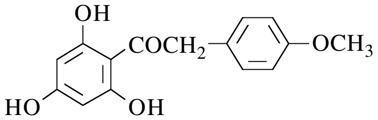
Syntheses

-Preparation by reaction of p-methoxyphenylacetonitrile with hydroxyhydroquinone (Hoesch reaction) [246] [530] [732] [1347], (80%) [707].
-Also refer to: [212] [731] [1580] [1581].

m.p. 180-181° [707] [1347]; TLC [707];
^1H NMR [707], ^{13}C NMR [732], UV [1347].

2-(4-Methoxyphenyl)-1-(2,4,6-trihydroxyphenyl)ethanone

[15485-66-2] $C_{15}H_{14}O_5$ mol.wt. 274.27



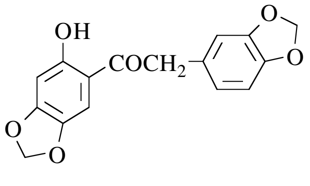
Syntheses

-Preparation by reaction of p-methoxyphenylacetonitrile with phloroglucinol (Hoesch reaction),
*in the presence of zinc chloride [141] [1019] [1145], (91-92%) [1168] [1169] [1354], (80%) [113], (66%) [771], (57%) [106], (55%) [1024];
*in the presence of boron trifluoride etherate (82%) [1024].
-Preparation by Fries rearrangement of 3,5-dihydroxyphenyl p-methoxyphenylacetate with aluminium chloride in nitrobenzene, first at 60°, then at 150° for 2 h (75%) [1354].
-Preparation by Friedel-Crafts acylation of phloroglucinol with p-methoxyphenylacetyl chloride in nitrobenzene at 100° for 2 h (50%) [1354].
-Preparation by reaction of p-methoxyphenylacetic acid with phloroglucinol in the presence of zinc chloride and phosphorous oxychloride for 24 h at r.t. (68%) [391].
-Also refer to: [559] [701] [873] [1165] [1166] [1182] [1183] [1188] [1419].

m.p. 198-200° [1169], 198-199° [1019], 195° [106], 194° [771],
192-193° [113] [1354], 192° [391]; monohydrate [113];
^1H NMR [1169], ^{13}C NMR [732] [1167] [1169], IR [771],
UV [771] [1019] [1169]; TLC [771].

2-(1,3-Benzodioxol-5-yl)-1-(6-hydroxy-1,3-benzodioxol-5-yl)ethanone

[2746-90-9] $C_{16}H_{12}O_6$ mol.wt. 300.27



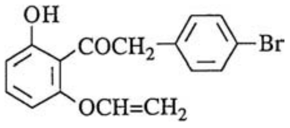
Syntheses

-Obtained by reaction of (3,4-methylenedioxy)phenylacetonitrile with *sesamol* (5-hydroxy-1,3-benzodioxol) (Hoesch reaction) (13%) [528].
-Also obtained by reaction of methylene sulfate with 2,4,5-trihydroxyphenyl (3,4-methylenedioxy)benzyl ketone in the presence of potassium hydroxide in dilute acetone for 70 min at 45-50° (9%) [528].

m.p. 172-173° [528]; IR [528], UV [528].

2-(4-Bromophenyl)-1-[2-(ethenyloxy)-6-hydroxyphenyl]ethanone

$C_{16}H_{13}BrO_3$ mol.wt. 333.18



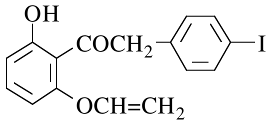
Synthesis

-Obtained (by-product) by reaction of diethylaminochloroethane with 2,6-dihydroxy-4'-bromodesoxybenzoin in the presence of sodium ethoxide in refluxing ethanol for 4 h [914].

m.p. 103° [914].

1-[2-(Ethenyloxy)-6-hydroxyphenyl]-2-(4-iodophenyl)ethanone

$C_{16}H_{13}IO_3$ mol.wt. 380.18



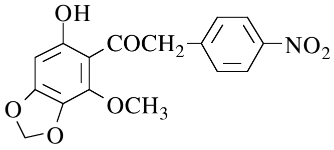
Synthesis

-Obtained (by-product) by reaction of diethylaminochloroethane with 2,6-dihydroxy-4'-iododesoxybenzoin in the presence of sodium ethoxide in refluxing ethanol for 4 h [914].

m.p. 131° [914].

1-(6-Hydroxy-4-methoxy-1,3-benzodioxol-5-yl)-2-(4-nitrophenyl)ethanone

$C_{16}H_{13}NO_7$ mol.wt. 331.28



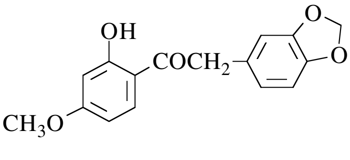
Synthesis

-Obtained by condensation of 3-methoxy-4,5-methylenedioxyphenol with 4-nitrophenylacetontrile (Hoesch reaction) (37%) [529].

m.p. 165-167° [529]; IR [529].

2-(1,3-Benzodioxol-5-yl)-1-(2-hydroxy-4-methoxyphenyl)ethanone

[5128-56-3] $C_{16}H_{14}O_5$ mol.wt. 286.28



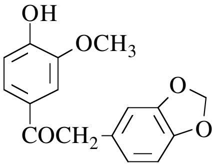
Syntheses

-Obtained by partial methylation of *pseudo-baptigenetin* in ethanol with diazomethane in ethyl ether for 24 h (82%) [1385].
-Also refer to: [699] [843].

m.p. 145° [1385].

2-(1,3-Benzodioxol-5-yl)-1-(4-hydroxy-3-methoxyphenyl)ethanone

[56766-87-1] $C_{16}H_{14}O_5$ mol.wt. 286.28



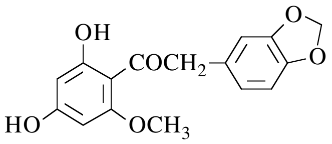
Synthesis

-Obtained by hydrogenolysis of 4-benzyloxy-3-methoxyphenyl 3,4-methylenedioxybenzyl ketone (oil) with hydrogen in the presence of 10% Pd/C in ethanol at r.t. for 1.5 h (87%) [434].

m.p. 132-133° [434];
^{1}H NMR [434], IR [434], UV [434], MS [434].

2-(1,3-Benzodioxol-5-yl)-1-(2,4-dihydroxy-6-methoxyphenyl)ethanone

[55607-36-8] $C_{16}H_{14}O_6$ mol.wt. 302.28



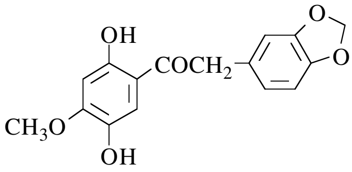
Synthesis

-Obtained by reaction of 3,4-methylenedioxyphenylacetonitrile with phloroglucinol monomethyl ether (Hoesch reaction) [559], (27%) [715].

m.p. 143-144° [559], 138-139° [715];
^{1}H NMR [715]; TLC [715].

2-(1,3-Benzodioxol-5-yl)-1-(2,5-dihydroxy-4-methoxyphenyl)ethanone

[2746-89-6] $C_{16}H_{14}O_6$ mol.wt. 302.28



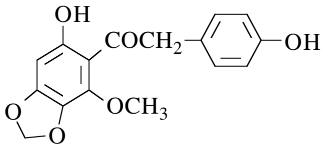
Synthesis

-Obtained by treatment of 2,4,5-trihydroxyphenyl (3,4-methylenedioxy)benzyl ketone in acetone with an ethereal diazomethane solution at r.t. overnight (76%) [528].

m.p. 194-196° [528]; UV [528].

1-(6-Hydroxy-4-methoxy-1,3-benzodioxol-5-yl)-2-(4-hydroxyphenyl)ethanone

[3207-38-3] $C_{16}H_{14}O_6$ mol.wt. 302.28



Syntheses

-Obtained by alkaline degradation of *irisolone* (4'-hydroxy-5-methoxy-6,7-methylenedioxyisoflavone) (m.p. 258-265°) (SM) with refluxing aqueous sodium hydroxide for 1.5 h. SM was isolated from the rhizomes of *iris nepalensis* D. DON (Iridaceae) [573].

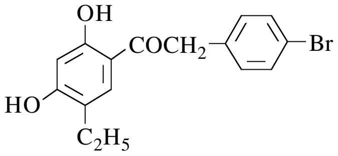
-Also obtained by reaction of 4-hydroxyphenylacetonitrile with 3-methoxy-4,5-methylenedioxyphenol (Hoesch reaction) (7%) [529].

-Also obtained by diazotization of 6-hydroxy-2-methoxy-3,4-methylenedioxyphenyl 4-aminobenzyl ketone, followed by hydrolysis of the diazonium salt obtained (10%) [529].

m.p. 159-160° [573], 152-153° [529]; IR [529], UV [529] [573].

2-(4-Bromophenyl)-1-(5-ethyl-2,4-dihydroxyphenyl)ethanone

[96643-99-1] $C_{16}H_{15}BrO_3$ mol.wt. 335.20



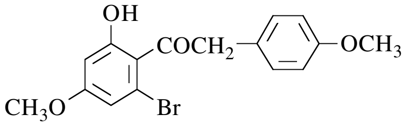
Synthesis

-Preparation by reaction of p-bromophenylacetonitrile with 4-ethylresorcinol in the presence of boron trifluoride etherate under hydrogen chloride atmosphere at r.t. overnight (80%) [936], (70%) [786].

m.p. 124-125° [786] [936]; ^{1}H NMR [786].

1-(2-Bromo-6-hydroxy-4-methoxyphenyl)-2-(4-methoxyphenyl)ethanone

[191847-25-3] $C_{16}H_{15}BrO_4$ mol.wt. 351.20



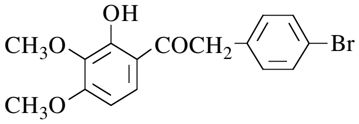
Synthesis

-Obtained by Friedel-Crafts acylation of 3,5-dimethoxybromobenzene with 4-methoxyphenylacetyl chloride in the presence of aluminium chloride (12%) [1578].

m.p. 180-182° [1578]; ^{1}H NMR [1578], MS [1578].

2-(4-Bromophenyl)-1-(2-hydroxy-3,4-dimethoxyphenyl)ethanone

$C_{16}H_{15}BrO_4$ mol.wt. 351.20



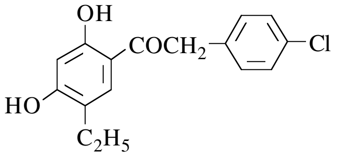
Synthesis

-Refer to: [758] (Japanese paper).

m.p. 134-135° [758].

2-(4-Chlorophenyl)-1-(5-ethyl-2,4-dihydroxyphenyl)ethanone

[96644-00-7] $C_{16}H_{15}ClO_3$ mol.wt. 290.75



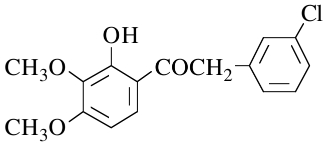
Synthesis

-Preparation by reaction of p-chlorophenylacetonitrile with 4-ethylresorcinol in the presence of boron trifluoride etherate under hydrogen chloride atmosphere at r.t. overnight (80%) [936], (70%) [786].

m.p. 130-131° [786] [936]; ^{1}H NMR [786].

2-(3-Chlorophenyl)-1-(2-hydroxy-3,4-dimethoxyphenyl)ethanone

[24863-50-1] $C_{16}H_{15}ClO_4$ mol.wt. 306.75



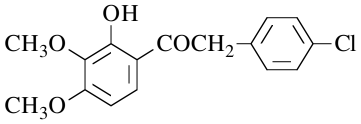
Synthesis

-Obtained by Friedel-Crafts acylation of pyrogallol trimethyl ether with m-chlorophenylacetyl chloride in the presence of aluminium chloride in carbon disulfide for 30 min (54%) [758].

m.p. 111-112° [758]; ^{1}H NMR [758].

2-(4-Chlorophenyl)-1-(2-hydroxy-3,4-dimethoxyphenyl)ethanone

[24852-34-4] $C_{16}H_{15}ClO_4$ mol.wt. 306.75



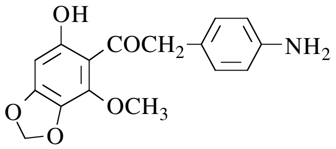
Synthesis

-Obtained by Friedel-Crafts acylation of pyrogallol trimethyl ether with p-chlorophenylacetyl chloride in carbon disulfide in the presence of aluminium chloride for 30 min (59%) [758].

m.p. 113-114° [758].

2-(4-Aminophenyl)-1-(6-hydroxy-4-methoxy-1,3-benzodioxol-5-yl)ethanone

$C_{16}H_{15}NO_5$ mol.wt. 301.30



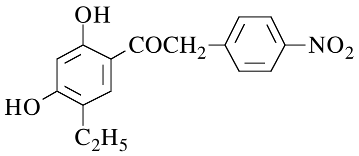
Synthesis

-Obtained by catalytic reduction of 6-hydroxy-2-methoxy-3,4-methylenedioxyphenyl 4-nitrobenzyl ketone in ethyl acetate with hydrogen in the presence of 10% Pd/C at r.t. (82%) [529].

m.p. 170-172° [529]; IR [529].

1-(5-Ethyl-2,4-dihydroxyphenyl)-2-(4-nitrophenyl)ethanone

[96644-02-9] $C_{16}H_{15}NO_5$ mol.wt. 301.30



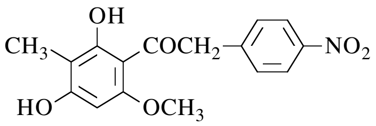
Synthesis

-Obtained by reaction of p-nitrophenylacetonitrile with 4-ethylresorcinol in the presence of boron trifluoride etherate under hydrogen chloride atmosphere (8-10 h), then at r.t. overnight (94%) [786].

m.p. 159-160° [786]; ^{1}H NMR [786].

1-(2,4-Dihydroxy-6-methoxy-3-methylphenyl)-2-(4-nitrophenyl)ethanone

$C_{16}H_{15}NO_6$ mol.wt. 317.30



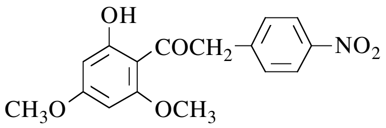
Synthesis

-Obtained by reaction of p-nitrophenylacetonitrile with 2,6-dihydroxy-4-methoxytoluene (Hoesch reaction) [764].

m.p. 201° [764].

1-(2-Hydroxy-4,6-dimethoxyphenyl)-2-(4-nitrophenyl)ethanone

[56982-36-6] $C_{16}H_{15}NO_6$ mol.wt. 317.30



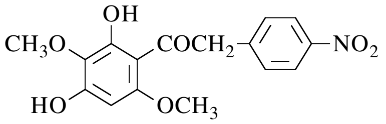
Syntheses

-Obtained by partial methylation of 4-nitrobenzyl 2,4,6-trihydroxyphenyl ketone,
*with diazomethane in ethyl ether at 0° for 48 h (57%) [686];
*with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone [585].
-Also refer to: [688].

m.p. 150° [585], 148-149° [688], 148° [686].

1-(2,4-dihydroxy-3,6-dimethoxyphenyl)-2-(4-Nitrophenyl)ethanone

$C_{16}H_{15}NO_7$ mol.wt. 333.30



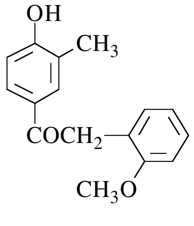
Synthesis

-Obtained by reaction of p-nitrophenylacetonitrile with 2,5-dimethoxyresorcinol (Hoesch reaction) [746].

m.p. 174° [746].

1-(2-Hydroxy-3-methylphenyl)-2-(2-methoxyphenyl)ethanone

[74384-36-4] $C_{16}H_{16}O_3$ mol.wt. 256.30



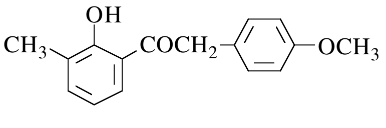
Synthesis

-Preparation by Fries rearrangement of o-cresyl o-methoxyphenylacetate with aluminium chloride in nitromethane for 170 h at 20° (60%) [971].

m.p. 167° [971];
^{1}H NMR (Sadtler: standard n° 44610 M);
IR (Sadtler: standard n° 71638 K) [971],
UV [971], MS [971].

1-(2-Hydroxy-3-methylphenyl)-2-(4-methoxyphenyl)ethanone

[74384-33-1] $C_{16}H_{16}O_3$ mol.wt. 256.30



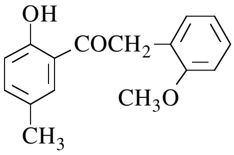
Synthesis

-Obtained (by-product) by Fries rearrangement of o-cresyl p-methoxyphenylacetate with aluminium chloride in nitromethane for 25 h at 20° (11%) [971].

oil [971]; IR [971], UV [971], MS [971].

1-(2-Hydroxy-5-methylphenyl)-2-(2-methoxyphenyl)ethanone

[74384-38-6] $C_{16}H_{16}O_3$ mol.wt. 256.30



Synthesis

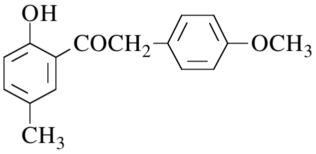
-Obtained by Fries rearrangement of p-cresyl o-methoxyphenylacetate with aluminium chloride in nitromethane for 170 h at 20° (41%) [971].

m.p. 95° [971];

^{1}H NMR (Sadtler: standard n° 44606 M), IR (Sadtler: standard n°71634 K) [971], UV [971], MS [971].

1-(2-Hydroxy-5-methylphenyl)-2-(4-methoxyphenyl)ethanone

[74384-34-2] $C_{16}H_{16}O_3$ mol.wt. 256.30



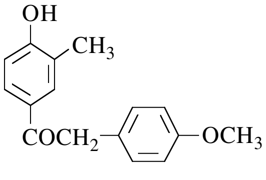
Synthesis

-Obtained by Fries rearrangement of p-cresyl p-methoxyphenylacetate with aluminium chloride in nitromethane for 25 h at 20° (22%) [971].

m.p. 55° [971];
IR [971], UV [971], MS [971].

1-(4-Hydroxy-3-methylphenyl)-2-(4-methoxyphenyl)ethanone

[74384-31-9] $C_{16}H_{16}O_3$ mol.wt. 256.30



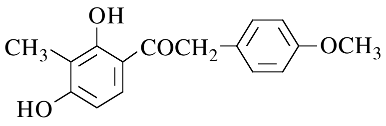
Synthesis

-Preparation by Fries rearrangement of o-cresyl p-methoxyphenylacetate with aluminium chloride in nitromethane for 25 h at 20° (71%) [971].

m.p. 160° [971];
^{1}H NMR (Sadtler: standard n° 44612 M), IR (Sadtler: standard n° 71640 K) [971], UV [971], MS [971].

1-(2,4-Dihydroxy-3-methylphenyl)-2-(4-methoxyphenyl)ethanone

[93434-89-0] $C_{16}H_{16}O_4$ mol.wt. 272.30



Syntheses

-Preparation by hydrogenation of 2,4-dihydroxy-3-formylphenyl 4-methoxybenzyl ketone (m.p. 114-115°) in acetic acid in the presence of 5% Pd/C in an atmosphere of hydrogen at r.t. and at atmospheric pressure (79%) [594].

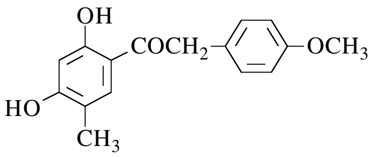
-Preparation by reaction of p-methoxyphenylacetonitrile with 2-methylresorcinol (48%) (Hoesch reaction) [841].

Also refer to: [28].

m.p. 175° [841], 172-173° [594].

1-(2,4-Dihydroxy-5-methylphenyl)-2-(4-methoxyphenyl)ethanone

[56308-10-2] $C_{16}H_{16}O_4$ mol.wt. 272.30



Syntheses

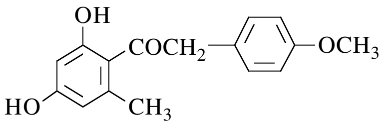
-Obtained by reaction of 4-methoxyphenylacetonitrile with 4-methylresorcinol (Hoesch reaction) (44%) [173], (36%) [1534].

-Also refer to: [1419] (Hungarian paper).

m.p. 155° [1534], 139-140° [173]. One of the reported melting points is obviously wrong.

1-(2,4-Dihydroxy-6-methylphenyl)-2-(4-methoxyphenyl)ethanone

[15485-71-9] $C_{16}H_{16}O_4$ mol.wt. 272.30



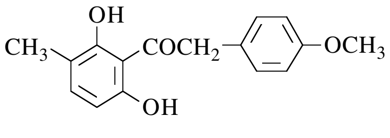
Synthesis

-Obtained by treatment of orcinol with p-methoxyphenylacetonitrile in ethyl ether in the presence of zinc chloride and hydrogen chloride (Hoesch reaction) [1019].

m.p. 109-110° [1019]; UV [1019].

1-(2,6-Dihydroxy-3-methylphenyl)-2-(4-methoxyphenyl)ethanone

[131196-70-8] $C_{16}H_{16}O_4$ mol.wt. 272.30



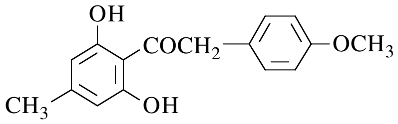
Synthesis

-Obtained from 2,6-dihydroxy-4'-methoxy-5-methoxycarbonyl-3-methyldeoxybenzoin (m.p. 116°) which was simultaneously hydrolysed and decarboxylated by treatment with potassium hydroxide in refluxing dilute ethanol for 1.5 h (84%) [1534].

m.p. 164° [1534].

1-(2,6-Dihydroxy-4-methylphenyl)-2-(4-methoxyphenyl)ethanone

[128672-42-4] $C_{16}H_{16}O_4$ mol.wt. 272.30

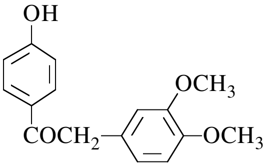


Synthesis

-Refer to: [1565] (Chinese paper).

2-(3,4-Dimethoxyphenyl)-1-(4-hydroxyphenyl)ethanone

[183054-34-4] $C_{16}H_{16}O_4$ mol.wt. 272.30



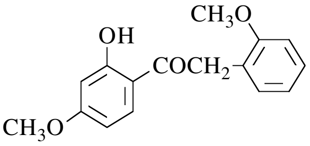
Synthesis

-Obtained by Friedel-Crafts acylation of isopropyl phenyl ether with homoveratryl chloride in ethylene dichloride in the presence of aluminium chloride, first at 20°, then at 40° for 2-3 h and at r.t. overnight (31%) [1487].

m.p. 165-167° [1487];
^{1}H NMR [1487], ^{13}C NMR [1487], IR [1487], MS [1487].

1-(2-Hydroxy-4-methoxyphenyl)-2-(2-methoxyphenyl)ethanone

[18440-00-1] $C_{16}H_{16}O_4$ mol.wt. 272.30



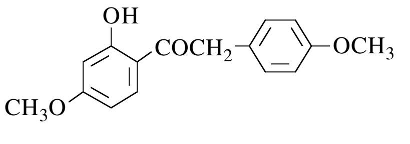
Syntheses

-Preparation by partial methylation of 2,4-dihydroxy-2'-methoxydeoxybenzoin,
*with methyl iodide in the presence of potassium carbonate in boiling acetone during 1.5 h (quantitative yield) [1536];
*with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 5 h (83%) [590].
-Also obtained by Friedel-Crafts acylation of resorcinol dimethyl ether with o-methoxyphenylacetyl chloride in the presence of aluminium chloride, first in carbon disulfide, then on steam bath for 2.5 h after solvent elimination (40%) [733].
-Also obtained by hydrolysis of 2,4-dimethoxybenzoyl-2-methoxyphenylacetonitrile (m.p. 114-115°) in acetic acid with concentrated hydrochloric acid on a steam bath for 15 h (43%) [777].
-Also obtained by hydrolysis of ethyl 2,4-dimethoxybenzoyl-2-methoxyphenylacetate (m.p. 94-96°) in acetic acid with concentrated hydrochloric acid on a steam bath for 15 h (40%) [777].
-Also obtained by degradation of 7,2'-dimethoxy-3-phenyl-4-hydroxycoumarin with refluxing 30% alcoholic hydrogen chloride for 1 h (36%) [387].
-Also refer to: [724] [1165] [1291] [1364] [1530].

m.p. 94° [1536], 93-95° [733], 93-94° [590], 92° [387], 90-91° [777];
b.p.$_{0.001}$ 180° [777].

1-(2-Hydroxy-4-methoxyphenyl)-2-(4-methoxyphenyl)ethanone

[39604-64-3] $C_{16}H_{16}O_4$ mol.wt. 272.30



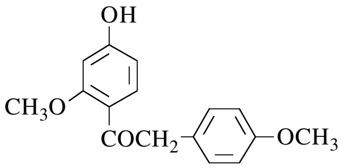
Syntheses

-Preparation by partial methylation of 2,4-dihydroxyphenyl 4-methoxybenzyl ketone,
*with methyl iodide in the presence of potassium carbonate in boiling acetone during 3 h (83%) [106];
*with dimethyl sulfate [86], in the presence of potassium carbonate in boiling acetone [13];
*with diazomethane in ethyl ether [221] [1526].
-Also obtained by alkaline degradation of *formononetin methyl ether* (7,4'-dimethoxyisoflavone) [221], (m.p. 156°) with boiling 10% sodium hydroxide for 1 h [1526].
-Also obtained by hydrolysis of 2,4-dimethoxybenzoyl-4-methoxyphenyl-acetonitrile (m.p. 105-106°) in acetic acid with concentrated hydrochloric acid on a steam bath for 15 h (38%) [777].
-Also obtained by hydrolysis of ethyl 2,4-dimethoxybenzoyl-4-methoxyphenyl-acetate (m.p. 48-50°) in acetic acid with concentrated hydrochloric acid on a steam bath for 15 h (33%) [777].
-Also obtained by reaction of p-methoxyphenylacetonitrile with resorcinol monomethyl ether (Hoesch reaction) [1528].
-Also refer to: [11] [12] [117] [169] [701] [724] [870] [1076] [1165] [1168] [1169] [1291] [1364] [1490].

m.p. 104° [106] [1526], 102° [221], 100-100°5 [777], 92-93° [1528];
b.p.$_{0.001}$ 190° [777]; ^{13}C NMR [732] [1167].

1-(4-Hydroxy-2-methoxyphenyl)-2-(4-methoxyphenyl)ethanone

$C_{16}H_{16}O_4$ mol.wt. 272.30



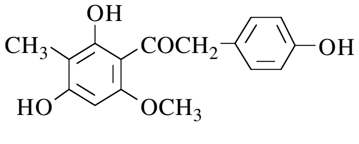
Syntheses

-Obtained by heating 1-[4-(glucopyranosyloxy)-2-methoxyphenyl]-2-(4-methoxyphenyl)ethanone (SM) with concentrated sulfuric acid for 20 min. SM was obtained by methylation of synthetic *onospin* (m.p. 179°5) with excess methyl iodide in the presence of potassium carbonate in boiling methanol for 2 h. This same methylation can be realized by using diazomethane [1528].
-Also obtained by reaction of p-methoxyphenylacetonitrile with resorcinol monomethyl ether (Hoesch reaction) [1528].

m.p. 173-175° [1528].

1-(2,4-Dihydroxy-6-methoxy-3-methylphenyl)-2-(4-hydroxyphenyl)ethanone

$C_{16}H_{16}O_5$ mol.wt. 288.30



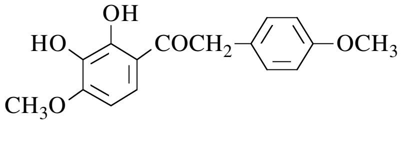
Syntheses

-Obtained by reaction of p-hydroxyphenylacetonitrile with 2,6-dihydroxy-4-methoxytoluene (m.p. 124°) (Hoesch reaction) (50%) [1531].
-Also refer to: [1534].

m.p. 207° [1531].

1-(2,3-Dihydroxy-4-methoxyphenyl)-2-(4-methoxyphenyl)ethanone

[38412-65-6] $C_{16}H_{16}O_5$ mol.wt. 288.30



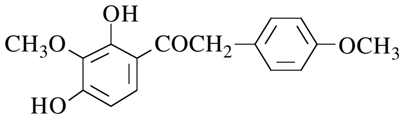
Synthesis

-Obtained by reaction of 4-methoxyphenylacetic acid with 3-methoxycatechol in chloroform in the presence of excess boron trifluoride, first at 0°, then at r.t. for 2 days (97%) [744].

m.p. 137° [744].

1-(2,4-Dihydroxy-3-methoxyphenyl)-2-(4-methoxyphenyl)ethanone

[61243-80-9] $C_{16}H_{16}O_5$ mol.wt. 288.30



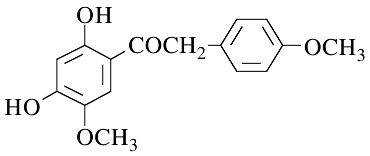
Synthesis

-Obtained by mild base hydrolysis of *8-O-methyl-retusin* (7-hydroxy-8,4'-dimethoxyisoflavone) (SM) (m.p. 229-232°), itself isolated from heartwood of *Xanthocercis zambesiaca* (Bak.) (Leguminosae) [615].

m.p. 140-142° [615]; ^{1}H NMR [615], IR [615], UV [615], MS [615].

1-(2,4-Dihydroxy-5-methoxyphenyl)-2-(4-methoxyphenyl)ethanone

[5128-54-1] $C_{16}H_{16}O_5$ mol.wt. 288.30



Syntheses

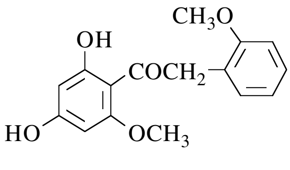
-Obtained by alkaline degradation of *afromosin* (7-hydroxy-6,4'-dimethoxyisoflavone), (69%) [1347], (64%) [986]. *Afromosin* (m.p. 228-229°), was isolated from *afromosia elata* Harms [986]. *Afromosin* is the aglycone of *wistin* (m.p. 209-210°), itself isolated from the bark of *wistaria floribunda* DC [1347].

-Also obtained by reaction of 4-methoxyphenyl-acetonitrile with 4-methoxyresorcinol (Hoesch reaction) (20%) [986].

m.p. 128-129° [986], 127° [1347]; ^{13}C NMR [732], IR [986], UV [986] [1347].

1-(2,4-Dihydroxy-6-methoxyphenyl)-2-(2-methoxyphenyl)ethanone

$C_{16}H_{16}O_5$ mol.wt. 288.30

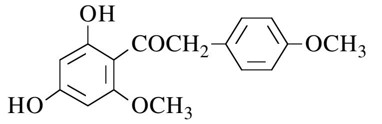


Synthesis

-Refer to: [559].

1-(2,4-Dihydroxy-6-methoxyphenyl)-2-(4-methoxyphenyl)ethanone

[13539-34-9] $C_{16}H_{16}O_5$ mol.wt. 288.30



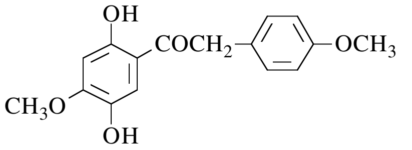
Syntheses

-Preparation by reaction of p-methoxyphenylacetonitrile with phloroglucinol monomethyl ether (Hoesch reaction) [559] [700], (39%) [85], (31%) [1531].
-Also obtained by alkaline degradation of *genistein 5,4'-dimethyl ether* (7-hydroxy-5,4'-dimethoxyisoflavone) (m.p. 290-293°) in boiling 30% potassium hydroxide for 15 min (93%) [1520].

crystals [1520]; m.p. 166-167° [559], 129-130° [1531], 126-127° [85]. One of the reported melting points is obviously wrong. UV [85].

1-(2,5-Dihydroxy-4-methoxyphenyl)-2-(4-methoxyphenyl)ethanone

[79744-55-1] $C_{16}H_{16}O_5$ mol.wt. 288.30



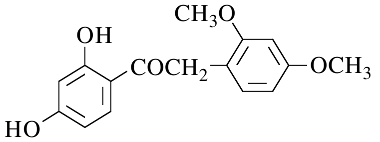
Syntheses

-Obtained by alkaline persulfate oxidation of 2-hydroxy-4-methoxyphenyl 4-methoxybenzyl ketone (Elbs reaction) (21%) [86].
-Also obtained by partial methylation of 2,4,5-trihydroxyphenyl 4-methoxybenzyl ketone with excess diazomethane in ethyl ether at r.t. overnight (14%) [530].
-Also obtained by reaction of 4-methoxyphenylacetonitrile with 2-methoxyhydroquinone so called methoxyquinol (24%) (Hoesch reaction) [986].

m.p. 150° [986], 148-149° [530], 133-134° [86].
One of the reported melting points is obviously wrong.
^{13}C NMR [732], IR [986], UV [86] [986].

1-(2,4-Dihydroxyphenyl)-2-(2,4-dimethoxyphenyl)ethanone

[1855-30-7] $C_{16}H_{16}O_5$ mol.wt. 288.30



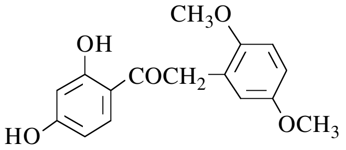
Syntheses

-Obtained by reaction of 2,4-dimethoxyphenylacetonitrile with resorcinol (Hoesch reaction) [1145], (55%) [1304], (37%) [218] [314], (5%) [1384].
-Also refer to: [702] [703].

m.p. 158-159° [1304], 155-156° [1384], 154° [314], 152° [218];
b.p.$_{0.02}$ 200-210° [1384]; IR [314].

1-(2,4-Dihydroxyphenyl)-2-(2,5-dimethoxyphenyl)ethanone

[18086-25-4] $C_{16}H_{16}O_5$ mol.wt. 288.30



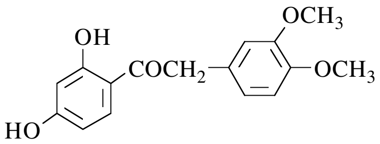
Synthesis

-Obtained by reaction of 2,5-dimethoxyphenylacetonitrile (m.p. 56-57°) with resorcinol (40%) (Hoesch reaction) [751].

m.p. 144-145° [751].

1-(2,4-Dihydroxyphenyl)-2-(3,4-dimethoxyphenyl)ethanone

[24126-98-5] $C_{16}H_{16}O_5$ mol.wt. 288.30



Syntheses

-Preparation by Friedel-Crafts acylation of resorcinol with 3,4-dimethoxyphenylacetyl chloride in nitrobenzene in the presence of aluminium chloride for 24 h at r.t. (56%) [106].

-Preparation by reaction of 3,4-dimethoxyphenylacetonitrile with resorcinol (Hoesch reaction) [158], (60%) [392], (49%) [218].

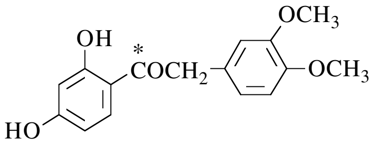
-Obtained by heating *Cladrin* (7-hydroxy-3',4'-dimethoxyisoflavone) (m.p. 257-258°) with 10% aqueous barium hydroxide at reflux for 2 h (73%). *Cladrin* was isolated from *Cladrastis lutea* (Mich. f.) K. Koch (Leguminosae) [1330].

-Also refer to: [467] [723] [1140].

m.p. 182-183° [1330], 180° [218], 177°5 [106], 177-178° [392], 176°5 [158].

1-(2,4-Dihydroxyphenyl)-2-(3,4-dimethoxyphenyl)ethanone-*1*-^{14}*C*

[142050-41-7] $C_{16}H_{16}O_5$ mol.wt. 290.29



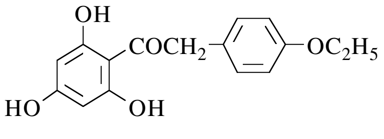
Synthesis

-Obtained by reaction of 3,4-dimethoxybenzyl [^{14}C] nitrile with resorcinol (Hoesch reaction) (38%) [174].

m.p. 183-184° [174]; TLC [174].

2-(4-Ethoxyphenyl)-1-(2,4,6-trihydroxyphenyl)ethanone

$C_{16}H_{16}O_5$ mol.wt. 288.30



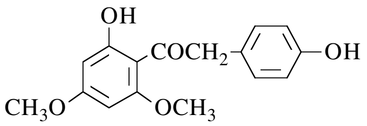
Synthesis

-Preparation by condensation of p-ethoxyphenylacetonitrile with phloroglucinol (Hoesch reaction) [1074].

m.p. 208-210° [1074].

1-(2-Hydroxy-4,6-dimethoxyphenyl)-2-(4-hydroxyphenyl)ethanone

[69127-79-3] $C_{16}H_{16}O_5$ mol.wt. 288.30



Syntheses

-Obtained by alkaline degradation of *genistein 5,7-dimethyl ether* (5,7-dimethoxy-4'-hydroxyisoflavone) (m.p. 266°) with 40% potassium hydroxide in a water bath for 15 min (41%) [1571].

-Also obtained by diazotization of 4-aminobenzyl 2-hydroxy-4,6-dimethoxyphenyl ketone hydrochloride, followed by hydrolysis of the diazonium salt obtained (33%) [686].

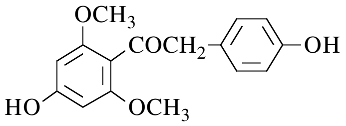
-Also obtained by reaction of p-hydroxyphenylacetonitrile with phloroglucinol dimethyl ether (Hoesch reaction) (25%) [829], (19%) [1571].

-Also refer to: [559] [1166].

m.p. 112° [829] [1571], 110° [686].

1-(4-Hydroxy-2,6-dimethoxyphenyl)-2-(4-hydroxyphenyl)ethanone

$C_{16}H_{16}O_5$ mol.wt. 288.30



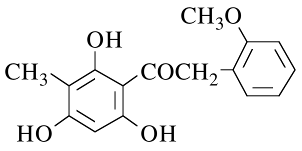
Synthesis

-Obtained by reaction of p-hydroxyphenylacetonitrile with phloroglucinol dimethyl ether (Hoesch reaction) [829] [1571].

m.p. 182° [1571], 181° [829].

2-(2-Methoxyphenyl)-1-(2,4,6-trihydroxy-3-methylphenyl)ethanone

$C_{16}H_{16}O_5$ mol.wt. 288.30



Syntheses

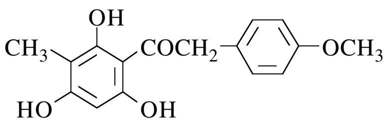
-Preparation by reaction of o-methoxyphenylacetonitrile with 2-methylphloroglucinol (m.p. 215°) (Hoesch reaction), (45%) [1531], (35%) [989].

-Also refer to: [1208].

m.p. 206° [1531], 198-200° [989]; sublimation at 160°/0.01 mm [1531].

2-(4-Methoxyphenyl)-1-(2,4,6-trihydroxy-3-methylphenyl)ethanone

$C_{16}H_{16}O_5$ mol.wt. 288.30



Syntheses

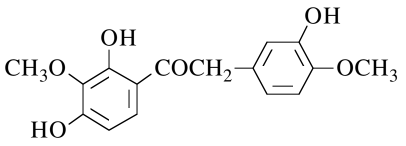
-Obtained by reaction of p-methoxyphenylacetonitrile with 2-methylphloroglucinol (m.p. 215°) [1531] (Hoesch reaction), (54%) [1317], (26%) [1531].

-Also refer to: [988] [1208] [1209].

m.p. 228° [1531], 220-221° [1317]; sublimation at 160°/ 0.01 mm [1531].

1-(2,4-Dihydroxy-3-methoxyphenyl)-2-(3-hydroxy-4-methoxyphenyl)ethanone

[61243-85-4] $C_{16}H_{16}O_6$ mol.wt. 304.30



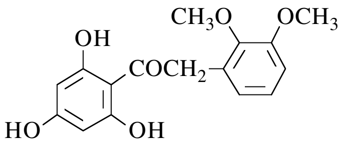
Syntheses

-Obtained by mild base hydrolysis of 7,3'-dihydroxy-8,4'-dimethoxyisoflavone (m.p. 212-213°), (71%) [615].
-Also refer to: [297].

m.p. 127-129° [615]; ^{1}H NMR [615], IR [615], UV [615], MS [615].

2-(2,3-Dimethoxyphenyl)-1-(2,4,6-trihydroxyphenyl)ethanone

$C_{16}H_{16}O_6$ mol.wt. 304.30



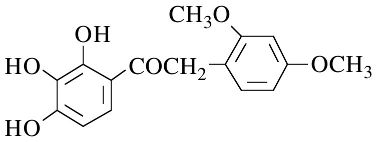
Syntheses

-Obtained by reaction of 2,3-dimethoxyphenylacetonitrile with phloroglucinol (Hoesch reaction) (44%) [1536].
-Also refer to: [1530].

m.p. 193° [1536].

2-(2,4-Dimethoxyphenyl)-1-(2,3,4-trihydroxyphenyl)ethanone

[14756-83-3] $C_{16}H_{16}O_6$ mol.wt. 304.30



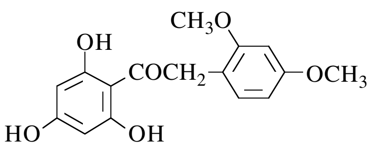
Syntheses

-Obtained by reaction of phenylacetic acid with pyrogallol in the presence of zinc chloride at 130° for 2 h (Nencki reaction) (39%) [754].
-Also obtained (poor yield) by reaction of 2,4-dimethoxyphenylacetonitrile with pyrogallol (Hoesch reaction) (4%) [754].

m.p. 134-135° [754].

2-(2,4-Dimethoxyphenyl)-1-(2,4,6-trihydroxyphenyl)ethanone

[65568-08-3] $C_{16}H_{16}O_6$ mol.wt. 304.30



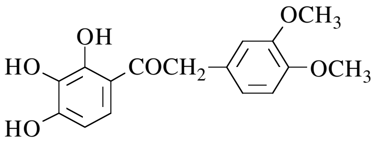
Syntheses

-Obtained by condensation of 2,4-dimethoxyphenylacetonitrile (m.p. 76°) with phloroglucinol (Hoesch reaction) [12] [839] [1016] [1080].
-Also refer to: [559] [716] [723] [1140] [1495] [1530].

m.p. 178° [1080], 175° [1016]; paper chromatography [393].

2-(3,4-Dimethoxyphenyl)-1-(2,3,4-trihydroxyphenyl)ethanone

[93435-58-6] $C_{16}H_{16}O_6$ mol.wt. 304.30



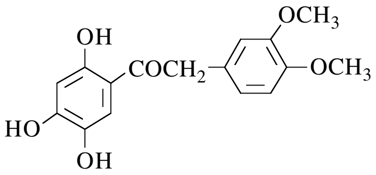
Synthesis

-Obtained by condensation of 3,4-dimethoxyphenylacetonitrile (m.p. 45-47°) [620] with pyrogallol (Hoesch reaction) [1147], (23%) [848].

m.p. 174° [848].

2-(3,4-Dimethoxyphenyl)-1-(2,4,5-trihydroxyphenyl)ethanone

[66116-74-3] $C_{16}H_{16}O_6$ mol.wt. 304.30



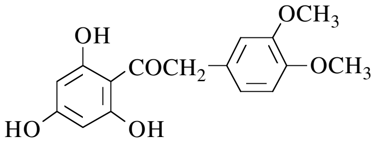
Syntheses

-Preparation by reaction of 3,4-dimethoxyphenylacetonitrile with hydroxyhydroquinone (Hoesch reaction) (81%) [707].
-Also refer to: [246].

m.p. 193-194° [707]; TLC [707];
^1H NMR [707], ^{13}C NMR [732].

2-(3,4-Dimethoxyphenyl)-1-(2,4,6-trihydroxyphenyl)ethanone

[53084-06-3] $C_{16}H_{16}O_6$ mol.wt. 304.30



Syntheses

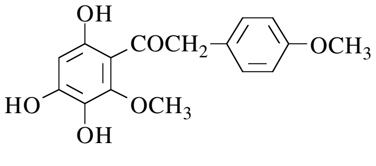
-Preparation by reaction of 3,4-dimethoxyphenylacetonitrile with phloroglucinol (Hoesch reaction),
*in the presence of zinc chloride [559] [1073], (47%) [106], (42%) [771], (38%) [1024];
*in the presence of boron trifluoride etherate (59%) [1024].

-Also refer to: [873].
N.B.: The monohydrate of this ketone was at first obtained [106]. The water of crystallisation is lost on heating the crystals at 90°.

m.p. 208-210° [1073], 184-186° [559], 182-184° [1024], 181° [106], 180-181° [771].
One of the reported melting points is obviously wrong.
^{13}C NMR [732], IR [771], UV [771]; TLC [771].

2-(4-Methoxyphenyl)-1-(3,4,6-trihydroxy-2-methoxyphenyl)ethanone

[14701-83-8] $C_{16}H_{16}O_6$ mol.wt. 304.30



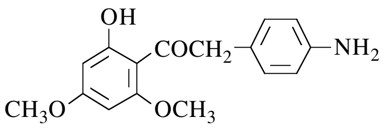
Synthesis

-Obtained by persulfate oxidation of 2,4-dihydroxy-6-methoxyphenyl 4-methoxybenzyl ketone (Elbs reaction) [85].

m.p. 144° [85]; UV [85].

2-(4-Aminophenyl)-1-(2-hydroxy-4,6-dimethoxyphenyl)ethanone

$C_{16}H_{17}NO_4$ mol.wt. 287.32



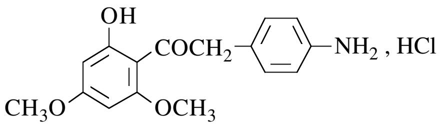
Synthesis

-Preparation by hydrogenation of 2-hydroxy-4,6-dimethoxyphenyl 4-nitrobenzyl ketone in ethanol in the presence of Raney nickel as catalyst with hydrogen for 8 h [686].

m.p. 103-104° [686].

2-(4-Aminophenyl)-1-(2-hydroxy-4,6-dimethoxyphenyl)ethanone *(Hydrochloride)*

$C_{16}H_{17}NO_4$, HCl mol.wt. 323.78



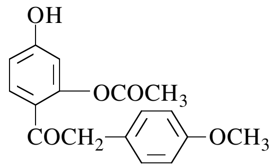
Synthesis

-Obtained by treatment of the above base with hot dilute hydrochloric acid [686].

m.p. 198-200° [686].

1-[2-(Acetyloxy)-4-hydroxyphenyl]-2-(4-methoxyphenyl)ethanone

[145747-28-0] $C_{17}H_{16}O_5$ mol.wt. 300.31



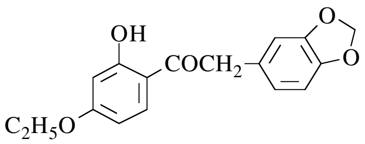
Syntheses

-Obtained by selective deacetylation catalyzed by porcine pancreas lipase in THF at 42-45° of,
*2,4-diacetoxyphenyl 4-methoxybenzyl ketone during 48 h (73%) [1144] [1145] [1146];
*1-acetoxy-1-(2,4-diacetoxyphenyl)-2-(4-methoxyphenyl)-ethene during 72 h (18%) [1145].

semi solid [1145]; TLC [1145];
^{1}H NMR [1145], IR [1145], UV [1145], MS [1145].

2-(1,3-Benzodioxol-5-yl)-1-(4-ethoxy-2-hydroxyphenyl)ethanone
(Pseudo-baptigenetin monoethyl ether)

$C_{17}H_{16}O_5$ mol.wt. 300.31



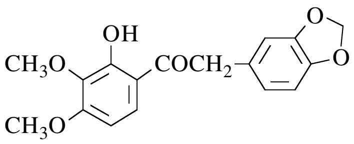
Syntheses

-Obtained by partial ethylation of *pseudo-baptigenetin* in ethanol with diazoethane in ethyl ether for 1.25 h [1385].
-Also obtained by alkaline degradation of *pseudo-baptigenin monoethyl ether* (m.p. 172°) with potassium hydroxide in boiling dilute ethanol [1385].

m.p. 129° [1385].

2-(1,3-Benzodioxol-5-yl)-1-(2-hydroxy-3,4-dimethoxyphenyl)ethanone

[84018-73-5] $C_{17}H_{16}O_6$ mol.wt. 316.31

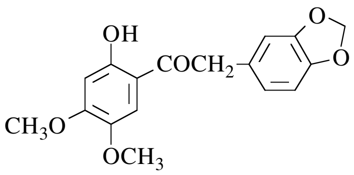


Synthesis

-Obtained by reaction of 3,4-(methylenedioxy)phenylacetonitrile with pyrogallol (Hoesch reaction) and subsequent partial methylation of the 2,3,4-trihydroxyphenyl 3,4-methylenedioxybenzyl ketone so obtained with dimethyl sulfate [706] according to the method [528].

2-(1,3-Benzodioxol-5-yl)-1-(2-hydroxy-4,5-dimethoxyphenyl)ethanone

[2746-88-5] $C_{17}H_{16}O_6$ mol.wt. 316.31



Syntheses

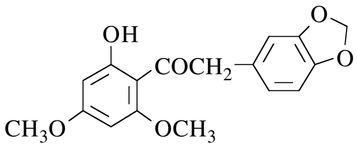
-Obtained by partial methylation of 3,4-(methylenedioxy)benzyl 2,4,5-trihydroxyphenyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 6 h (40%) [528] or according to [701], (90%) [707].

-Also obtained by partial demethylation of 3,4-(methylenedioxy)benzyl 2,4,5-trimethoxyphenyl ketone (m.p. 153-154°) with aluminium chloride in refluxing acetonitrile for 45 min (43%) [262].
-Also obtained (trace) by reaction of 3,4-(methylenedioxy)phenylacetyl chloride with 1,2,4-trimethoxybenzene in the presence of aluminium chloride in ethyl ether at 0° overnight (< 1%) [262].
-Also refer to: [12].

m.p. 153-154° [528], 119° [707], 118-119° [262]. One of the reported melting points is obviously wrong.
IR [262] [528], UV [262] [528], MS [262].

2-(1,3-Benzodioxol-5-yl)-1-(2-hydroxy-4,6-dimethoxyphenyl)ethanone

[22044-73-1] $C_{17}H_{16}O_6$ mol.wt. 316.31



Syntheses

-Preparation by partial methylation of 3,4-(methylenedioxy)benzyl 2,4,6-trihydroxyphenyl ketone with dimethyl sulfate in the presence of potassium carbonate in boiling acetone [559], for 14 h (73%) [687].

-Also refer to: [699] [1419].

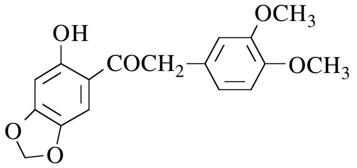
Isolation from natural sources

-Obtained (major product) by alkaline hydrolysis of *Derrustone* (5,7-dimethoxy-3',4'-methylenedioxyisoflavone) (m.p. 153-154°) (SM) with 25% aqueous potassium hydroxide in refluxing methanol for 2 h (69%). SM was isolated from the root material of *Derris robusta* (Roxb.) Benth [438].

m.p. 102-103° [438], 98-99° [559], 97° [687]; IR [438].

2-(3,4-Dimethoxyphenyl)-1-(6-hydroxy-1,3-benzodioxol-5-yl)ethanone

[61243-78-5] $C_{17}H_{16}O_6$ mol.wt. 316.31



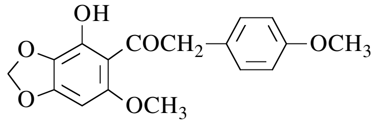
Synthesis

-Obtained by mild base hydrolysis of 3',4'-dimethoxy-6,7-methylenedioxyisoflavone [615].

m.p. 148-151° [615];
^{1}H NMR [615], IR [615], UV [615], MS [615];
TLC [615].

1-(4-Hydroxy-6-methoxy-1,3-benzodioxol-5-yl)-2-(4-methoxyphenyl)ethanone

$C_{17}H_{16}O_6$ mol.wt. 316.31



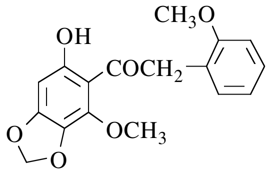
Synthesis

-Obtained by alkali degradation of 5,4'-dimethoxy-7,8-methylenedioxy-2-methylisoflavone (m.p. 214-215°) with potassium hydroxide in refluxing dilute ethanol for 2 h under a stream of nitrogen gas (88%) [529].

m.p. 133-134° [529]; IR [529], UV [529].

1-(6-Hydroxy-4-methoxy-1,3-benzodioxol-5-yl)-2-(2-methoxyphenyl)ethanone

$C_{17}H_{16}O_6$ mol.wt. 316.31



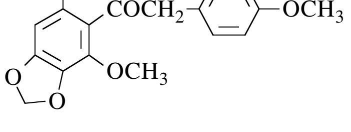
Synthesis

-Obtained by alkaline degradation of *tlatlancuayin* (5,2'-dimethoxy-6,7-methylenedioxyisoflavone) (SM) with refluxing aqueous sodium hydroxide for 1.5 h (quantitative yield). SM was isolated from *Iresine celosioides* L. (Amarantaceae) [335].

m.p. 115-116° [335]; IR [335], UV [335].

1-(6-Hydroxy-4-methoxy-1,3-benzodioxol-5-yl)-2-(4-methoxyphenyl)ethanone

[3207-42-9] $C_{17}H_{16}O_6$ mol.wt. 316.31



Syntheses

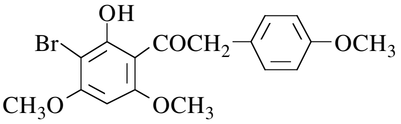
-Obtained by methylenation of 2,4,5-trihydroxy-6-methoxyphenyl 4-methoxybenzyl ketone with methylene iodide in the presence of potassium carbonate in refluxing acetone for 40 h [85].
-Also obtained by alkaline degradation of *irisolone methyl ether* (4',5-dimethoxy-6,7-methylenedioxy-isoflavone) (m.p. 184-185°) with refluxing aqueous sodium hydroxide for 1.5 h [573].
-Also obtained by reaction of 4-methoxyphenylacetonitrile with 3-methoxy-4,5-methylenedioxy-phenol (Hoesch reaction) (12%) [529].

-Also obtained in two steps: First, methylation of 6-benzyloxy-2-hydroxy-3,4-methylenedioxyphenyl 4-methoxybenzyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 27 h. The obtained methyl ether was debenzylated with hydrogen in ethanol in the presence of 10% Pd/C for 5 h at r.t. (31%) [529].

m.p. 114-115° [529], 113-114° [85] [573];
IR [529], UV [85] [529] [573].

1-(3-Bromo-2-hydroxy-4,6-dimethoxyphenyl)-2-(4-methoxyphenyl)ethanone

[28750-74-5] $C_{17}H_{17}BrO_5$ mol.wt. 381.22



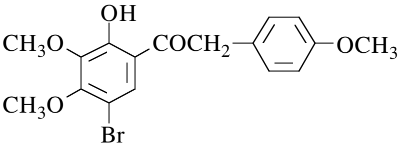
Synthesis

-Preparation by bromination of 2-hydroxy-4,6,4'-trimethoxydeoxybenzoin with bromine in chloroform under UV light at r.t. overnight (52%) [771].

m.p. 158-159° [771]; TLC [771];
^1H NMR [771], IR [771], UV [771].

1-(5-Bromo-2-hydroxy-3,4-dimethoxyphenyl)-2-(4-methoxyphenyl)ethanone

[24852-43-5] $C_{17}H_{17}BrO_5$ mol.wt. 381.22



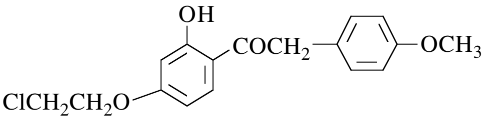
Synthesis

-Obtained by bromination of 2-hydroxy-3,4-dimethoxyphenyl 4-methoxybenzyl ketone with bromine in the presence of sodium acetate in chloroform for 5 h (70%) [758].

m.p. 81-82° [758]; ^1H NMR [758].

1-[4-(2-Chloroethoxy)-2-hydroxyphenyl]-2-(4-methoxyphenyl)ethanone

[247931-29-9] $C_{17}H_{17}ClO_4$ mol.wt. 320.77



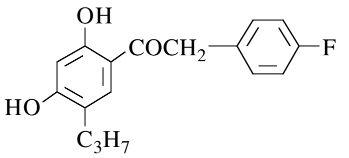
Synthesis

-Obtained by partial alkylation of 1-(2,4-dihydroxyphenyl)-2-(4-methoxyphenyl)ethanone with 1-bromo-2-chloroethane in the presence of potassium carbonate in refluxing acetone for 24 h (70%) [1490].

m.p. 87-89° [1490]; ^1H NMR [1490].

1-(2,4-Dihydroxy-5-propylphenyl)-2-(4-fluorophenyl)ethanone

[96644-01-8] $C_{17}H_{17}FO_3$ mol.wt. 288.32



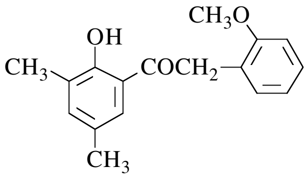
Synthesis

-Obtained by reaction of p-fluorophenylacetonitrile with 4-propylresorcinol in the presence of boron trifluoride etherate under hydrogen chloride at r.t. for 8-10 h, then at r.t. overnight (63%) [786].

m.p. 100-101° [786]; ^{1}H NMR [786].

1-(2-Hydroxy-3,5-dimethylphenyl)-2-(2-methoxyphenyl)ethanone

[74384-39-7] $C_{17}H_{18}O_3$ mol.wt. 270.33



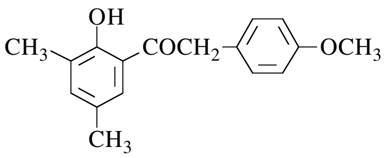
Synthesis

-Obtained by Fries rearrangement of 2,4-dimethylphenyl 2-methoxyphenylacetate with aluminium chloride in nitromethane at 20° for 170 h (39%) [971].

m.p. 85° [971];
^{1}H NMR (Sadtler: standard n° 44603 M), [971],
IR (Sadtler: standard n° 71631 K), [971], UV [971],
MS [971].

1-(2-Hydroxy-3,5-dimethylphenyl)-2-(4-methoxyphenyl)ethanone

[74384-35-3] $C_{17}H_{18}O_3$ mol.wt. 270.33



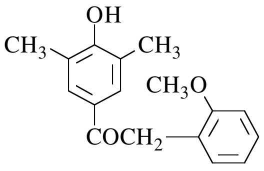
Synthesis

-Preparation by Fries rearrangement of 2,4-dimethylphenyl 4-methoxyphenylacetate with aluminium chloride in nitromethane at 20° for 170 h (59%) [971].

m.p. 23° [971]; IR [971], UV [971], MS [971].

1-(4-Hydroxy-3,5-dimethylphenyl)-2-(2-methoxyphenyl)ethanone

[74384-37-5] $C_{17}H_{18}O_3$ mol.wt. 270.33



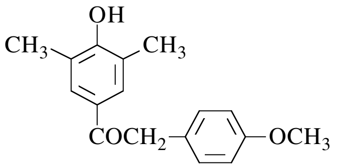
Synthesis

-Obtained by Fries rearrangement of 2,6-dimethylphenyl 2-methoxyphenylacetate in the presence of ferric chloride or aluminium chloride in nitromethane at 20° for 50 h (29% and 6% yields, respectively) [971].

m.p. 160° [971];
^{1}H NMR (Sadtler: standard n° 44607 M), [971],
IR (Sadtler: standard n° 71635 K), [971], UV [971], MS [971].

1-(4-Hydroxy-3,5-dimethylphenyl)-2-(4-methoxyphenyl)ethanone

[74384-32-0] $C_{17}H_{18}O_3$ mol.wt. 270.33



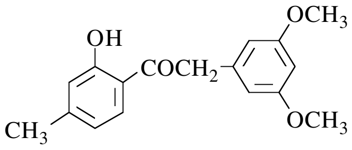
Synthesis

-Preparation by Fries rearrangement of 2,6-dimethylphenyl 4-methoxyphenylacetate with aluminium chloride in nitromethane at 20° for 50 h (76%) [971].

m.p. 177° [971];
^{1}H NMR (Sadtler: standard n° 44604 M), [971],
IR (Sadtler: standard n° 71632 K), [971], UV [971], MS [971].

2-(3,5-Dimethoxyphenyl)-1-(2-hydroxy-4-methylphenyl)ethanone

[111191-98-1] $C_{17}H_{18}O_4$ mol.wt. 286.33



Synthesis

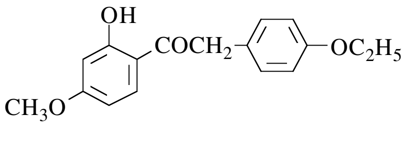
-Obtained (poor yield) by Fries rearrangement of m-cresyl 3,5-dimethoxyphenylacetate (b.p.$_{0.05}$ 95°) in the presence of aluminium chloride, first in carbon disulfide, then at 130-145° for 2 h after solvent elimination (15%) [495].

brown gum [495].

N.B.: Methyl ether: m.p. 199-200° [495], ^{1}H NMR [495], IR [495], MS [495].

2-(4-Ethoxyphenyl)-1-(2-hydroxy-4-methoxyphenyl)ethanone

[89019-87-4] $C_{17}H_{18}O_4$ mol.wt. 286.33



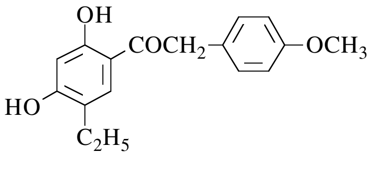
Synthesis

-Obtained (by-product) by reaction of p-hydroxyphenylacetic acid with m-methoxyphenol in ethylene dichloride in the presence of boron trifluoride at 80° for 2 h under an argon atmosphere (2%) [937].

m.p. 95-97° [937]; ^{1}H NMR [937], IR [937], UV [937], MS [937].

1-(5-Ethyl-2,4-dihydroxyphenyl)-2-(4-methoxyphenyl)ethanone

[96644-03-0] $C_{17}H_{18}O_4$ mol.wt. 286.33



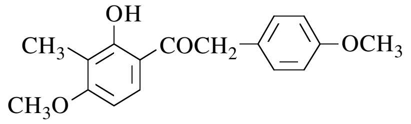
Synthesis

-Preparation by condensation of p-methoxyphenylacetonitrile with 4-ethylresorcinol in the presence of boron trifluoride etherate under hydrogen chloride atmosphere (8-10 h) at r.t. overnight (86%) [786].

m.p. 95-96° [786]; ^{1}H NMR [786].

1-(2-Hydroxy-4-methoxy-3-methylphenyl)-2-(4-methoxyphenyl)ethanone

[39604-65-4] $C_{17}H_{18}O_4$ mol.wt. 286.33



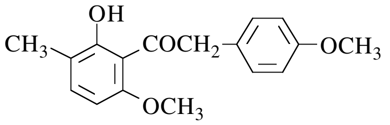
Syntheses

-Preparation by partial methylation of,
*2,4-dihydroxy-3-methylphenyl 4-methoxybenzyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 6 h [594], (86%) [841];
*2,4-dihydroxyphenyl 4-methoxybenzyl ketone with methyl iodide in methanolic potash, first in a bath of ice-salt mixture, then at r.t. overnight and at reflux for 7 h (39%) [594].
-Also refer to: [12].

m.p. 121-122° [841], 116-117° [594].

1-(2-Hydroxy-6-methoxy-3-methylphenyl)-2-(4-methoxyphenyl)ethanone

$C_{17}H_{18}O_4$ mol.wt. 286.33



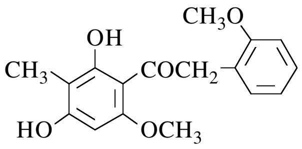
Synthesis

-Obtained by partial methylation of 2,6-dihydroxy-3-methylphenyl 4-methoxybenzyl ketone with dimethyl sulfate in the presence of potassium carbonate in boiling acetone for 1 h (71%) [1534].

oil [1534].

1-(2,4-Dihydroxy-6-methoxy-3-methylphenyl)-2-(2-methoxyphenyl)ethanone

$C_{17}H_{18}O_5$ mol.wt. 302.33



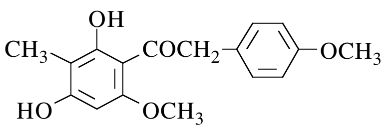
Synthesis

-Obtained by reaction of o-methoxyphenylacetonitrile with 2,6-dihydroxy-4-methoxyyoluene (m.p. 124°) (Hoesch reaction) (36%) [767], (31%) [1531].

m.p. 195° [1531], 194° [767].

1-(2,4-Dihydroxy-6-methoxy-3-methylphenyl)-2-(4-methoxyphenyl)ethanone

[56308-09-9] $C_{17}H_{18}O_5$ mol.wt. 302.33



Syntheses

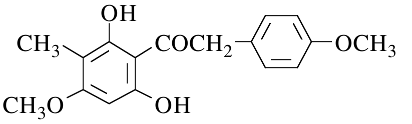
-Obtained by reaction of p-methoxyphenyl-acetonitrile with 2,6-dihydroxy-4-methoxytoluene (m.p. 124°) (Hoesch reaction) [1318], (44%) [1353], (33%) [1531].

-Also refer to: [1419].

m.p. 162-164° [1318], 162° [1531], 125-127° [1353]. One of the reported melting points is obviously wrong.

1-(2,6-Dihydroxy-4-methoxy-3-methylphenyl)-2-(4-methoxyphenyl)ethanone

$C_{17}H_{18}O_5$ mol.wt. 302.33



Syntheses

-Obtained by alkaline hydrolysis of 5-hydroxy-7,4'-dimethoxy-8-methylisoflavone (m.p. 164-166°) with potassium hydroxide in refluxing ethanol for 30 min (31%) [672].

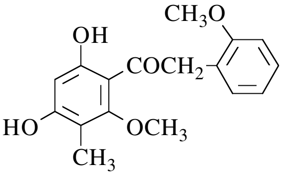
-Also obtained by reaction of p-methoxyphenylacetonitrile with 2,4-dihydroxy-6-methoxytoluene (m.p. 119°) (Hoesch reaction) (41%) [1531].

-Also obtained by alkaline hydrolysis of 5-hydroxy-7,4'-dimethoxy-2,6-dimethylisoflavone (m.p. 198-200°) with 8% alcoholic potassium hydroxide at reflux for 30 min [672].

m.p. 196-197° [672], 192° [1531].

1-(4,6-Dihydroxy-2-methoxy-3-methylphenyl)-2-(2-methoxyphenyl)ethanone

$C_{17}H_{18}O_5$ mol.wt. 302.33



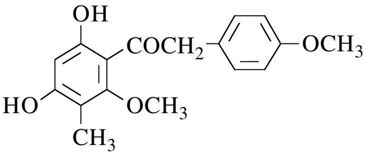
Synthesis

-Obtained by catalytic debenzylation of 4,6-bis(benzyloxy)-2-methoxy-3-methylphenyl 2-methoxybenzyl ketone (m.p. 107°) in acetic acid in the presence of Pd/C for 20 min (quantitative yield) [1532].

m.p. 118° [1532].

1-(4,6-Dihydroxy-2-methoxy-3-methylphenyl)-2-(4-methoxyphenyl)ethanone

$C_{17}H_{18}O_5$ mol.wt. 302.33



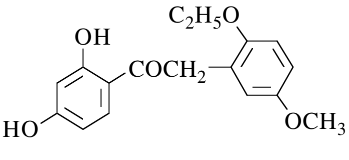
Synthesis

-Obtained by hydrogenolysis of 4,6-bis(benzyloxy)-2-methoxy-3-methylphenyl 4-methoxybenzyl ketone (m.p. 106°) in the presence of Pd/C in acetic acid for 10 min (quantitative yield) [1532].

m.p. 176° [1532].

1-(2,4-Dihydroxyphenyl)-2-(2-ethoxy-5-methoxyphenyl)ethanone

[18086-36-7] $C_{17}H_{18}O_5$ mol.wt. 302.33



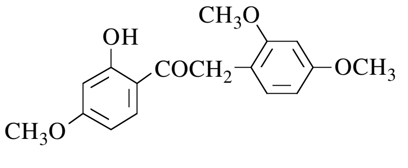
Synthesis

-Obtained by reaction of 2-ethoxy-5-methoxyphenylacetonitrile (m.p. 46-48°) with resorcinol (34%) (Hoesch reaction) [751].

m.p. 114-115° [751].

2-(2,4-Dimethoxyphenyl)-1-(2-hydroxy-4-methoxyphenyl)ethanone

[70779-11-2] $C_{17}H_{18}O_5$ mol.wt. 302.33



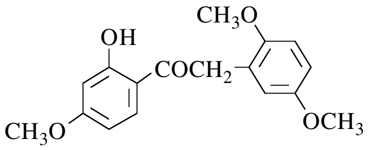
Syntheses

-Preparation by partial methylation of 2,4-dihydroxyphenyl 2,4-dimethoxybenzyl ketone [1145],
*with methyl iodide in the presence of potassium carbonate in boiling acetone for 70 min (95%) [218];
*with diazomethane in ethyl ether for 30 min (quantitative yield) [1384].
-Also refer to: [723] [1140].

m.p. 116° [218], 114-115° [1384]; b.p.$_{0.05}$ 170-180° [1384];
^{1}H NMR [788], UV [1410].

2-(2,5-Dimethoxyphenyl)-1-(2-hydroxy-4-methoxyphenyl)ethanone

[18086-26-5] $C_{17}H_{18}O_5$ mol.wt. 302.33



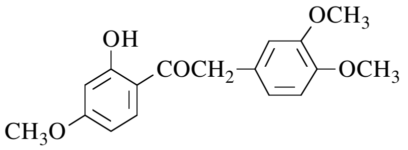
Synthesis

-Preparation by partial methylation of 2,4-dihydroxyphenyl 2,5-dimethoxybenzyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 6 h (92%) [751].

m.p. 113-114° [751]; ^{1}H NMR [788].

2-(3,4-Dimethoxyphenyl)-1-(2-hydroxy-4-methoxyphenyl)ethanone

[53084-05-2] $C_{17}H_{18}O_5$ mol.wt. 302.33



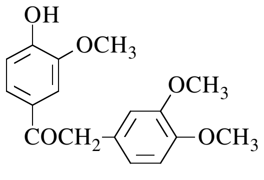
Syntheses

-Preparation by partial methylation of 2,4-dihydroxyphenyl 3,4-dimethoxybenzyl ketone,
*with methyl iodide in the presence of potassium carbonate in boiling acetone for 70 min (86-91%) [218] or for 3 h (81%) [106];
*with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 6 h (69%) [392] or in boiling 10% alcoholic sodium hydroxide for 1 h (31%) [158].
-Also obtained by reaction of 3,4-dimethoxyphenylacetyl chloride with 1,3-dimethoxybenzene in the presence of aluminium chloride in boiling benzene for 1 h (52%) [158].
-Also refer to: [277] [724] [1291] [1419].

m.p. 119° [106] [158], 118° [218], 116-117° [392].

2-(3,4-Dimethoxyphenyl)-1-(4-hydroxy-3-methoxyphenyl)ethanone

[114847-19-7] $C_{17}H_{18}O_5$ mol.wt. 302.33



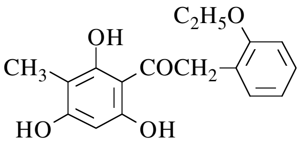
Syntheses

-Preparation by reaction of 3,4-dimethoxyphenylacetic acid with guaiacol in the presence of zinc chloride and phosphorous oxychloride for 24 h at r.t. (40%) [391].
-Also refer to: [273].

m.p. 142-144° [391].

2-(2-Ethoxyphenyl)-1-(2,4,6-trihydroxy-3-methylphenyl)ethanone

$C_{17}H_{18}O_5$ mol.wt. 302.33



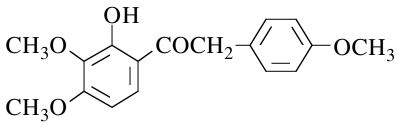
Synthesis

-Obtained by reaction of o-ethoxyphenylacetonitrile with 2-methylphloroglucinol (Hoesch reaction) (11%) [1536].

m.p. 174° [1536].

1-(2-Hydroxy-3,4-dimethoxyphenyl)-2-(4-methoxyphenyl)ethanone

[3606-32-4] $C_{17}H_{18}O_5$ mol.wt. 302.33



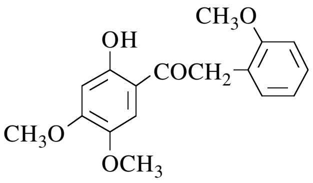
Syntheses

-Obtained by alkaline hydrolysis of *di-O-methylretusin* (7,8,4'-trimethoxyisoflavone) (m.p. 151°) (SM) with 10% aqueous potassium hydroxide in refluxing ethanol for 1 h (67%). SM was obtained by partial methylation of *retusin* (m.p. 249°) (7,8-dihydroxy-4'-methoxyisoflavone), itself isolated from *Dalbergia retusa* heartwood (cocobolo) (Leguminosae) [744].
-Also obtained by Friedel-Crafts reaction of 4-methoxyphenylacetyl chloride with pyrogallol trimethyl ether in the presence of aluminium chloride [759].
-Also refer to: [731] [732] [758].

m.p. 122-123° [744], 121-122° [759]; ^{13}C NMR [732].

1-(2-Hydroxy-4,5-dimethoxyphenyl)-2-(2-methoxyphenyl)ethanone

[24195-30-0] $C_{17}H_{18}O_5$ mol.wt. 302.33



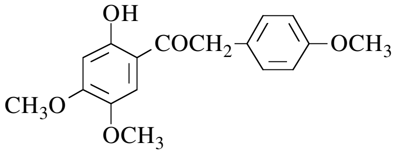
Syntheses

-Obtained by reaction of o-methoxyphenylacetonitrile with 3,4-dimethoxyphenol (Hoesch reaction) [864], (35%) [262].
-Also refer to: [954] [1364].

m.p. 108-109° [262];
IR [262], UV [262], MS [262].

1-(2-Hydroxy-4,5-dimethoxyphenyl)-2-(4-methoxyphenyl)ethanone

[5128-49-4] $C_{17}H_{18}O_5$ mol.wt. 302.33



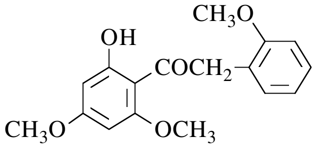
Syntheses

-Preparation by partial methylation of,
*2,4-dihydroxy-5-methoxyphenyl 4-methoxybenzyl ketone with methyl iodide in the presence of potassium carbonate in boiling acetone [1347];
*2,5-dihydroxy-4-methoxyphenyl 4-methoxybenzyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 4 h (80%) [86];
*2,4,5-trihydroxyphenyl 4-methoxybenzyl ketone with excess diazomethane in ethyl ether at r.t. overnight (45%) [530] or with methyl iodide in the presence of potassium carbonate in refluxing acetone for 1.5 h [1347] or according to [701], (86%) [707].
-Also obtained by Friedel-Crafts acylation of 1,2,4-trimethoxybenzene with p-methoxyphenylacetyl chloride in the presence of aluminium chloride in ethyl ether [86].
-Also obtained by reaction of p-methoxyphenylacetonitrile with 3,4-dimethoxyphenol (Hoesch reaction) (25%) [986].
-Also obtained by alkaline degradation of *afromosin 7-methyl ether* (6,7,4'-trimethoxyisoflavone) (SM) (m.p. 178°) [1347], (m.p. 174-175°) [986] with potassium hydroxide in refluxing ethanol [1347] for 40 min under nitrogen (61%) [986]. SM was obtained by methylation of *afromosin* (7-hydroxy-6,4'-dimethoxyisoflavone) (m.p. 228-229°), itself isolated from *Afromosia elata* Harms [986].

m.p. 100-101° [707], 99-100° [86] [986] [1347], 98-100° [530];
^{1}H NMR [707], ^{13}C NMR [732], IR [1347], UV [86] [1347]; TLC [707].

1-(2-Hydroxy-4,6-dimethoxyphenyl)-2-(2-methoxyphenyl)ethanone

[56308-08-8] $C_{17}H_{18}O_5$ mol.wt. 302.33



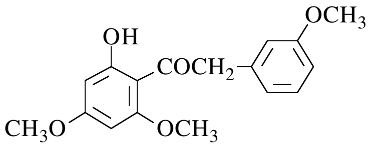
Syntheses

-Preparation by partial methylation of 2,4,6-trihydroxyphenyl 2-methoxybenzyl ketone,
*with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 14 h (86%) [767], for 4 h (70%) [1319] or for 3.5 h (58%) [1531];
*with methyl iodide and of potassium carbonate in refluxing acetone for 4 h (54%) [1320].
-Also obtained by partial methylation of 2-hydroxy-4,6-dimethoxyphenyl 2-hydroxybenzyl ketone (95%) [1530].
-Also refer to: [559] [590] [989] [1419].

m.p. 122° [1531], 116-118° [1319] [1320], 116° [767].

1-(2-Hydroxy-4,6-dimethoxyphenyl)-2-(3-methoxyphenyl)ethanone

[109089-92-1] $C_{17}H_{18}O_5$ mol.wt. 302.33



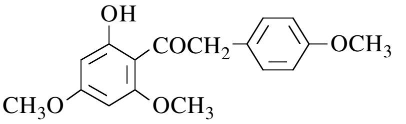
Synthesis

-Preparation by partial methylation of 3-methoxybenzyl 2,4,6-trihydroxyphenyl ketone with dimethyl sulfate in the presence of potassium carbonate in boiling acetone for 3 h (70%) [559].

m.p. 66-67° [559].

1-(2-Hydroxy-4,6-dimethoxyphenyl)-2-(4-methoxyphenyl)ethanone

[39604-68-7] $C_{17}H_{18}O_5$ mol.wt. 302.33



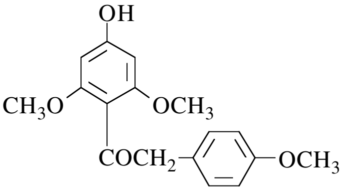
Syntheses

-Preparation by partial methylation of 2,4,6-trihydroxyphenyl 4-methoxybenzyl ketone,
*with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone [771] [1074] [1075], for 3 h (64%) [106];
*with diazomethane in ethyl ether at 0° (80%) [1169] or in methanol [1168];
*with methyl iodide in the presence of potassium carbonate in refluxing acetone for 3 h (42%) [1317].
-Also obtained by reaction of 4-methoxyphenylacetonitrile with phloroglucinol dimethyl ether (Hoesch reaction) [1573], (19%) [1239].
-Also obtained by alkaline degradation of 3-(p-anisoyl)-4,6-dimethoxybenzofuran with potassium hydroxide in refluxing dilute methanol for 1.5 h (78%) [200].
-Also obtained by alkaline hydrolysis of 5,7,4'-trimethoxyisoflavone (m.p. 162-163°) with 1 N aqueous sodium hydroxide in refluxing ethanol for 2 h [221].
-Also refer to: [12] [180] [559] [701] [724] [949] [1001] [1076] [1165] [1364] [1490] [1530].

monohydrate [200];
m.p. 140° [200], 139-140° [1169];
m.p. 89° [106] [1573], 88-89° [221] [1074] [1239] [1317], 86-87° [771]. One of the reported melting points is obviously wrong.
^{1}H NMR [1169], IR [771], UV [771] [1169]; TLC [771], HPLC [1169].

1-(4-Hydroxy-2,6-dimethoxyphenyl)-2-(4-methoxyphenyl)ethanone

[109089-93-2] $C_{17}H_{18}O_5$ mol.wt. 302.33



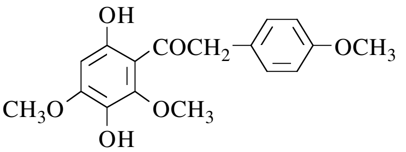
Syntheses

-Obtained by reaction of p-methoxyphenylacetonitrile with phloroglucinol dimethyl ether (Hoesch reaction) [1573].
-Also obtained by saponification of 4-acetoxy-2,6-dimethoxyphenyl 4-methoxybenzyl ketone (m.p. 137°) in ethanol with 3% aqueous sodium hydroxide [1573].
-Also refer to: [1001].

m.p. 73° [1573].

1-(3,6-Dihydroxy-2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)ethanone

$C_{17}H_{18}O_6$ mol.wt. 318.33



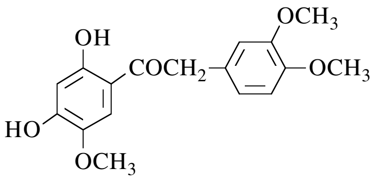
Synthesis

-Obtained (poor yield) by condensation of 2,6-dimethoxyhydroquinone with the complex p-methoxyphenylacetic acid and boron trifluoride in chloroform at r.t. overnight (< 2%) [766].

m.p. 110° [766].

1-(2,4-Dihydroxy-5-methoxyphenyl)-2-(3,4-dimethoxyphenyl)ethanone

[24126-91-8] $C_{17}H_{18}O_6$ mol.wt. 318.33



Syntheses

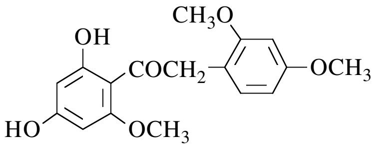
-Obtained by condensation of 3,4-dimethoxyphenylacetonitrile with 4-methoxyresorcinol (Hoesch reaction) (14%) [1330].

-Also obtained by heating *Cladrastin* (7-hydroxy-6,3',4'-trimethoxyisoflavone) (m.p. 206-207°) with 10% aqueous barium hydroxide at reflux for 2 h under nitrogen (62%). *Cladrastin* was isolated from *Cladrastis lutea* (Mich. f.) K. Koch (Leguminosae) [1330].

m.p. 166-167° [1330]; UV [1330], MS [1330].

1-(2,4-Dihydroxy-6-methoxyphenyl)-2-(2,4-dimethoxyphenyl)ethanone

[109091-12-5] $C_{17}H_{18}O_6$ mol.wt. 318.33



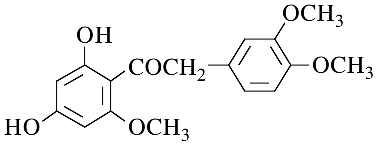
Synthesis

-Preparation by reaction of 2,4-dimethoxyphenylacetonitrile with phloroglucinol monomethyl ether (Hoesch reaction) [559].

m.p. 169-171° [559].

1-(2,4-Dihydroxy-6-methoxyphenyl)-2-(3,4-dimethoxyphenyl)ethanone

[109092-83-3] $C_{17}H_{18}O_6$ mol.wt. 318.33



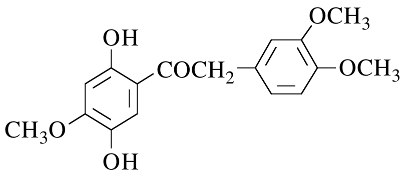
Synthesis

-Obtained by reaction of 3,4-dimethoxyphenylacetonitrile with phloroglucinol monomethyl ether (Hoesch reaction) [559] [1342], (20%) [1239].

m.p. 180° [1239], 179-180° [559], 108-109° [1342]. One of the reported melting points is obviously wrong. IR [1342].

1-(2,5-Dihydroxy-4-methoxyphenyl)-2-(3,4-dimethoxyphenyl)ethanone

[24126-94-1] $C_{17}H_{18}O_6$ mol.wt. 318.33



Syntheses

-Obtained by reaction of 3,4-dimethoxyphenylacetonitrile with methoxyquinol (2-methoxyhydroquinone) (Hoesch reaction) (16%) [1330].

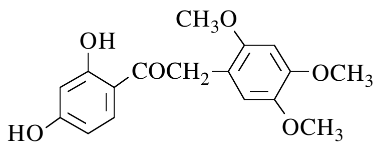
-Also refer to: [246].

m.p. 188-189° [1330];

^{13}C NMR [732], UV [1330], MS [1330].

1-(2,4-Dihydroxyphenyl)-2-(2,4,5-trimethoxyphenyl)ethanone

$C_{17}H_{18}O_6$ mol.wt. 318.33



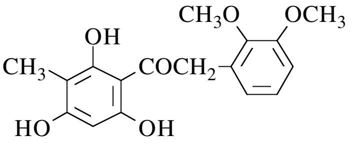
Syntheses

-Obtained by reaction of 2,4,5-trimethoxyphenylacetonitrile with resorcinol (Hoesch reaction) (13%) [536].
-Also obtained by reaction of resorcinol with homoasaronic acid (2,4,5-trimethoxyphenylacetic acid) (m.p. 102-103°),
*in the presence of zinc chloride at 130-140° for 2 h (31%) (Nencki reaction) [536];
*in the presence of phosphorous oxychloride and zinc chloride at 50-60° for 2 h (24%) [536];
*in the presence of polyphosphoric acid on a steam bath for 15 min (46%) [536].

m.p. 201-202° [536].

2-(2,3-Dimethoxyphenyl)-1-(2,4,6-trihydroxy-3-methylphenyl)ethanone

$C_{17}H_{18}O_6$ mol.wt. 318.33



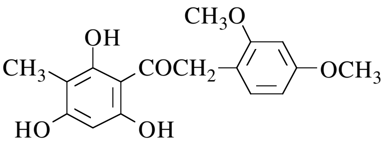
Synthesis

-Obtained by reaction of 2,3-dimethoxyphenylacetonitrile with 2-methylphloroglucinol (Hoesch reaction) (47%) [1536].

m.p. 201° [1536].

2-(2,4-Dimethoxyphenyl)-1-(2,4,6-trihydroxy-3-methylphenyl)ethanone

$C_{17}H_{18}O_6$ mol.wt. 318.33



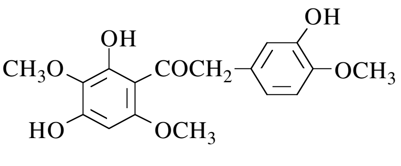
Syntheses

-Obtained by reaction of 2,4-dimethoxyphenylacetonitrile with 2-methylphloroglucinol (Hoesch reaction) (56%) [125].
-Also refer to: [465].

m.p. 188-189° [125]; UV [125].

1-(2,4-Dihydroxy-3,6-dimethoxyphenyl)-2-(3-hydroxy-4-methoxyphenyl)ethanone

[64640-60-4] $C_{17}H_{18}O_7$ mol.wt. 334.33



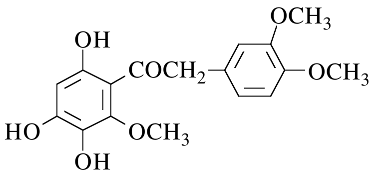
Synthesis

-Preparation by reaction of 3-(benzyloxy)-4-methoxyphenylacetonitrile with 1,3-(dibenzyloxy)-2,5-dimethoxybenzene (Hoesch reaction) [1341], (61%) [843].

m.p. 278-279° [843], 277-279° [1341]; ^1H NMR [843], IR [1341], UV [843].

2-(3,4-Dimethoxyphenyl)-1-(3,4,6-trihydroxy-2-methoxyphenyl)ethanone

[129207-80-3] $C_{17}H_{18}O_7$ mol.wt. 334.33



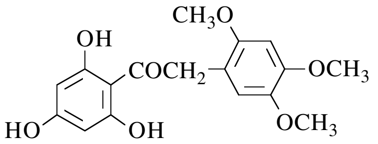
Synthesis

-Obtained by reaction of potassium persulfate with 2,4-dihydroxy-6-methoxyphenyl 3,4-dimethoxybenzyl ketone in 40% aqueous potassium hydroxide at r.t. overnight (Elbs reaction) [1342].

m.p. 135-137° [1342].

1-(2,4,6-Trihydroxyphenyl)-2-(2,4,5-trimethoxyphenyl)ethanone

[72545-40-5] $C_{17}H_{18}O_7$ mol.wt. 334.33



Synthesis

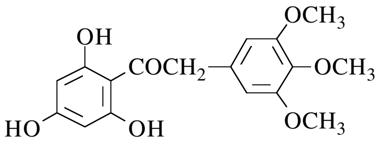
-Obtained by reaction of 2,4,5-trimethoxyphenylacetonitrile with phloroglucinol (Hoesch reaction) [839], (40%) [582].

N.B.: The phloroglucinol could not be condensed with 2,4,5-trimethoxyphenylacetyl chloride in the presence of aluminium chloride [496] [582].

m.p. 208-209° [582].

1-(2,4,6-Trihydroxyphenyl)-2-(3,4,5-trimethoxyphenyl)ethanone

[79744-61-9] $C_{17}H_{18}O_7$ mol.wt. 334.33



Syntheses

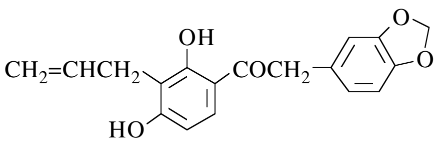
-Preparation by reaction of 3,4,5-trimethoxyphenylacetonitrile with phloroglucinol in ethyl ether (63%) (Hoesch reaction) [208].

-Also refer to: [246].

m.p. 197-198° [208]; ^{1}H NMR [208], ^{13}C NMR [732], IR [208], MS [208].

2-(1,3-Benzodioxol-5-yl)-1-[2,4-dihydroxy-3-(2-propenyl)phenyl]ethanone

[117951-99-2] $C_{18}H_{16}O_5$ mol.wt. 312.32



Syntheses

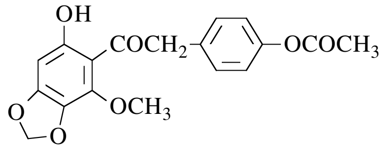
-Obtained by reaction of allyl bromide with 2,4-dihydroxy-3',4'-methylenedioxydesoxybenzoin in the presence of methanolic potassium hydroxide (16%) [711].

-Also refer to: [1140].

m.p. 121-122° [711]; ^{1}H NMR [711], IR [711], UV [711].

2-[4-(Acetyloxy)phenyl]-1-(6-hydroxy-4-methoxy-1,3-benzodioxol-5-yl)ethanone

$C_{18}H_{16}O_7$ mol.wt. 344.32



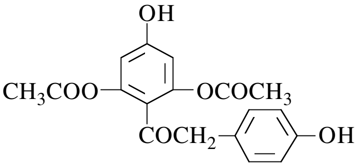
Synthesis

-Obtained by reaction of acetic anhydride with 4'-hydroxybenzyl 2-hydroxy-4,5-methylenedioxy-6-methoxyphenyl ketone in pyridine at r.t. for 1 h [573].

m.p. 162-163° [573].

1-[2,6-Bis(acetyloxy)-4-hydroxyphenyl]-2-(4-hydroxyphenyl)ethanone

[147747-31-5] $C_{18}H_{16}O_7$ mol.wt. 344.32



Syntheses

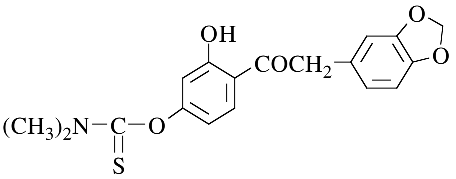
-Obtained (poor yields) by regioselective enzyme-catalyzed deacetylation of 4-acetoxybenzyl 2,4,6-triacetoxyphenyl ketone in the dry organic solvents hereafter mentioned containing n-butanol with lipase at 42-45° [1146].

lipase	solvent	time (h)	yields (%)
PPL	THF/n-BuOH	45	15
CCL	DIPE/n-BuOH	46	15

PPL = porcine pancreas lipase; CCL = candida cylindracea lipase; DIPE = diisopropyl ether.

O-[4-(1,3-Benzodioxol-5-ylacetyl)-3-hydroxyphenyl] dimethylcarbamothioate

[142751-39-1] $C_{18}H_{17}NO_5S$ mol.wt. 359.40



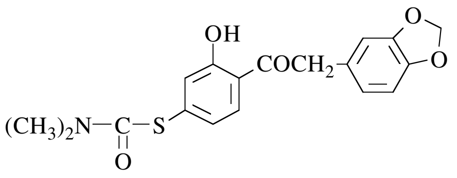
Synthesis

-Obtained by stirring a mixture of 2-(1,3-benzodioxol-5-yl)-1-(2,4-dihydroxyphenyl)ethanone (1 mol), dimethylthiocarbamoyl chloride (2 mol), 1,4-diazabicyclo[2,2,2]octane and N,N-dimethylformamide at r.t. for 2 h (92%) [907].

m.p. 168-169° [907]; ^{1}H NMR [907], MS [907].

S-[4-(1,3-Benzodioxol-5-ylacetyl)-3-hydroxyphenyl] dimethylcarbamothioate

[142751-43-7] $C_{18}H_{17}NO_5S$ mol.wt. 359.40



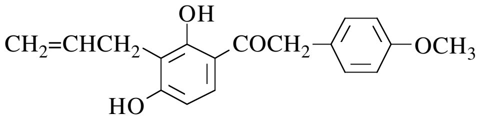
Synthesis

-Obtained by refluxing a solution of O-[4-(1,3-Benzodioxol-5-ylacetyl)-3-hydroxyphenyl] dimethylcarbamothioate [142751-39-1] in N,N-dimethylaniline for 1 h (91%) (Newman-Kwart rearrangement) [907].

m.p. 160-161° [907]; ^{1}H NMR [907], MS [907].

1-[2,4-Dihydroxy-3-(2-propenyl)phenyl]-2-(4-methoxyphenyl)ethanone

[117951-88-9] $C_{18}H_{18}O_4$ mol.wt. 298.34



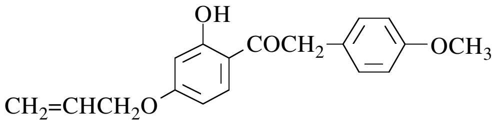
Syntheses

-Obtained by reaction of allyl bromide with 2,4-dihydroxy-4'-methoxydesoxybenzoin in methanolic potassium hydroxide at r.t. overnight (27%) [711].
-Also refer to: [1140].

m.p. 97-98° [711]; ^{1}H NMR [711], IR [711], UV [711].

1-[2-Hydroxy-4-(2-propenyloxy)phenyl]-2-(4-methoxyphenyl)ethanone

[73937-48-1] $C_{18}H_{18}O_4$ mol.wt. 298.34

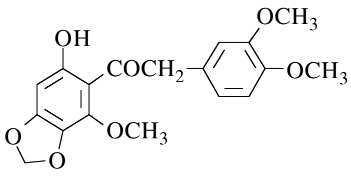


Syntheses

-Refer to: [1258] and [1328] (compound X).

2-(3,4-Dimethoxyphenyl)-1-(6-hydroxy-4-methoxy-1,3-benzodioxol-5-yl)ethanone

[2631-85-8] $C_{18}H_{18}O_7$ mol.wt. 346.34



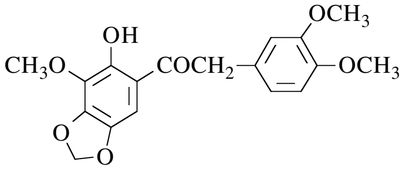
Syntheses

-Obtained by reaction of methylene iodide with 2,4,5-trihydroxy-6-methoxyphenyl 3,4-dimethoxybenzyl ketone in the presence of potassium carbonate in refluxing acetone for 45 h [1342].
-Also obtained (poor yield) by reaction of 3,4-dimethoxyphenylacetonitrile with 3-methoxy-4,5-methylenedioxyphenol (Hoesch reaction) (< 2%) [533].

m.p. 125-126° [1342], 121°5-122° [533]; UV [533].

2-(3,4-Dimethoxyphenyl)-1-(6-hydroxy-7-methoxy-1,3-benzodioxol-5-yl)ethanone

[61243-79-6] $C_{18}H_{18}O_7$ mol.wt. 346.34



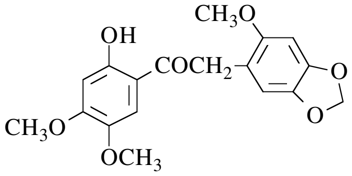
Synthesis

-Obtained by mild base hydrolysis of 8,3',4'-trimethoxy-6,7-methylenedioxyisoflavone [615].

m.p. 162-163° [615];
^{1}H NMR [615], IR [615], UV [615], MS [615]; TLC [615].

1-(2-Hydroxy-4,5-dimethoxyphenyl)-2-(6-methoxy-1,3-benzodioxol-5-yl)ethanone

[24195-24-2] $C_{18}H_{18}O_7$ mol.wt. 346.34



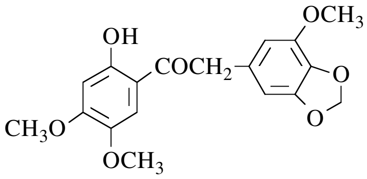
Synthesis

-Obtained by alkaline degradation of 6,7,2'-trimethoxy-4',5'-methylenedioxyisoflavone (m.p. 234°5-235°5) (SM) with sodium hydroxide in refluxing 50% aqueous ethanol (10-45 min) (88%). SM was isolated from the heartwood of *Cordyla africana* (Leguminosae, sub-family: Caesalpinioideae, tribe: Swartzieae) [262].

m.p. 161-162° [262]; IR [262], UV [262], MS [262].

1-(2-Hydroxy-4,5-dimethoxyphenyl)-2-(7-methoxy-1,3-benzodioxol-5-yl)ethanone

[24195-23-1] $C_{18}H_{18}O_7$ mol.wt. 346.34



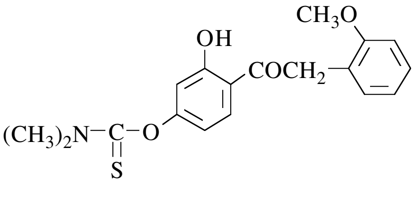
Synthesis

-Obtained by alkaline degradation of 6,7,3'-trimethoxy-4',5'-methylenedioxyisoflavone (m.p. 211-212°) (SM) with sodium hydroxide in refluxing 50% aqueous ethanol (10-45 min) (28%). SM was isolated from the heartwood of *Cordyla africana* (Leguminosae, sub-family: Caesalpinioideae, tribe: Swartzieae) [262].

m.p. 143-144° [262]; IR [262], UV [262], MS [262].

O-[3-Hydroxy-4-[(2-methoxyphenyl)acetyl]phenyl] dimethylcarbamothioate

[142751-37-9] $C_{18}H_{19}NO_4S$ mol.wt. 345.42



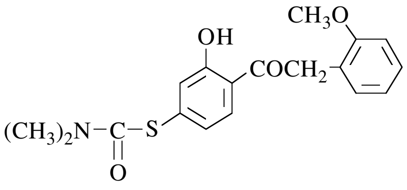
Synthesis

-Obtained by stirring a mixture of 2,4-dihydroxyphenyl 2-methoxybenzyl ketone (1 mol), dimethylthiocarbamoyl chloride (2 mol), 1,4-diazabicyclo[2,2,2]octane and DMF at r.t. for 2 h (91%) [907].

m.p. 168-169° [907];
^{1}H NMR [907], MS [907].

S-[3-Hydroxy-4-[(2-methoxyphenyl)acetyl]phenyl] dimethylcarbamothioate

[142751-41-5] $C_{18}H_{19}NO_4S$ mol.wt. 345.42



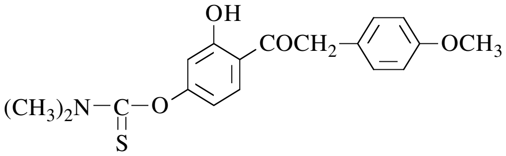
Synthesis

-Obtained by refluxing a solution of O-[3-Hydroxy-4-[(2-methoxyphenyl)acetyl]-phenyl] dimethylcarbamothioate [142751-37-9] in N,N-dimethylaniline for 1 h (89%) (Newman-Kwart rearrangement) [907].

m.p. 107-108° [907]; ¹H NMR [907], MS [907].

O-[3-Hydroxy-4-[(4-methoxyphenyl)acetyl]phenyl] dimethylcarbamothioate

[142751-38-0] $C_{18}H_{19}NO_4S$ mol.wt. 345.42



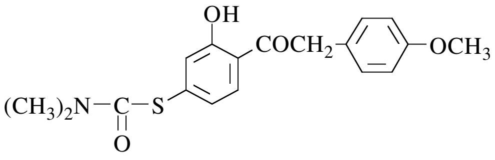
Synthesis

-Obtained by stirring a mixture of 2,4-dihydroxyphenyl 4-methoxybenzyl ketone (1 mol), dimethylthiocarbamoyl chloride (2 mol), 1,4-diazabicyclo[2,2,2] octane (2 mol) and N,N-dimethyl-formamide at r.t. for 2 h (96%) [907].

m.p. 114-115° [907]; ¹H NMR [907], MS [907].

S-[3-Hydroxy-4-[(4-methoxyphenyl)acetyl]phenyl] dimethylcarbamothioate

[142751-42-6] $C_{18}H_{19}NO_4S$ mol.wt. 345.42



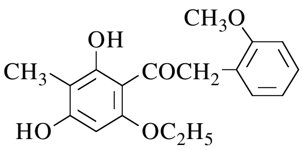
Synthesis

-Obtained by refluxing a solution of O-[3-Hydroxy-4-[(4-methoxyphenyl)-acetyl]phenyl] dimethylcarbamothioate [142751-38-0] in N,N-dimethylaniline for 1 h (92%) (Newman-Kwart rearrangement) [907].

m.p. 130-131° [907]; ¹H NMR [907], MS [907].

1-(6-Ethoxy-2,4-dihydroxy-3-methylphenyl)-2-(2-methoxyphenyl)ethanone

$C_{18}H_{20}O_5$ mol.wt. 316.35



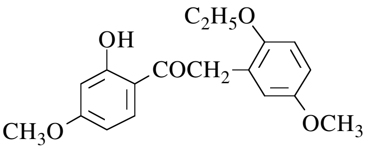
Synthesis

-Obtained by reaction of o-methoxyphenylacetonitrile with 4-ethoxy-2,6-dihydroxytoluene (Hoesch reaction) (32%) [1536].

m.p. 185° [1536].

2-(2-Ethoxy-5-methoxyphenyl)-1-(2-hydroxy-4-methoxyphenyl)ethanone

[18086-37-8] $C_{18}H_{20}O_5$ mol.wt. 316.35



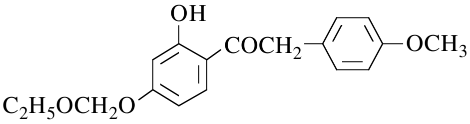
Synthesis

-Obtained by partial methylation of 2,4-dihydroxyphenyl 2-ethoxy-5-methoxybenzyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 6 h (87%) [751].

m.p. 107-108° [751].

1-[4-(Ethoxymethoxy)-2-hydroxyphenyl]-2-(4-methoxyphenyl)ethanone

[97714-80-2] $C_{18}H_{20}O_5$ mol.wt. 316.35



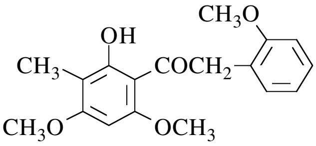
Syntheses

-Obtained by reaction of chloromethyl ethyl ether with 2,4-dihydroxyphenyl 4-methoxybenzyl ketone in acetone in the presence of potassium carbonate at r.t. for 15-45 min [710].

-Also refer to: [701].

1-(2-Hydroxy-4,6-dimethoxy-3-methylphenyl)-2-(2-methoxyphenyl)ethanone

$C_{18}H_{20}O_5$ mol.wt. 316.35



Syntheses

-Preparation by partial methylation of 2,4-dihydroxy-6-methoxy-3-methylphenyl 2-methoxybenzyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone (quantitative yield) [1531], for 14 h (89%) [767].

-Also obtained by partial methylation of 2,4,6-trihydroxy-3-methylphenyl 2-methoxybenzyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 4 h (82%) [989] or for 3 h (66%) [1531].

-Also obtained (by-product) by partial methylation of 2,4,6-trihydroxyphenyl 2-methoxybenzyl ketone with methyl iodide in the presence of potassium carbonate in refluxing acetone for 4 h (11%) [1320].

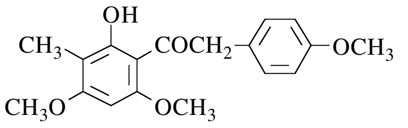
-Also obtained by reaction of o-methoxyphenylacetonitrile with 2-hydroxy-4,6-dimethoxytoluene (m.p. 67°) (Hoesch reaction) (38%) [1531].

-Also refer to: [590].

m.p. 150° [767], 148° [1531], 146-148° [989] [1320].

1-(2-Hydroxy-4,6-dimethoxy-3-methylphenyl)-2-(4-methoxyphenyl)ethanone

[56308-12-4] $C_{18}H_{20}O_5$ mol.wt. 316.35



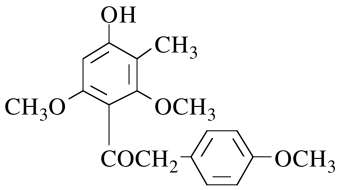
Syntheses

-Obtained by partial methylation of 2,4,6-trihydroxy-3-methylphenyl 4-methoxybenzyl ketone,
*with dimethyl sulfate in the presence of potassium carbonate in boiling acetone for 4 h (73%) [1317] or for 3 h (68%) [1531];
*with excess methyl iodide in the presence of potassium carbonate in boiling acetone for 4 h [1317].
-Also obtained by reaction of methyl iodide with 2,4,6-trihydroxyphenyl 4-methoxybenzyl ketone in the presence of potassium carbonate in refluxing acetone for 3 h (13%) [1317].
-Also obtained by partial methylation of 2,4-dihydroxy-6-methoxy-3-methylphenyl 4-methoxybenzyl ketone with methyl iodide in the presence of potassium carbonate in boiling acetone [1531] for 2 h (96%) [1317].
-Also obtained by partial methylation of 2,6-dihydroxy-4-methoxy-3-methylphenyl 4-methoxybenzyl ketone with dimethyl sulfate with of potassium carbonate in boiling acetone [1531].
-Also obtained by partial methylation of 2,4-dihydroxy-6-methoxy-3-methylphenyl 4-hydroxybenzyl ketone with dimethyl sulfate with potassium carbonate in boiling acetone [1531].
-Also obtained by reaction of p-methoxyphenylacetonitrile with 2-hydroxy-4,6-dimethoxytoluene (m.p. 67°) (Hoesch reaction) (38%) [1531].
-Also refer to: [988] [1419].

m.p. 116° [1531], 114-115° [1317] [1318].

1-(4-Hydroxy-2,6-dimethoxy-3-methylphenyl)-2-(4-methoxyphenyl)ethanone

$C_{18}H_{20}O_5$ mol.wt. 316.35

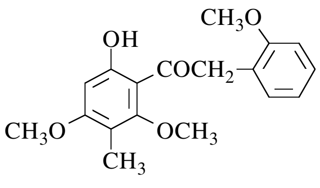


Synthesis

-Obtained (by-product) by reaction of p-methoxyphenylacetonitrile with 2-hydroxy-4,6-dimethoxytoluene (Hoesch reaction) (small amounts) [1531].

1-(6-Hydroxy-2,4-dimethoxy-3-methylphenyl)-2-(2-methoxyphenyl)ethanone

$C_{18}H_{20}O_5$ mol.wt. 316.35



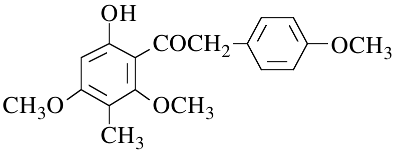
Syntheses

-Obtained by partial methylation of 4,6-dihydroxy-2-methoxy-3-methylphenyl 2-methoxybenzyl ketone with methyl iodide in the presence of potassium carbonate in boiling acetone for 30 min (96%) [1532].
-Preparation by alkaline degradation of 5,7,2'-trimethoxy-6-methylisoflavone (m.p. 220°) with sodium hydroxide in refluxing dilute methanol for 1.5 h (74%) [1536].
-Also refer to: [1076].

m.p. 134° [1536].

1-(6-Hydroxy-2,4-dimethoxy-3-methylphenyl)-2-(4-methoxyphenyl)ethanone

[22081-01-2] $C_{18}H_{20}O_5$ mol.wt. 316.35



Syntheses

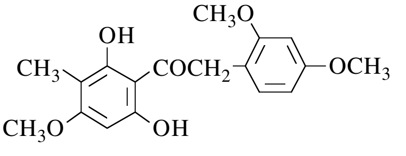
-Obtained by partial methylation of 4,6-dihydroxy-2-methoxy-3-methylphenyl 4-methoxybenzyl ketone with excess methyl iodide in the presence of potassium carbonate in boiling acetone for 1.5 h (96%) [1532].

-Also obtained by reaction of p-methoxyphenylacetyl chloride with 4-hydroxy-2,6-dimethoxytoluene in ethyl ether in the presence of aluminium chloride (18%) [717].

m.p. 88° [1532], 87-88° [717];
^{1}H NMR [788], IR [717]; TLC [717].

1-(2,6-Dihydroxy-4-methoxy-3-methylphenyl)-2-(2,4-dimethoxyphenyl)ethanone

$C_{18}H_{20}O_6$ mol.wt. 332.35



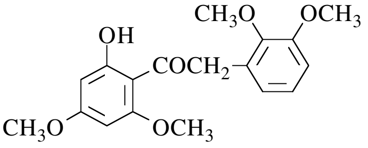
Synthesis

-Obtained by alkaline degradation of *dehydro-ougenin dimethyl ether acetate* (5-acetoxy-6-methyl-7,2',4'-trimethoxyisoflavanone) (m.p. 216-217°) with refluxing alcoholic potash for 2 h (83%) [125].

m.p. 174-175° [125]; UV [125].

2-(2,3-Dimethoxyphenyl)-1-(2-hydroxy-4,6-dimethoxyphenyl)ethanone

$C_{18}H_{20}O_6$ mol.wt. 332.35



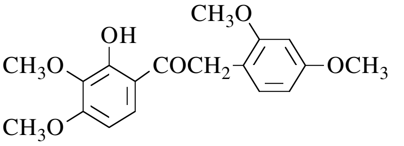
Synthesis

-Preparation by partial methylation of 2,4,6-trihydroxy-2',3'-dimethoxydeoxybenzoin with dimethyl sulfate in the presence of potassium carbonate in boiling acetone (92%) [1536].

m.p. 132° [1536].

2-(2,4-Dimethoxyphenyl)-1-(2-hydroxy-3,4-dimethoxyphenyl)ethanone

[6502-87-0] $C_{18}H_{20}O_6$ mol.wt. 332.35



Syntheses

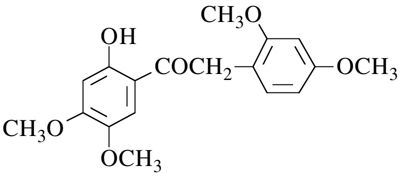
-Preparation by partial methylation of 2,3,4-trihydroxyphenyl 2,4-dimethoxybenzyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 6 h (82%) [754].

-Also obtained by Friedel-Crafts acylation of pyrogallol trimethyl ether with 2,4-dimethoxyphenylacetyl chloride [750], (41%) [754].
-Also refer to: [753].

m.p. 134-135° [750] [754]; ^{1}H NMR [788].

2-(2,4-Dimethoxyphenyl)-1-(2-hydroxy-4,5-dimethoxyphenyl)ethanone

[15402-24-1] $C_{18}H_{20}O_6$ mol.wt. 332.35



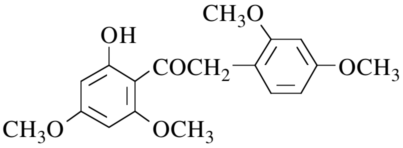
Syntheses

-Preparation by Hoesch condensations of 1,2,4-trihydroxybenzene with 2,4-dimethoxyphenylacetonitrile or with 2,4-dihydroxyphenylacetonitrile, followed by partial methylations of the ketones so obtained [1145].
-Also obtained by Friedel-Crafts acylation of 1,2,4-trimethoxybenzene with 2,4-dimethoxyphenylacetyl chloride in the presence of aluminium chloride [753] in ethyl ether [864], (31%) [752].
-Also refer to: [1140].

m.p. 122-123° [752] [753].

2-(2,4-Dimethoxyphenyl)-1-(2-hydroxy-4,6-dimethoxyphenyl)ethanone *(Albizoin)*

[39604-69-8] $C_{18}H_{20}O_6$ mol.wt. 332.35



Syntheses

-Preparation by partial methylation of 2,4-dimethoxybenzyl 2,4,6-trihydroxyphenyl ketone with dimethyl sulfate in the presence of potassium carbonate in boiling acetone [559], (92%) [583].
-Preparation by partial demethylation of 2,4-dimethoxybenzyl 2,4,6-trimethoxyphenyl ketone with aluminium chloride in refluxing ethyl ether for 10 h (65%) [799].
-Also obtained by alkaline degradation of 5,7,2',4'-tetramethoxyisoflavone (m.p. 203-204°) with potassium hydroxide in refluxing dilute ethanol for 1 h (93%) [799].
-Also obtained by alkaline degradation of *ferreirin* trimethyl ether (m.p. 163°) [799], so called *dihydrodalbergioidin tetramethyl ether* (m.p. 165-166°) [125], (5,7,2',4'-tetramethoxyisoflavanone) with potassium hydroxide in refluxing dilute ethanol for 1 h (21%) [799] or for 6 h (26%) [125].
-Also obtained by Friedel-Crafts acylation of 1,3,5-trimethoxybenzene with 2,4-dimethoxyphenylacetyl chloride in the presence of aluminium chloride in ethyl ether at 0° for 16 h [1278].
-Also refer to: [12] [723] [1140] [1495] [1536].

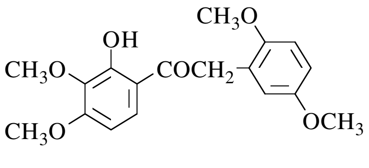
Isolation from natural sources

-From the marine mollusc *Nerita albicilla* (Class Gastropoda, family Neritidae) [1278].

m.p. 140-142° [1278], 139° [799], 138-139° [125], 137-138° [583], 136-137° [559];
^{1}H NMR [788] [1278], IR [125] [1278], UV [125] [1278], MS [1278];
HPLC [1278].

2-(2,5-Dimethoxyphenyl)-1-(2-hydroxy-3,4-dimethoxyphenyl)ethanone

[20569-19-1] $C_{18}H_{20}O_6$ mol.wt. 332.35



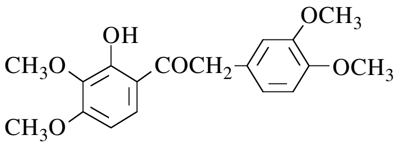
Synthesis

-Obtained by Friedel-Crafts acylation of pyrogallol trimethyl ether with 2,5-dimethoxyphenylacetyl chloride in the presence of aluminium chloride in ethyl ether at 0° overnight (39%) [752].

m.p. 153-154° [752].

2-(3,4-Dimethoxyphenyl)-1-(2-hydroxy-3,4-dimethoxyphenyl)ethanone

[61243-86-5] $C_{18}H_{20}O_6$ mol.wt. 332.35



Syntheses

-Obtained by partial methylation of 2,3,4-trihydroxyphenyl 3,4-dimethoxybenzyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 6 h (82%) [848].

-Also obtained by Friedel-Crafts acylation of pyrogallol trimethyl ether with 3,4-dimethoxyphenylacetyl chloride (homoveratroyl chloride) in ethyl ether in the presence of aluminium chloride, first at 0°, then at r.t. overnight (33-34%) [289] [848] or in refluxing methylene chloride for 2.5 h (70%) [408] [1507].

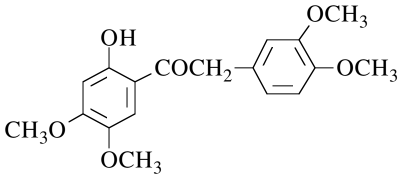
-Obtained by partial demethylation of 2,3,4-trimethoxyphenyl 3',4'-dimethoxybenzyl ketone (oil) with aluminium chloride in refluxing ethyl ether for 1 h (67%) [615].

-Also refer to: [1283].

m.p. 139-140° [1507], 135-137° [615], 134° [848], 133-134° [289], ^1H NMR [1507], IR [1507].

2-(3,4-Dimethoxyphenyl)-1-(2-hydroxy-4,5-dimethoxyphenyl)ethanone

[24195-22-0] $C_{18}H_{20}O_6$ mol.wt. 332.35



Syntheses

-Obtained by alkaline degradation of 6,7,3',4'-tetramethoxyisoflavone (m.p. 187-188°) (SM) with sodium hydroxide in refluxing 50% aqueous ethanol (45%) [262]. SM was isolated from the heartwood of *Cordyla africana* (Leguminosae).

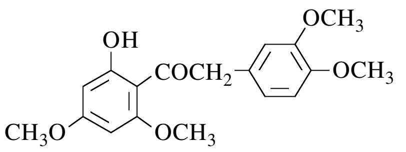
-Also obtained by partial demethylation of 3,4-dimethoxybenzyl 2,4,5-trimethoxyphenyl ketone (m.p. 120-121°) with aluminium chloride in refluxing acetonitrile for 45 min (10%) [262].

-Also obtained by partial methylation of 3,4-dimethoxybenzyl 2,4,5-trihydroxyphenyl ketone (85%) [707] according to [701].

m.p. 138-139° [707], 137-138° [262];
^1H NMR [788], ^{13}C NMR [732], IR [262], UV [262], MS [262]; TLC [707].

2-(3,4-Dimethoxyphenyl)-1-(2-hydroxy-4,6-dimethoxyphenyl)ethanone

[109250-71-7] $C_{18}H_{20}O_6$ mol.wt. 332.35



Syntheses

-Preparation by partial methylation of 2,4-dihydroxy-6,3',4'-trimethoxydeoxybenzoin with methyl iodide in the presence of potassium carbonate in boiling acetone for 1 h (80%) [1239].

-Also obtained by partial methylation of 2,4,6-trihydroxy-3',4'-dimethoxydeoxybenzoin with dimethyl sulfate in the presence of potassium carbonate in boiling acetone [771], (80%) [559], for 3 h [106] or for 10 h [1073].

-Also obtained by hydrolysis of *O-trimethylsantal* (5,7,3',4'-tetramethoxyisoflavone) (m.p. 155-156°) with potassium hydroxide in boiling dilute ethanol for 1 h (82%) [1239].

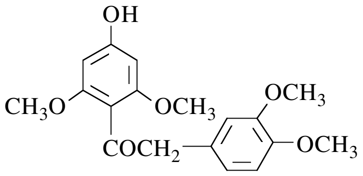
-Also obtained by reaction of 3,4-dimethoxyphenylacetonitrile with phloroglucinol dimethyl ether (Hoesch reaction) (12%) [1239].

-Also refer to: [1076] [1530].

m.p. 120-121° [1073], 117°5 [771], 117° [106] [1239], 101-103° [559];
One of the reported melting points is obviously wrong.
IR [771], UV [771]; TLC [771].

2-(3,4-Dimethoxyphenyl)-1-(4-hydroxy-2,6-dimethoxyphenyl)ethanone

$C_{18}H_{20}O_6$ mol.wt. 332.35



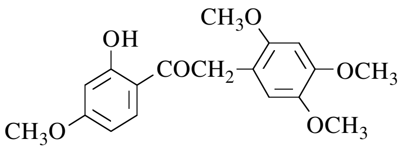
Synthesis

-Obtained (by-product) by reaction of 3,4-dimethoxyphenylacetonitrile with phloroglucinol dimethyl ether (Hoesch reaction) (< 3%) [1239].

m.p. 140° [1239].

1-(2-Hydroxy-4-methoxyphenyl)-2-(2,4,5-trimethoxyphenyl)ethanone

[85288-48-8] $C_{18}H_{20}O_6$ mol.wt. 332.35



Syntheses

-Obtained by partial methylation of 2,4-dihydroxyphenyl 2,4,5-trimethoxybenzyl ketone in acetone,

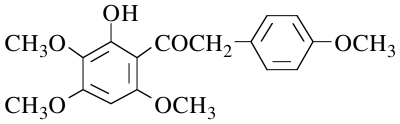
*with an etheral solution of diazomethane (96%) [536];

*with methyl iodide in the presence of potassium carbonate in refluxing acetone for 70 min (96%) [536].

m.p. 135-136° [536]; ^{1}H NMR [788].

1-(2-Hydroxy-3,4,6-trimethoxyphenyl)-2-(4-methoxyphenyl)ethanone

[13539-22-5] $C_{18}H_{20}O_6$ mol.wt. 332.35



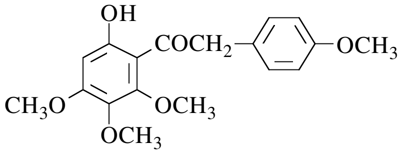
Synthesis

-Refer to: [788] (compound XII).

^{1}H NMR [788].

1-(6-Hydroxy-2,3,4-trimethoxyphenyl)-2-(4-methoxyphenyl)ethanone

[22110-04-9] $C_{18}H_{20}O_6$ mol.wt. 332.35



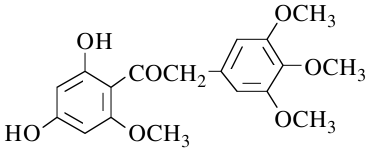
Syntheses

-Preparation by acylation of antiarol,
*with p-methoxyphenylacetyl chloride in ethyl ether in the presence of aluminium chloride at r.t. for 12 h (28%) [842] or for 24 h (55%) [601];
*with p-methoxyphenylacetic acid in chloroform in the presence of boron trifluoride at r.t. overnight (37%) [766].
-Also obtained by alkaline hydrolysis of *munigin* dimethyl ether (m.p. 176°) (5,6,7,4'-tetramethoxyisoflavone) with potassium hydroxide in refluxing ethanol for 30 min (84%) [802].

m.p. 91-92° [842], 73° [802], 69° [601] [766].
One of the reported melting points is obviously wrong.
b.p.$_1$ 190-200° [802], b.p.$_4$ 207-222° [601], b.p.$_2$ 210-220° [766].

1-(2,4-Dihydroxy-6-methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)ethanone

[129207-78-9] $C_{18}H_{20}O_7$ mol.wt. 348.35



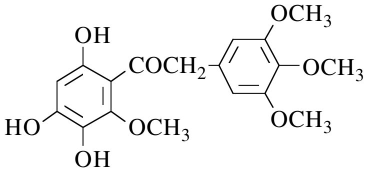
Synthesis

-Obtained by reaction of 3,4,5-trimethoxyphenylacetonitrile with phloroglucinol monomethyl ether (Hoesch reaction) [1342].

m.p. 130-131° [1342]; IR [1342].

1-(3,4,6-Trihydroxy-2-methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)ethanone

[129207-79-0] $C_{18}H_{20}O_8$ mol.wt. 364.35



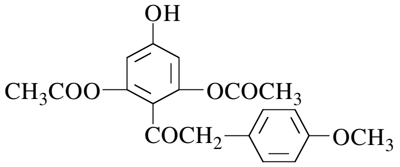
Synthesis

-Obtained by reaction of potassium persulfate with 2,4-dihydroxy-6-methoxyphenyl 3,4,5-trimethoxybenzyl ketone in 40% aqueous potassium hydroxide at r.t. overnight (Elbs reaction) (21%) [1342].

m.p. 164-165° [1342].

1-[2,6-Bis(acetyloxy)-4-hydroxyphenyl]-2-(4-methoxyphenyl)ethanone

[204068-63-3] $C_{19}H_{18}O_7$ mol.wt. 358.35

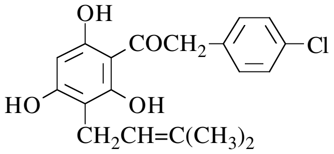


Synthesis

-Obtained (small amount) by selective deacetylation of 1-acetoxy-1-(2,4,6-triacetoxyphenyl)-2-(4-methoxyphenyl)ethene catalyzed by porcine pancreas lipase in THF at 42-45° for 72 h [1145].

2-(4-Chlorophenyl)-1-[2,4,6-trihydroxy-3-(3-methyl-2-butenyl)phenyl]ethanone

[85602-22-8] $C_{19}H_{19}ClO_4$ mol.wt. 346.81



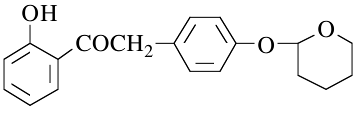
Synthesis

-Preparation by reaction of prenyl chloride with 2-(4-chlorophenyl)-1-(2,4,6-trihydroxyphenyl)-ethanone in ethyl ether in the presence of a saturated aqueous sodium carbonate solution and a catalytic amount of cuprous chloride for 3 h at r.t. (45%) [376].

m.p. 182-184° [376]; ^{13}C NMR [376], IR [376], MS [376].

1-(2-Hydroxyphenyl)-2-[4-[(tetrahydro-2*H*-pyran-2-yl)oxy]phenyl]ethanone

[130064-19-6] $C_{19}H_{20}O_4$ mol.wt. 312.37



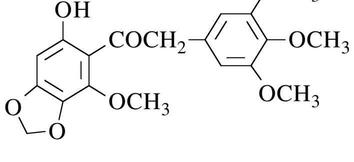
Synthesis

-Preparation by reaction of 3,4-dihydro-2*H*-pyran with 2,4'-dihydroxydeoxybenzoin in dioxane in the presence of PTSA (p-toluenesulfonic acid) at r.t. for 4 h (80%) [1335].

m.p. 95° [1335]; ^{1}H NMR [1335], IR [1335], MS [1335].

1-(6-Hydroxy-4-methoxy-1,3-benzodioxol-5-yl)-2-(3,4,5-trimethoxyphenyl)ethanone

[50901-33-2] $C_{19}H_{20}O_8$ mol.wt. 376.38



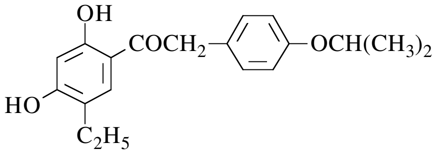
Synthesis

-Obtained by reaction of methylene iodide with 2,4,5-trihydroxy-6-methoxyphenyl 3,4,5-trimethoxybenzyl ketone in the presence of potassium carbonate in refluxing acetone for 50 h [1342].

m.p. 119-120° [1342].

1-(5-Ethyl-2,4-dihydroxyphenyl)-2-[4-(1-methylethoxy)phenyl]ethanone

[96644-04-1] $C_{19}H_{22}O_4$ mol.wt. 314.38



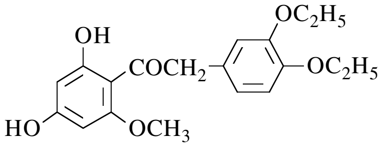
Synthesis

-Preparation by condensation of p-isopropyloxyphenylacetonitrile with 4-ethylresorcinol in the presence of boron trifluoride etherate under hydrogen chloride atmosphere (8-10 h) at r.t. overnight (62%) [786].

m.p. 95-96° [786]; ^{1}H NMR [786].

2-(3,4-Diethoxyphenyl)-1-(2,4-dihydroxy-6-methoxyphenyl)ethanone

$C_{19}H_{22}O_6$ mol.wt. 346.38



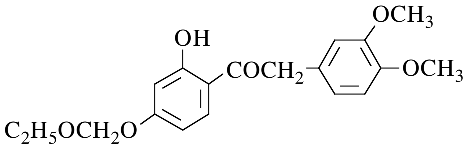
Synthesis

-Obtained by reaction of 3,4-diethoxyphenylacetonitrile with phloroglucinol monomethyl ether (Hoesch reaction) (24%) [1239].

m.p. 129-130° [1239].

2-(3,4-Dimethoxyphenyl)-1-(4-ethoxymethoxy-2-hydroxyphenyl)ethanone

$C_{19}H_{22}O_6$ mol.wt. 346.38



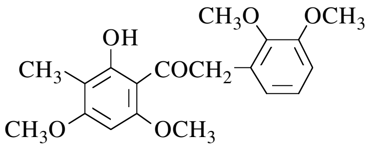
Synthesis

-Obtained by reaction of ethoxymethyl chloride with 2,4-dihydroxyphenyl 3,4-dimethoxybenzyl ketone in the presence of potassium carbonate in acetone for 45 min [723].

TLC [723].

2-(2,3-Dimethoxyphenyl)-1-(2-hydroxy-4,6-dimethoxy-3-methylphenyl)ethanone

$C_{19}H_{22}O_6$ mol.wt. 346.38



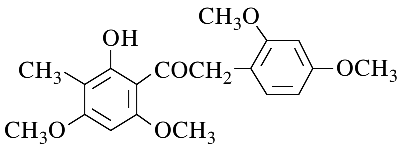
Synthesis

-Preparation by partial methylation of 2,4,6-trihydroxy-3-methylphenyl 2,3-dimethoxybenzyl ketone with dimethyl sulfate in the presence of potassium carbonate in boiling acetone (69%) [1536].

m.p. 160° [1536].

2-(2,4-Dimethoxyphenyl)-1-(2-hydroxy-4,6-dimethoxy-3-methylphenyl)ethanone

$C_{19}H_{22}O_6$ mol.wt. 346.38



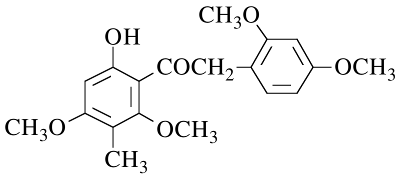
Syntheses

-Preparation by partial methylation of 2,4,6-trihydroxy-3-methylphenyl 2,4-dimethoxybenzyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 40 h (55%) [125].
-Also refer to: [465].

m.p. 142-143° [125]; UV [125].

2-(2,4-Dimethoxyphenyl)-1-(6-hydroxy-2,4-dimethoxy-3-methylphenyl)ethanone

[22081-04-5] $C_{19}H_{22}O_6$ mol.wt. 346.38



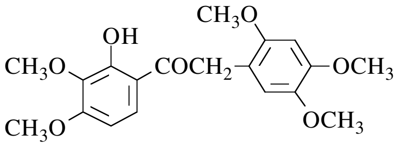
Synthesis

-Obtained by reaction of 2,4-dimethoxyphenylacetyl chloride with 4-hydroxy-2,6-dimethoxytoluene in ethyl ether in the presence of aluminium chloride [717].

m.p. 115-116° [717]; IR [717], UV [717].

1-(2-Hydroxy-3,4-dimethoxyphenyl)-2-(2,4,5-trimethoxyphenyl)ethanone

[20390-13-0] $C_{19}H_{22}O_7$ mol.wt. 362.38



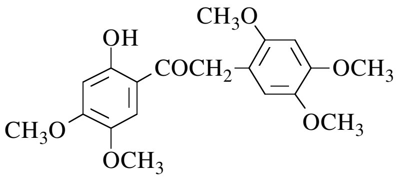
Synthesis

-Preparation by Friedel-Crafts acylation of pyrogallol trimethyl ether with 2,4,5-trimethoxyphenylacetyl chloride in the presence of aluminium chloride in ethyl ether at 0° overnight (68%) [752].

m.p. 170-171° [752].

1-(2-Hydroxy-4,5-dimethoxyphenyl)-2-(2,4,5-trimethoxyphenyl)ethanone

[24195-21-9] $C_{19}H_{22}O_7$ mol.wt. 362.38



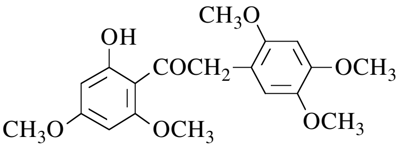
Synthesis

-Obtained by alkaline degradation of 6,7,2',4',5'-pentamethoxyisoflavone (m.p. 171-172°) (SM) with sodium hydroxide in refluxing 50% aqueous ethanol (10-45 min) (84%). SM was isolated from the heartwood of *Cordyla africana* (Leguminosae; sub-family: Caesalpinioideae, tribe: Swartzieae) [262].

m.p. 137-138° and 127°5-128°5 [262]; IR [262], UV [262], MS [262].

1-(2-Hydroxy-4,6-dimethoxyphenyl)-2-(2,4,5-trimethoxyphenyl)ethanone

$C_{19}H_{22}O_7$ mol.wt. 362.38



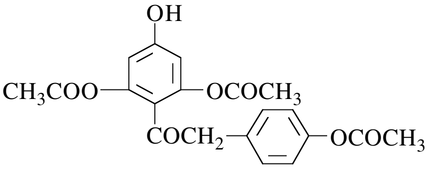
Synthesis

-Obtained by partial methylation of 2,4,6-trihydroxyphenyl 2,4,5-trimethoxybenzyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 14 h (74%) [582].

m.p. 144-145° [582].

2-[4-(Acetyloxy)phenyl]-1-[2,6-bis(acetyloxy)-4-hydroxyphenyl]ethanone

[145747-30-4] $C_{20}H_{18}O_8$ mol.wt. 386.36



Syntheses

-Obtained by regioselective enzyme-catalyzed deacetylation of 4-acetoxybenzyl 2,4,6-triacetoxyphenyl ketone in the dry organic solvents hereafter mentioned containing n-butanol with lipase at 42-45° [1146].

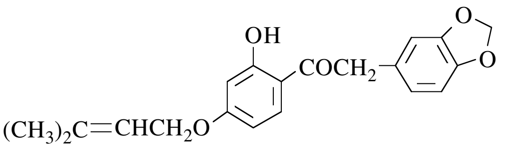
lipase	solvent	time (h)	yields (%)
PPL	acetone/n-BuOH	48	18
PPL	CH_3CN/n-BuOH	48	18
PPL	THF/n-BuOH	45	55
CCL	DIPE/n-BuOH	46	52

PPL = porcine pancreas lipase; CCL = candida cylindracea lipase; DIPE = diisopropyl ether.

TLC [1146].

2-(1,3-Benzodioxol-5-yl)-1-[2-hydroxy-4-[(3-methyl-2-butenyl)oxy]phenyl]ethanone

[94683-36-0] $C_{20}H_{20}O_5$ mol.wt. 340.38



Syntheses

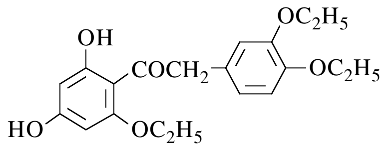
-Obtained by alkaline degradation of *Tephrosia maxima* Pers. (7-γ,γ-dimethylallyloxy)-3',4'-methylenedioxyisoflavone so called *7-O-γ,γ-dimethylallylpseudobaptigenin* (m.p. 126-128°) $C_{21}H_{18}O_5$, with sodium hydroxide (12%) in refluxing dilute ethanol for 15 min [1217].

-Also obtained by partial allylation of Ψ*-baptigenetin* (2,4-dihydroxyphenyl 3,4-methylenedioxybenzyl ketone) with γ,γ-dimethylallyl bromide in the presence of potassium carbonate in refluxing acetone for 8 h (64%) [848].

m.p. 81-82° [848], 73-74° [1217].

2-(3,4-Diethoxyphenyl)-1-(2-ethoxy-4,6-dihydroxyphenyl)ethanone

$C_{20}H_{24}O_6$ mol.wt. 360.41



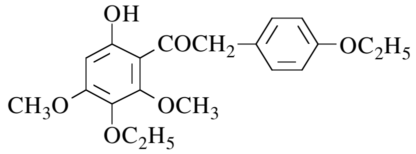
Synthesis

-Obtained by condensation of 3,4-diethoxyphenylacetonitrile with phloroglucinol monoethyl ether (Hoesch reaction) (16%) [1239].

rhombic prisms [1239];
4-methyl ether m.p. 99° [1239]

1-(3-Ethoxy-6-hydroxy-2,4-dimethoxyphenyl)-2-(4-ethoxyphenyl)ethanone

$C_{20}H_{24}O_6$ mol.wt. 360.41



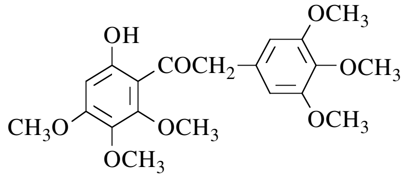
Syntheses

-Obtained by acylation of 4-ethoxy-3,5-dimethoxyphenol,
*with p-ethoxyphenylacetic acid in chloroform in the presence of boron trifluoride at r.t. overnight (31%) [766];
*with p-ethoxyphenylacetyl chloride in ethyl ether in the presence of aluminium chloride at 0° for 2 h, then at r.t. overnight (9%) [840].

m.p. 104° [766] [840]; b.p.$_{0.5}$ 220-230° [766].

1-(6-hydroxy-2,3,4-trimethoxyphenyl)-2-(3,4,5-trimethoxyphenyl)ethanone

[64554-42-3] $C_{20}H_{24}O_8$ mol.wt. 392.41



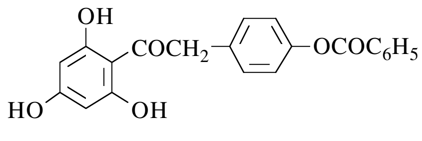
Synthesis

-Obtained by alkaline degradation of *irigenin trimethyl ether* (5,6,7,3',4',5'-hexamethoxyisoflavone) (m.p. 163°) with potassium hydroxide in refluxing dilute ethanol for 3 h (82%). *Irigenin* (5,7,3'-trihydroxy-6,4',5'-trimethoxyisoflavone) (m.p. 185°) was prepared by acidic hydrolysis of *iridin* (7-glucopyranosyloxy-5,3'-dihydroxy-6,4',5'-trimethoxyisoflavone) (m.p. 216-217°), itself isolated from *iris kumaonensis* Wall. [749].

m.p. 92° [749]; IR [749], UV [749]; TLC [749].

2-[4-(Benzoyloxy)phenyl]-1-(2,4,6-trihydroxyphenyl)ethanone

$C_{21}H_{16}O_6$ mol.wt. 364.35



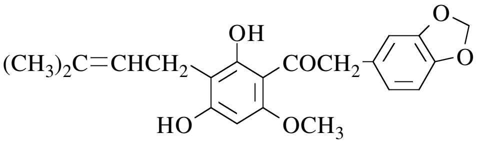
Synthesis

-Preparation by reaction of 4-benzoyloxyacetonitrile with phloroglucinol (Hoesch reaction) (44%) [117].

m.p. 224° [117].

2-(1,3-Benzodioxol-5-yl)-1-[2,4-dihydroxy-6-methoxy-3-(3-methyl-2-butenyl)phenyl]-ethanone

[55607-37-9] $C_{21}H_{22}O_6$ mol.wt. 370.95



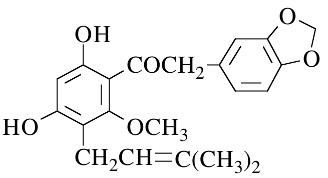
Synthesis

-Obtained (poor yield) by prenylation of 2,4-dihydroxy-6-methoxyphenyl 3,4-methylenedioxybenzyl ketone with 2-hydroxy-2-methyl-3-butene in dioxane in the presence of boron trifluoride etherate for 1 h at r.t. (4%) [715].

m.p. 155-156° [715]; ^{1}H NMR [715]; TLC [715].

2-(1,3-Benzodioxol-5-yl)-1-[4,6-dihydroxy-2-methoxy-3-(3-methyl-2-butenyl)phenyl]-ethanone

[55607-38-0] $C_{21}H_{22}O_6$ mol.wt. 370.95



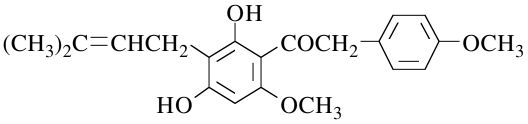
Synthesis

-Obtained (poor yield) by prenylation of 2,4-dihydroxy-6-methoxyphenyl 3,4-methylenedioxybenzyl ketone with 2-hydroxy-2-methyl-3-butene in dioxane in the presence of boron trifluoride etherate for 1 h at r.t. (3%) [715].

m.p. 105-106° [715]; ^{1}H NMR [715]; TLC [715].

1-[2,4-Dihydroxy-6-methoxy-3-(3-methyl-2-butenyl)phenyl]-2-(4-methoxyphenyl)-ethanone

[35817-95-9] $C_{21}H_{24}O_5$ mol.wt. 356.42



Syntheses

-Obtained by nuclear prenylation of 2,4-dihydroxy-6-methoxyphenyl 4-methoxybenzyl ketone,

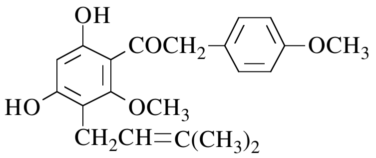
*using 2-methyl-2-hydroxy-3-methylbutene in dioxane in the presence of boron trifluoride etherate, first at 0°, then for 1 h at r.t. (9%) [700];

*with prenyl bromide in the presence methanolic potassium hydroxide, first with cooling, then keeping the reaction mixture for 20 h at r.t. (12%) [700].

m.p. 153-154° [700]; ^{1}H NMR [700]; TLC [700].

1-[4,6-Dihydroxy-2-methoxy-3-(3-methyl-2-butenyl)phenyl]-2-(4-methoxyphenyl)-ethanone

[35817-96-0] $C_{21}H_{24}O_5$ mol.wt. 356.42



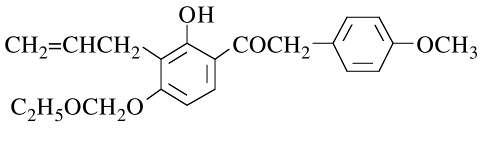
Synthesis

-Obtained by nuclear prenylation of 2,4-dihydroxy-6-methoxyphenyl 4-methoxybenzyl ketone using 2-methyl-2-hydroxy-3-methylbutene in dioxane in the presence of boron trifluoride etherate, first at 0°, then for 1 h at r.t. (7%) [700].

m.p. 91-92° [700]; ^{1}H NMR [700]; TLC [700].

1-[4-(Ethoxymethoxy)-2-hydroxy-3-(2-propenyl)phenyl]-2-(4-methoxyphenyl)ethanone

[117951-89-0] $C_{21}H_{24}O_5$ mol.wt. 356.42



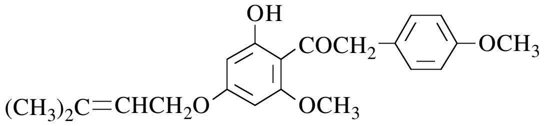
Synthesis

-Obtained by reaction of ethoxymethyl chloride with 3-allyl-2,4-dihydroxy-4'-methoxydesoxybenzoin in the presence of potassium carbonate in acetone for 10 min at r.t. [711].

TLC [711].

1-[2-Hydroxy-6-methoxy-4-[(3-methyl-2-butenyl)oxy]phenyl]-2-(4-methoxyphenyl)-ethanone

[35817-38-0] $C_{21}H_{24}O_5$ mol.wt. 356.42



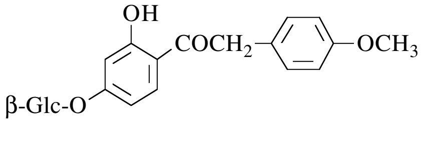
Synthesis

-Obtained by reaction of prenyl bromide with 2,4-dihydroxy-6,4'-dimethoxydesoxybenzoin in the presence of potassium carbonate in refluxing acetone for 3 h (81%) or in the presence of methanolic potassium hydroxide, first with cooling, then keeping the reaction mixture for 20 h at r.t. (2%) [700].

m.p. 76-77° [700]; ^{1}H NMR [700]; TLC [700].

1-[4-(β-D-Glucopyranosyloxy)-2-hydroxyphenyl]-2-(4-methoxyphenyl)ethanone
(Onospin)

$C_{21}H_{24}O_9$ mol.wt. 420.42



Syntheses

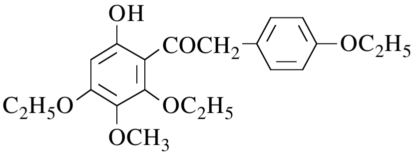
-Obtained by reaction of acetobromoglucose with 1-(2,4-dihydroxyphenyl)-2-(4-methoxyphenyl)ethanone in acetone in the presence of 10% aqueous sodium hydroxide at r.t. for 12 h (25%) [1528].

-Also obtained by alkaline degradation of *Ononin* — 7-(β-D-glucopyranosyloxy)-4'-methoxy isoflavone (SM) — [601] with boiling aqueous barium hydroxide [1528]. SM was isolated from the roots of thorny restharrow (*Ononis spinosa*) (Leguminosae, sub-family Fabaceae) [601] [1528].

m.p. 179°5 [1528]; $(\alpha)_D = 65°9\text{-}67°2$ (methanol) [1528].

1-(2,4-Diethoxy-6-hydroxy-3-methoxyphenyl)-2-(4-ethoxyphenyl)ethanone

$C_{21}H_{26}O_6$ mol.wt. 374.43



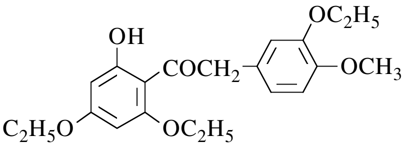
Synthesis

-Obtained by Friedel-Crafts acylation of 3,5-diethoxy-4-methoxyphenol with p-ethoxyphenylacetyl chloride in ethyl ether in the presence of aluminium chloride at r.t. for 12 h [842].

oil [842].

1-(2,4-Diethoxy-6-hydroxyphenyl)-2-(3-ethoxy-4-methoxyphenyl)ethanone

$C_{21}H_{26}O_6$ mol.wt. 374.43



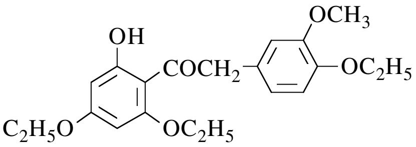
Synthesis

-Obtained by condensation of 3-ethoxy-4-methoxyphenylacetonitrile with phloroglucinol diethyl ether (Hoesch reaction) (16%) [1239].

m.p. 117° [1239].

1-(2,4-Diethoxy-6-hydroxyphenyl)-2-(4-ethoxy-3-methoxyphenyl)ethanone

$C_{21}H_{26}O_6$ mol.wt. 374.43



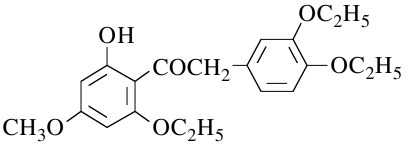
Synthesis

-Obtained by condensation of 4-ethoxy-3-methoxyphenylacetonitrile with phloroglucinol diethyl ether (Hoesch reaction) (16%) [1239].

m.p. 138° [1239].

2-(3,4-Diethoxyphenyl)-1-(2-ethoxy-6-hydroxy-4-methoxyphenyl)ethanone

$C_{21}H_{26}O_6$ mol.wt. 374.43



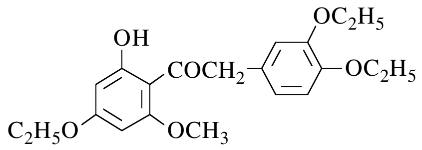
Syntheses

-Obtained by alkaline degradation of *O-triethylsantal* (7-methoxy-5,3',4'-triethoxyisoflavone) (m.p. 111-112°) with potassium hydroxide in boiling dilute ethanol for 1.5 h (67%) [1239].
-Also obtained by partial methylation of 2,4-dihydroxy-6,3',4'-triethoxydeoxybenzoin [1239].

m.p. 99° [1239].

2-(3,4-Diethoxyphenyl)-1-(4-ethoxy-2-hydroxy-6-methoxyphenyl)ethanone

$C_{21}H_{26}O_6$ mol.wt. 374.43



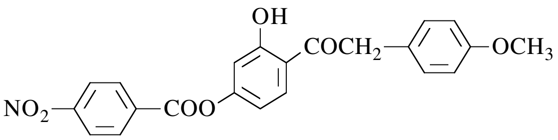
Synthesis

-Obtained by partial ethylation of 2,4-dihydroxy-6-methoxyphenyl 3,4-diethoxybenzyl ketone with ethyl iodide in the presence of potassium carbonate in boiling acetone for 2 h (77%) [1239].

m.p. 111-112° [1239].

1-[2-Hydroxy-4-(4-nitrobenzoyloxy)phenyl]-2-(4-methoxyphenyl)ethanone

$C_{22}H_{17}NO_7$ mol.wt. 407.38



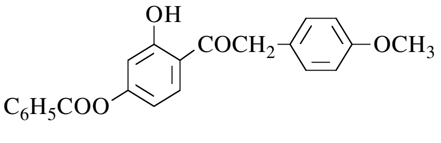
Synthesis

-Obtained by partial esterification of 2,4-dihydroxyphenyl 4-methoxybenzyl ketone with p-nitrobenzoyl chloride in the presence of pyridine [585].

m.p. 166-167° [585].

1-[4-(Benzoyloxy)-2-hydroxyphenyl]-2-(4-methoxyphenyl)ethanone

[102706-12-7] $C_{22}H_{18}O_5$ mol.wt. 362.38



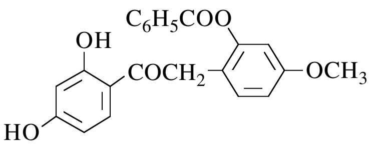
Syntheses

-Obtained by partial esterification of 2,4-dihydroxyphenyl 4-methoxybenzyl ketone with benzoyl chloride (Schotten-Baumann method) [585].
-Also refer to: [1123].

m.p. 120-121° [585].

2-[2-(Benzoyloxy)-4-methoxyphenyl]-1-(2,4-dihydroxyphenyl)ethanone

[52250-27-8] $C_{22}H_{18}O_6$ mol.wt. 378.38



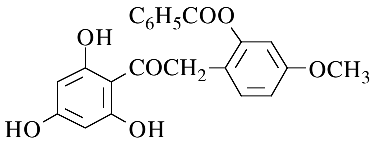
Synthesis

-Preparation by reaction of 2-benzoyloxy-4-methoxyphenylacetonitrile with resorcinol (Hoesch reaction) [466].

oil [466].

2-[2-(Benzoyloxy)-4-methoxyphenyl]-1-(2,4,6-trihydroxyphenyl)ethanone

[32884-28-9] $C_{22}H_{18}O_7$ mol.wt. 394.38



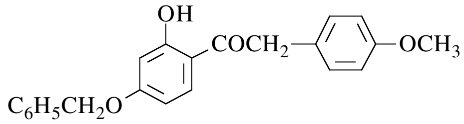
Synthesis

-Obtained by reaction of 2-benzoyloxy-4-methoxyphenylacetonitrile with phloroglucinol [465].

m.p. 207-208° [465]; IR [465].

1-[2-Hydroxy-4-(phenylmethoxy)phenyl]-2-(4-methoxyphenyl)ethanone

[95307-71-4] $C_{22}H_{20}O_4$ mol.wt. 348.40



Syntheses

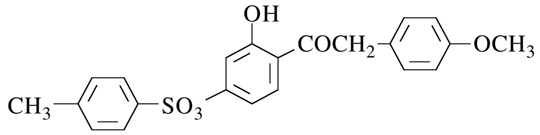
-Preparation by partial alkylation of 2,4-dihydroxyphenyl 4-methoxybenzyl ketone with benzyl chloride in the presence of potassium carbonate in refluxing acetone for 6 h (80%) [1490] or 8 h [26], (37%) [944].

-Also refer to: [13] [1140].

m.p. 103° [944], 93-95° [1490]; ^{1}H NMR [1490].

1-[2-Hydroxy-4-[[(4-methylphenyl)sulfonyl]oxy]phenyl]-2-(4-methoxyphenyl)ethanone

[102599-68-8] $C_{22}H_{20}O_6S$ mol.wt. 412.46



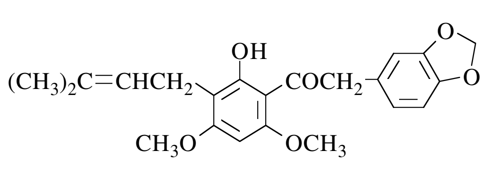
Synthesis

-Obtained by partial esterification of 2,4-dihydroxyphenyl 4-methoxybenzyl ketone with p-toluenesulfonyl chloride in acetone in the presence of potassium carbonate [585].

m.p. 91° [585].

2-(1,3-Benzodioxol-5-yl)-1-[2-hydroxy-4,6-dimethoxy-3-(3-methyl-2-butenyl)phenyl]-ethanone

[55607-39-1] $C_{22}H_{24}O_6$ mol.wt. 384.43



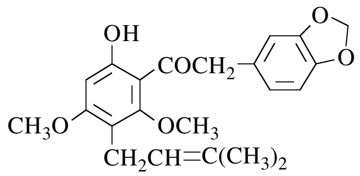
Synthesis

-Obtained by partial methylation of 2,4-dihydroxy-6-methoxy-3-prenylphenyl 3,4-methylenedioxybenzyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 3.5 h (96%) [715].

m.p. 118-119° [715]; ^{1}H NMR [715]; TLC [715].

2-(1,3-Benzodioxol-5-yl)-1-[6-hydroxy-2,4-dimethoxy-3-(3-methyl-2-butenyl)phenyl]-ethanone

[55607-41-5] $C_{22}H_{24}O_6$ mol.wt. 384.43



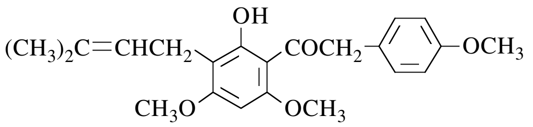
Synthesis

-Obtained by partial methylation of 2,4-dihydroxy-6-methoxy-5-prenylphenyl 3,4-methylenedioxybenzyl ketone with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 4 h (96%) [715].

m.p. 83-84° [715]; ^{1}H NMR [715]; TLC [715].

1-[2-Hydroxy-4,6-dimethoxy-3-(3-methyl-2-butenyl)phenyl]-2-(4-methoxyphenyl)-ethanone

[51323-85-4] $C_{22}H_{26}O_5$ mol.wt. 370.45



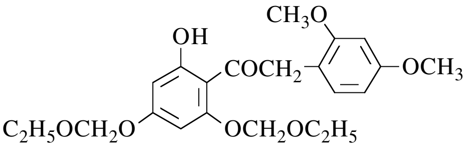
Synthesis

-Obtained by partial methylation of 3-prenyl-2,4-dihydroxy-6,4'-dimethoxydesoxybenzoin with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 3.5 h [700].

m.p. 94-95° [700].

2-(2,4-Dimethoxyphenyl)-1-[4,6-bis(ethoxymethoxy)-2-hydroxyphenyl]ethanone

$C_{22}H_{28}O_8$ mol.wt. 420.46

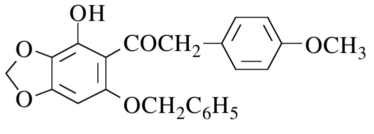


Synthesis

-Refer to: [723] (compound 1d).

1-[4-Hydroxy-6-(phenylmethoxy)-1,3-benzodioxol-5-yl]-2-(4-methoxyphenyl)ethanone

$C_{23}H_{20}O_6$ mol.wt. 392.41



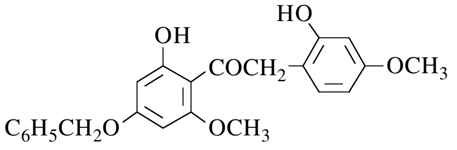
Synthesis

-Obtained by alkaline degradation of 5-benzyloxy-4'-methoxy-7,8-methylenedioxy-2-methylisoflavone with 10% aqueous potassium hydroxide in refluxing ethanol for 2 h under a stream of nitrogen gas (74%) [529].

m.p. 148-149° [529]; IR [529], UV [529].

1-[2-Hydroxy-6-methoxy-4-(phenylmethoxy)phenyl]-2-(2-hydroxy-4-methoxyphenyl)-ethanone

[32884-33-6] $C_{23}H_{22}O_6$ mol.wt. 394.42



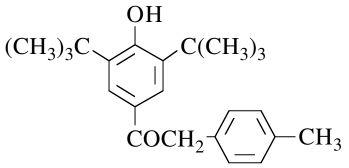
Synthesis

-Obtained by alkaline degradation of 2'-benzoyloxy-7-benzyloxy-4',5-dimethoxy-2-methoxycarbonylisoflavone (m.p. 183-184°) with potassium hydroxide in refluxing dilute ethanol for 2 h (98%) [465].

m.p. 120-122° [465]; ^{1}H NMR [465], IR [465].

1-[3,5-Bis(1,1-dimethylethyl)-4-hydroxyphenyl]-2-(4-methylphenyl)ethanone

[81116-01-0] $C_{23}H_{30}O_2$ mol.wt. 338.49



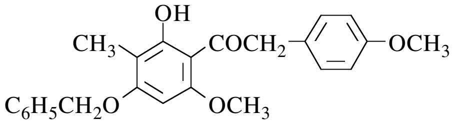
Syntheses

-Obtained by acylation of 2,6-di-tert-butylphenol with p-methylphenylacetyl chloride according to [1192], (35%) [1316].
-Also refer to: [1343].

m.p. 114-115° [1316]; IR [1316].

1-[2-Hydroxy-6-methoxy-3-methyl-4-(phenylmethoxy)phenyl]-2-(4-methoxyphenyl)-ethanone

[102749-29-1] $C_{24}H_{24}O_5$ mol.wt. 392.45



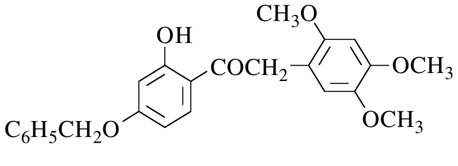
Synthesis

-Obtained by reaction of benzyl bromide with 2,4-dihydroxy-6-methoxy-3-methylphenyl 4-methoxybenzyl ketone in the presence of potassium carbonate in boiling acetone for 3 h (77%) [1534].

m.p. 118° [1534].

1-[2-Hydroxy-4-(phenylmethoxy)phenyl]-2-(2,4,5-trimethoxyphenyl)ethanone

$C_{24}H_{24}O_6$ mol.wt. 408.45



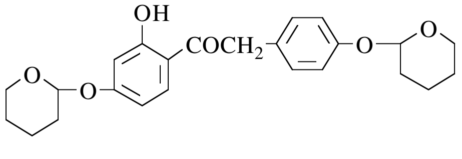
Synthesis

-Obtained by reaction of 2,4-dihydroxyphenyl 2,4,5-trimethoxybenzyl ketone with benzyl chloride in the presence of potassium carbonate in refluxing acetone for 8 h (94%) [536].

m.p. 149-150° [536].

1-[2-Hydroxy-4-[(tetrahydro-2*H*-pyran-2-yl)oxy]phenyl]-2-[4-[(tetrahydro-2*H*-pyran-2-yl)oxy]phenyl]ethanone

[130064-21-0] $C_{24}H_{28}O_6$ mol.wt. 412.48



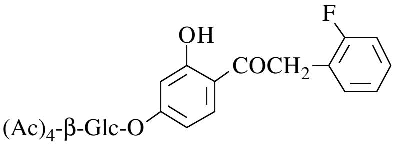
Synthesis

-Preparation by reaction of 3,4-dihydro-2*H*-pyran with 1-(2,4-dihydroxyphenyl)-2-(4-hydroxyphenyl)ethanone in concentrated hydrochloric acid and stirring in an ice bath for 4 h (87%) [1335].

m.p. 118° [1335]; ^{1}H NMR [1335], IR [1335], MS [1335].

2-(2-Fluorophenyl)-1-[2-hydroxy-4-[(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)oxy]-phenyl]ethanone

[121060-06-8] $C_{28}H_{29}FO_{12}$ mol.wt. 576.53

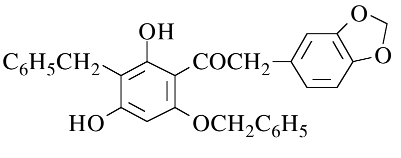


Synthesis

-Obtained by glycosidation of 1-(2,4-dihydroxyphenyl)-2-(2-fluorophenyl)ethanone with acetobromo-α-D-glucose in aqueous acetone containing potassium hydroxide [1186].

2-(1,3-Benzodioxol-5-yl)-1-[2,4-dihydroxy-6-(phenylmethoxy)-3-(phenylmethyl)phenyl]-ethanone

[39549-01-4] $C_{29}H_{24}O_6$ mol.wt. 468.51



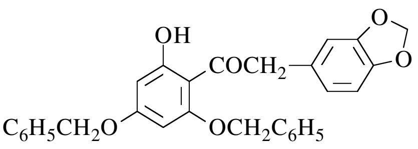
Synthesis

-Obtained by benzylation of 2,4,6-trihydroxyphenyl 3,4-methylenedioxybenzyl ketone with benzyl chloride in the presence of potassium carbonate in refluxing acetone for 7 h (10%) [714].

m.p. 145-146° [714]; ^{1}H NMR [714], UV [714].

2-(1,3-Benzodioxol-5-yl)-1-[2-hydroxy-4,6-bis(phenylmethoxy)phenyl]ethanone

[39549-00-3] $C_{29}H_{24}O_6$ mol.wt. 468.51



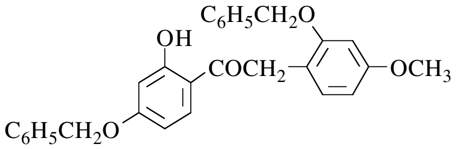
Synthesis

-Obtained by benzylation of 2,4,6-trihydroxyphenyl 3,4-methylenedioxy-benzyl ketone with benzyl chloride in the presence of potassium carbonate in refluxing acetone for 7 h (17%) [714].

m.p. 78-79° [714]; ^{1}H NMR [714], UV [714].

1-[2-Hydroxy-4-(phenylmethoxy)phenyl]-2-[4-methoxy-2-(phenylmethoxy)phenyl]-ethanone

[67685-29-4] $C_{29}H_{26}O_5$ mol.wt. 454.52



Syntheses

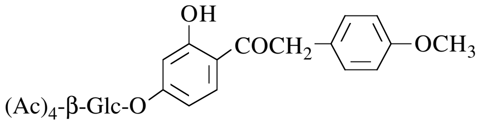
-Obtained by decarbonylation of the acetal — 2-(2-benzyloxy-4-methoxyphenyl)-1-(2,4-dibenzyloxyphenyl)-3,3-dimethoxy-propan-1-one — (colourless oil) in refluxing methanol (200 ml) containing 60% perchloric acid (30 ml) for 1.5 h (12%) [169].

-Also obtained by selective debenzylation of 2,2',4-tribenzyloxy-4'-methoxydeoxybenzoin (m.p. 111°) in acetonitrile in the presence of boron trifluoride etherate and sodium iodide at r.t. (88%) [169].

m.p. 101° [169]; ^{1}H NMR [169], MS [169]; TLC [169].

1-[2-Hydroxy-4-[(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)oxy]phenyl]-2-(4-methoxyphenyl)ethanone

[42868-73-5] $C_{29}H_{32}O_{13}$ mol.wt. 588.57

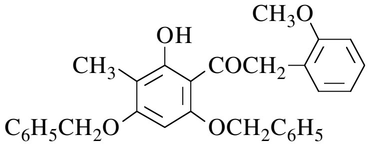


Synthesis

-Obtained by glycosidation of 1-(2,4-dihydroxyphenyl)-2-(4-methoxyphenyl)ethanone with acetobromo-α-D-glucose in aqueous acetone containing potassium hydroxide [1186].

1-[2-Hydroxy-3-methyl-4,6-bis(phenylmethoxy)phenyl]-2-(2-methoxyphenyl)ethanone

$C_{30}H_{28}O_5$ mol.wt. 468.55



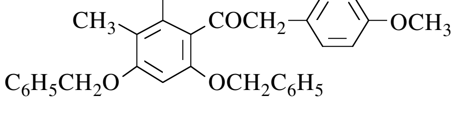
Synthesis

-Obtained by reaction of benzyl bromide (2 mol) with 2,4,6-trihydroxy-3-methylphenyl 2-methoxybenzyl ketone in the presence of potassium carbonate in boiling acetone for 3 h (31%) [1532].

m.p. 146° [1532].

1-[2-Hydroxy-3-methyl-4,6-bis(phenylmethoxy)phenyl]-2-(4-methoxyphenyl)ethanone

$C_{30}H_{28}O_5$ mol.wt. 468.55



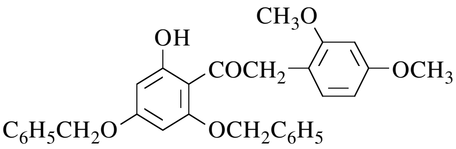
Synthesis

-Obtained by reaction of benzyl bromide (2 mol) with 2,4,6-trihydroxy-3-methylphenyl 4-methoxybenzyl ketone in the presence of potassium carbonate in boiling acetone for 3 h (37%) [1532].

m.p. 129° [1532].

2-(2,4-Dimethoxyphenyl)-1-[2-hydroxy-4,6-bis(phenylmethoxy)phenyl]ethanone

[39604-84-7] $C_{30}H_{28}O_6$ mol.wt. 484.55



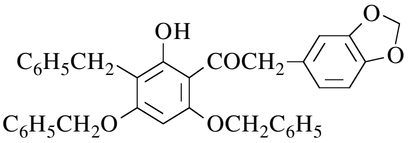
Synthesis

-Obtained by reaction of benzyl chloride with 2,4,6-trihydroxyphenyl 2,4-dimethoxybenzyl ketone in the presence of potassium carbonate in refluxing acetone for 5 h (38%) [12].

m.p. 136-137° [12].

2-(1,3-Benzodioxol-5-yl)-1-[2-hydroxy-4,6-bis(phenylmethoxy)-3-(phenylmethyl)phenyl]-ethanone

[39548-99-7] $C_{36}H_{30}O_6$ mol.wt. 558.63



Synthesis

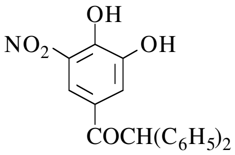
-Obtained (poor yield) by benzylation of 2,4,6-trihydroxyphenyl 3',4'-methylenedioxybenzyl ketone with benzyl chloride in the presence of potassium carbonate in refluxing acetone for 7 h (10%) [714].

m.p. 135-136° [714]; ^{1}H NMR [714], UV [714].

9.3. *Compounds derived from di- and triphenylacetic acids*

1-(3,4-Dihydroxy-5-nitrophenyl)-2,2-diphenylethanone

[400871-22-9] $C_{20}H_{15}NO_5$ mol.wt. 349.34



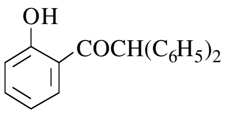
Synthesis

-Preparation by treatment of 2,2-diphenyl-1-(4-hydroxy-3-methoxy-5-nitrophenyl)ethanone with aluminium chloride in refluxing ethyl acetate/pyridine mixture for 2 h (90-96%) [887].

m.p. 204-205° [887]; ^{1}H NMR [887], ^{13}C NMR [887], IR [887].

1-(2-Hydroxyphenyl)-2,2-diphenylethanone

[4970-24-5] $C_{20}H_{16}O_2$ mol.wt. 288.34



Syntheses

-Obtained (by-product) by Fries rearrangement of phenyl diphenylacetate with aluminium chloride in nitrobenzene for 4 h at 60° (3%) [1551].

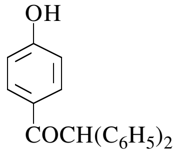
-Also obtained (poor yield) by refluxing phenyl diphenylacetate (pyrolysis, 300°) [1369]. **N.B.**: By using

"*Kupferbronze*" or various silicates ("*Bleicherde*", for example) as catalysts, the yield increases with appreciable change from 140°.

m.p. 99-100° [1551].

1-(4-Hydroxyphenyl)-2,2-diphenylethanone

[4873-38-5] $C_{20}H_{16}O_2$ mol.wt. 288.34



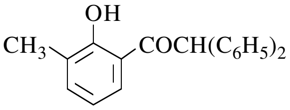
Syntheses

-Preparation by Fries rearrangement of phenyl diphenylacetate with aluminium chloride,
*in nitrobenzene at 60° for 4 h (70%) [1551];
*in nitroethane at r.t. for 24 h (86%) or at 60° for 4 h (79%) [1550].

m.p. 178-180° [1550], 174-177° [1551].

1-(2-Hydroxy-3-methylphenyl)-2,2-diphenylethanone

[133859-03-7] $C_{21}H_{18}O_2$ mol.wt. 302.37



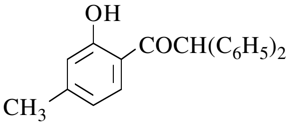
Synthesis

-Obtained by Fries rearrangement of o-tolyl diphenylacetate with aluminium chloride in nitrobenzene at 60° for 4 h (20%) [1551].

IR [1551].

1-(2-Hydroxy-4-methylphenyl)-2,2-diphenylethanone

[133859-04-8] $C_{21}H_{18}O_2$ mol.wt. 302.37



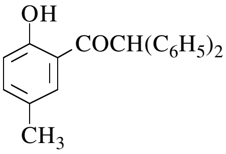
Synthesis

-Obtained by Fries rearrangement of m-tolyl diphenylacetate with aluminium chloride in nitrobenzene at 60° for 4 h (7%) [1551].

m.p. 179-180° [1551]; IR [1551].

1-(2-Hydroxy-5-methylphenyl)-2,2-diphenylethanone

[133859-05-9] $C_{21}H_{18}O_2$ mol.wt. 302.37



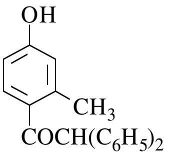
Syntheses

-Obtained by Fries rearrangement of p-tolyl diphenylacetate (m.p. 76°) [101] with aluminium chloride,
*without solvent in boiling water bath for 1 h [101];
*in nitrobenzene at 60° for 4 h (22%) [1551].

IR [1551].

1-(4-Hydroxy-2-methylphenyl)-2,2-diphenylethanone

[133859-06-0] $C_{21}H_{18}O_2$ mol.wt. 302.37



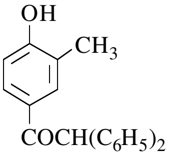
Syntheses

-Obtained (poor yields) by Fries rearrangement of m-tolyl diphenylacetate with aluminium chloride,
*in nitromethane or in nitroethane at r.t. for 12 h (19-21%) [1550];
*in nitrobenzene at r.t. for 10 h (10%) or at 60° for 4 h (10%) [1550], (6%) [1551].

m.p. 150-151° [1550], 125-127° [1551].
One of the reported melting points is obviously wrong.

1-(4-Hydroxy-3-methylphenyl)-2,2-diphenylethanone

[122918-54-1] $C_{21}H_{18}O_2$ mol.wt. 302.37



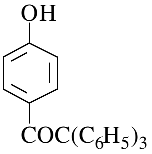
Synthesis

-Preparation by Fries rearrangement of o-cresyl diphenylacetate with aluminium chloride in nitrobenzene at 60° for 4 h (49%) [1551] or in nitroethane at r.t. for 12 h (73%) [1550].

m.p. 211-212° [1551].

1-(4-Hydroxyphenyl)-2,2,2-triphenylethanone

[133859-07-1] $C_{26}H_{20}O_2$ mol.wt. 364.44



Synthesis

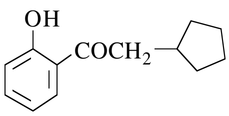
-Obtained (poor yield) by Fries rearrangement of phenyl triphenylacetate with aluminium chloride in nitrobenzene for 4 h at 60° (5%) [1551].

IR [1551].

9.4. *Compounds derived from cycloalkylacetic acids*

2-Cyclopentyl-1-(2-hydroxyphenyl)ethanone

[56234-70-9] $C_{13}H_{16}O_2$ mol.wt. 204.27



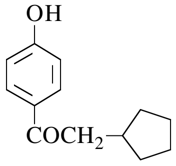
Synthesis

-Obtained by reaction of cyclopentylacetyl chloride with phenol in the presence of aluminium chloride at 140° for 15 min (46%) [1093].

b.p.$_1$ 112-114° [1093].

2-Cyclopentyl-1-(4-hydroxyphenyl)ethanone

[56184-10-2] $C_{13}H_{16}O_2$ mol.wt. 204.27



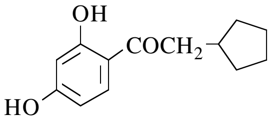
Synthesis

-Obtained by reaction of cyclopentylacetyl chloride with phenol in the presence of aluminium chloride at 140° for 15 min (36%) [1093].

b.p.$_1$ 175-185° [1093].

2-Cyclopentyl-1-(2,4-dihydroxyphenyl)ethanone

[59108-69-9] $C_{13}H_{16}O_3$ mol.wt. 220.27

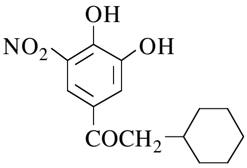


Synthesis

-Obtained by reaction of cyclopentylacetonitrile with resorcinol (Hoesch reaction) [141].

2-Cyclohexyl-1-(3,4-dihydroxy-5-nitrophenyl)ethanone

[400871-12-7] $C_{14}H_{17}NO_5$ mol.wt. 279.29



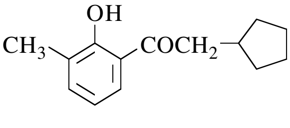
Synthesis

-Preparation by treatment of 2-cyclohexyl-1-(4-hydroxy-3-methoxy-5-nitrophenyl)ethanone with aluminium chloride in refluxing ethyl acetate/pyridine mixture for 2 h (90-96%) [887].

m.p. 113-114° [887];
^{1}H NMR [887], ^{13}C NMR [887], IR [887].

2-Cyclopentyl-1-(2-hydroxy-3-methylphenyl)ethanone

[56184-11-3] $C_{14}H_{18}O_2$ mol.wt. 218.30



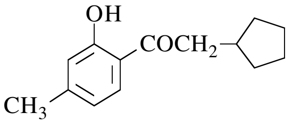
Synthesis

-Preparation by reaction of cyclopentylacetyl chloride with o-cresol in the presence of aluminium chloride at 180° for 15 min (40-45%) [1093].

b.p.$_1$ 121-123° [1093].

2-Cyclopentyl-1-(2-hydroxy-4-methylphenyl)ethanone

[56184-13-5] $C_{14}H_{18}O_2$ mol.wt. 218.30



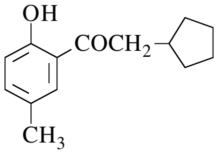
Synthesis

-Preparation by reaction of cyclopentylacetyl chloride with m-cresol in the presence of aluminium chloride at 140° for 15 min (81%) [1093].

b.p.$_1$ 126-128° [1093].

2-Cyclopentyl-1-(2-hydroxy-5-methylphenyl)ethanone

[56184-14-6] $C_{14}H_{18}O_2$ mol.wt. 218.30



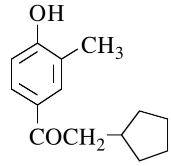
Synthesis

-Preparation by reaction of cyclopentylacetyl chloride with p-cresol in the presence of aluminium chloride at 140° for 15 min (80%) [1093].

b.p.$_1$ 124-126° [1093].

2-Cyclopentyl-1-(4-hydroxy-3-methylphenyl)ethanone

[56184-12-4] $C_{14}H_{18}O_2$ mol.wt. 218.30



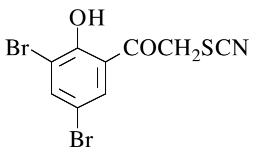
Synthesis

-Preparation by reaction of cyclopentylacetyl chloride with o-cresol in the presence of aluminium chloride at 140° for 15 min (56%) [1093].

b.p.$_1$ 180-190° [1093].

2-(3,5-Dibromo-2-hydroxyphenyl)-2-oxoethyl thiocyanate

$C_9H_5Br_2NO_2S$ mol.wt. 351.02



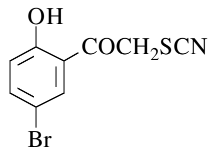
Synthesis

-Obtained by reaction of ammonium thiocyanate with 3,5,α-tribromo-2-hydroxyacetophenone in aqueous acetone at r.t. for 6 h (69%) [1308].

m.p. 142-143° [1308]; IR [1308].

2-(5-Bromo-2-hydroxyphenyl)-2-oxoethyl thiocyanate

[260430-29-3] $C_9H_6BrNO_2S$ mol.wt. 272.12



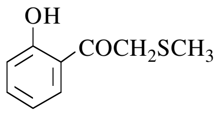
Synthesis

-Obtained by reaction of ammonium thiocyanate with 5,α-dibromo-2-hydroxyacetophenone in aqueous acetone at r.t. for 6 h (88%) [1308].

m.p. 131-132° [1308]; IR [1308].

1-(2-Hydroxyphenyl)-2-(methylthio)ethanone

[56986-82-4] $C_9H_{10}O_2S$ mol.wt. 182.96



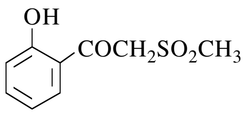
Synthesis

-Preparation by adding a solution of 15% sodium methylmercaptide to a solution of 2-hydroxy-α-bromoacetophenone in methanol in an ice bath. The reaction mixture was stirred for 30 min at r.t. (98%) [1113].

yellow liquid [1113]; MS [1113].

1-(2-Hydroxyphenyl)-2-(methylsulfonyl)ethanone

[39068-36-5] $C_9H_{10}O_4S$ mol.wt. 214.24



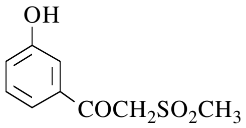
Synthesis

-Obtained by condensation of methyl 2-hydroxybenzoate with dimethylsulfone carbanion in DMSO (65%) [1162].

m.p. 139-140° [1162].

1-(3-Hydroxyphenyl)-2-(methylsulfonyl)ethanone

[52945-17-2] $C_9H_{10}O_4S$ mol.wt. 214.24



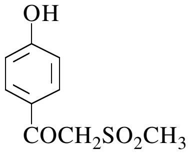
Synthesis

-Obtained by condensation of methyl 3-hydroxybenzoate with dimethylsulfone carbanion in DMSO (60%) [1162].

m.p. 168-169° [1162].

1-(4-Hydroxyphenyl)-2-(methylsulfonyl)ethanone

[52945-18-3] $C_9H_{10}O_4S$ mol.wt. 214.24



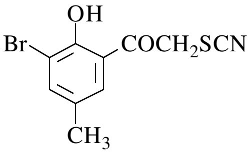
Synthesis

-Obtained by condensation of methyl 4-hydroxybenzoate with dimethylsulfone carbanion in DMSO (58%) [1162].

m.p. 173-174° [1162].

2-(3-Bromo-2-hydroxy-5-methylphenyl)-2-oxoethyl thiocyanate

$C_{10}H_8BrNO_2S$ mol.wt. 286.15



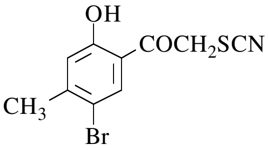
Synthesis

-Obtained by reaction of ammonium thiocyanate with 3,α-dibromo-2-hydroxy-5-methylacetophenone in aqueous acetone at r.t. for 6 h (66%) [1308].

m.p. 148-149° [1308]; IR [1308].

2-(5-Bromo-2-hydroxy-4-methylphenyl)-2-oxoethyl thiocyanate

$C_{10}H_8BrNO_2S$ mol.wt. 286.15



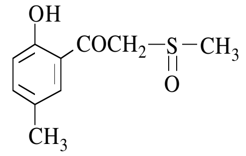
Synthesis

-Obtained by reaction of ammonium thiocyanate with 5,α-dibromo-2-hydroxy-4-methylacetophenone in aqueous acetone at r.t. for 6 h (73%) [1308].

m.p. 122-123° [1308]; IR [1308].

1-(2-Hydroxy-5-methylphenyl)-2-(methylsulfinyl)ethanone

[52159-50-9] $C_{10}H_{12}O_3S$ mol.wt. 212.27

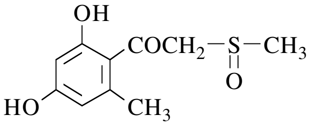


Synthesis

-Refer to: [316].

1-(2,4-Dihydroxy-6-methylphenyl)-2-(methylsulfinyl)ethanone

[478795-87-8] $C_{10}H_{12}O_4S$ mol.wt. 228.27



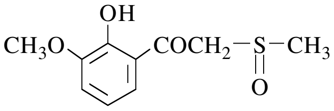
Synthesis

-Obtained by reaction of ethyl 2,4-dihydroxy-6-methylbenzoate with sodium methylsulfinylmethide [1178] according to [587].

oil [1178].

1-(2-Hydroxy-3-methoxyphenyl)-2-(methylsulfinyl)ethanone

[65220-47-5] $C_{10}H_{12}O_4S$ mol.wt. 228.27



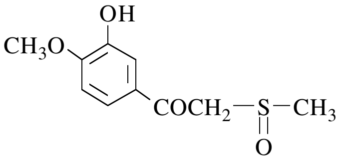
Synthesis

-Preparation by reaction of methyl 3-methoxysalicylate (methyl 2-hydroxy-3-methoxybenzoate) with methylsulfinyle carbanion, itself obtained from DMSO and sodium hydride (83%) [1000].

m.p. 140-142° [1000]; TLC [1000].

1-(3-Hydroxy-4-methoxyphenyl)-2-(methylsulfinyl)ethanone

[66100-55-8] $C_{10}H_{12}O_4S$ mol.wt. 228.27



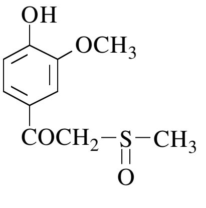
Synthesis

-Preparation by reaction of methyl isovanillinate (methyl 3-hydroxy-4-methoxybenzoate) with methylsulfinyle carbanion, itself obtained from DMSO and sodium hydride (89%) [1179].

m.p. 158-161° [1179];
^{1}H NMR [1179], IR [1179].

1-(4-Hydroxy-3-methoxyphenyl)-2-(methylsulfinyl)ethanone

[66100-54-7] $C_{10}H_{12}O_4S$ mol.wt. 228.27



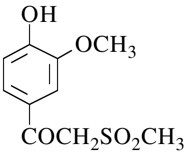
Synthesis

-Preparation by reaction of methyl vanillinate (methyl 4-hydroxy-3-methoxybenzoate) with methylsulfinyle, carbanion itself obtained from DMSO and sodium hydride (90%) [1179].

m.p. 151-152° [1179];
^{1}H NMR [1179], IR [1179].

1-(4-Hydroxy-3-methoxyphenyl)-2-(methylsulfonyl)ethanone

[52945-22-9] $C_{10}H_{12}O_5S$ mol.wt. 244.27



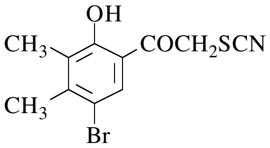
Synthesis

-Obtained by condensation of methyl 4-hydroxy-3-methoxybenzoate with dimethylsulfone carbanion in DMSO (76%) [1162].

m.p. 157-158° [1162].

2-(5-Bromo-2-hydroxy-3,4-dimethylphenyl)-2-oxoethyl thiocyanate

[260430-31-7] $C_{11}H_{10}BrNO_2S$ mol.wt. 300.18



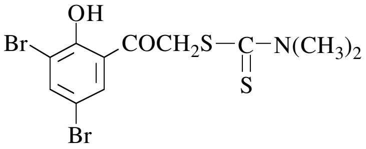
Synthesis

-Obtained by reaction of ammonium thiocyanate with 5,α-dibromo-2-hydroxy-3,4-dimethylacetophenone in aqueous acetone at r.t. for 6 h (52%) [1308].

m.p. 149-150° [1308]; IR [1308].

2-(3,5-Dibromo-2-hydroxyphenyl)-2-oxoethyl dimethylcarbamodithioate

[214959-26-9] $C_{11}H_{11}Br_2NO_2S_2$ mol.wt. 413.15



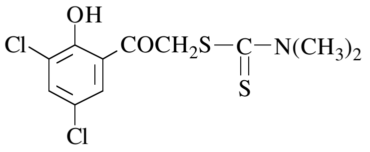
Synthesis

-Obtained by reaction of 3,5-dibromo-2-hydroxy-α-bromoacetophenone with sodium or piperidinium N,N-dimethyldithiocarbamate in methanol at r.t. for 12 h (72%) [490].

m.p. 164° [490];
^{1}H NMR [490], IR [490], UV [490].

2-(3,5-Dichloro-2-hydroxyphenyl)-2-oxoethyl dimethylcarbamodithioate

[87669-75-8] $C_{11}H_{11}Cl_2NO_2S_2$ mol.wt. 324.2

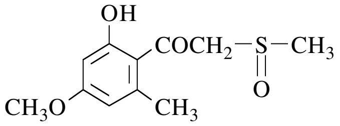


Syntheses

-Refer to: [267] [269].

1-(2-Hydroxy-4-methoxy-6-methylphenyl)-2-(methylsulfinyl)ethanone

[104783-89-3] $C_{11}H_{14}O_4S$ mol.wt. 242.30



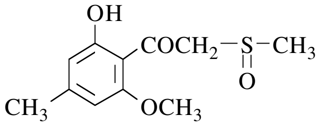
Syntheses

-Preparation by reaction of ethyl 2-hydroxy-4-methoxy-6-methylbenzoate (m.p. 73-74°) with sodium methylsulfinylmethide, itself obtained from DMSO and sodium hydride (85%) [587].
-Also refer to: [1178].

m.p. 146-148° [587]; ^{1}H NMR [587], IR [587].

1-(2-Hydroxy-6-methoxy-4-methylphenyl)-2-(methylsulfinyl)ethanone

[205880-83-7] $C_{11}H_{14}O_4S$ mol.wt. 242.30



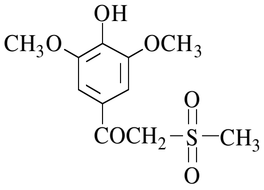
Syntheses

-Preparation by treatment of methyl 2-hydroxy-6-methoxy-4-methylbenzoate (methyl mono-O-methyl-p-orsellinate) (m.p. 94-96°) with sodium methylsulfinylmethide (SM) formed *in situ*. SM was obtained by action of sodium hydride (3 equiv) with DMSO (7 equiv) in benzene at 50° for 1 h. (78%) [1032].
-Also refer to: [820].

m.p. 62-64° [1032].

1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-(methylsulfonyl)ethanone

[52945-23-0] $C_{11}H_{14}O_6S$ mol.wt. 274.29



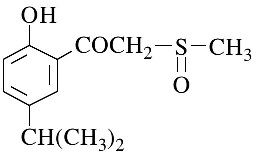
Synthesis

-Obtained by condensation of methyl 4-hydroxy-3,5-dimethoxybenzoate with dimethylsulfonyl carbanion in DMSO (74%) [1162].

m.p. 154-155° [1162].

1-[2-Hydroxy-5-(1-methylethyl)phenyl]-2-(methylsulfinyl)ethanone

[63220-58-6] $C_{12}H_{16}O_3S$ mol.wt. 240.32

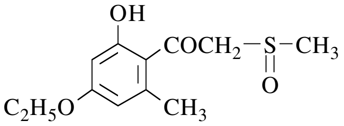


Syntheses

-Refer to: [315] [316].

1-(4-Ethoxy-2-hydroxy-6-methylphenyl)-2-(methylsulfinyl)ethanone

[478795-93-6] $C_{12}H_{16}O_4S$ mol.wt. 256.32



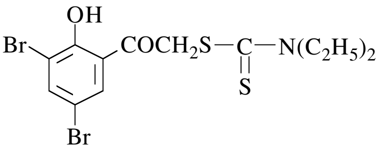
Synthesis

-Obtained by reaction of ethyl 4-ethoxy-2-hydroxy-6-methylbenzoate with sodium methylsulfinylmethide [1178] according to [587].

oil [1178].

2-(3,5-Dibromo-2-hydroxyphenyl)-2-oxoethyl diethylcarbamodithioate

[214959-27-0] $C_{13}H_{15}Br_2NO_2S_2$ mol.wt. 441.21



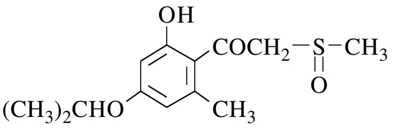
Synthesis

-Obtained by action of 3,5-dibromo-2-hydroxy-α-bromoacetophenone with sodium or piperidinium N,N-diethyldithiocarbamate in methanol at r.t. for 12 h (58%) [490].

m.p. 132° [490]; ^1H NMR [490], IR [490], UV [490].

1-[2-Hydroxy-6-methyl-4-(1-methylethoxy)phenyl]-2-(methylsulfinyl)ethanone

[478795-95-8] $C_{13}H_{18}O_4S$ mol.wt. 270.35



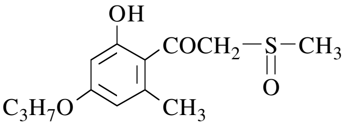
Synthesis

-Obtained by reaction of ethyl 2-hydroxy-4-isopropoxy-6-methylbenzoate with sodium methylsulfinylmethide [1178] according to [587].

oil [1178].

1-(2-Hydroxy-6-methyl-4-propoxyphenyl)-2-(methylsulfinyl)ethanone

[478795-94-7] $C_{13}H_{18}O_4S$ mol.wt. 270.35



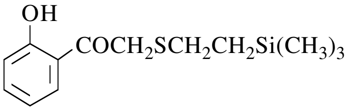
Synthesis

-Obtained by reaction of ethyl 2-hydroxy-6-methyl-4-propoxybenzoate with sodium methylsulfinylmethide [1178] according to [587].

oil [1178].

1-(2-Hydroxyphenyl)-2-[2-(trimethylsilyl)ethylthio]ethanone

[193075-79-5] $C_{13}H_{20}O_2SSi$ mol.wt. 268.45



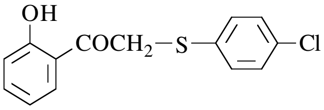
Synthesis

-Preparation by adding an ethanolic solution of sodium 2-(trimethylsilyl)ethanethiolate in a solution of 2-chloro-1-(2-hydroxyphenyl)ethanone in dioxane at r.t. for 2 h under nitrogen (99%) [161].

pale yellow oil [161]; ¹H NMR [161], IR [161].

2-[(4-Chlorophenyl)thio]-1-(2-hydroxyphenyl)ethanone

[113272-14-3] $C_{14}H_{11}ClO_2S$ mol.wt. 278.76



Syntheses

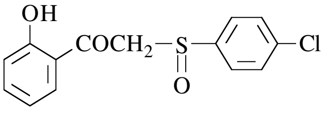
-Preparation by adding dropwise at r.t. an ethanolic solution of sodium 4-chlorothiophenoxide to a solution of 2-hydroxy-α-bromoacetophenone in dioxane and stirring the mixture for a further hour (84%) [338].

-Also refer to: [1273].

m.p. 83-84° [338]; ¹H NMR [338], IR [338], MS [338].

2-[(4-Chlorophenyl)sulfinyl]-1-(2-hydroxyphenyl)ethanone

[113272-15-4]
[131137-71-8] (±) $C_{14}H_{11}ClO_3S$ mol.wt. 294.76



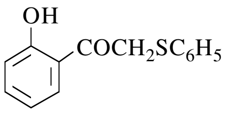
Syntheses

-Preparation by oxidation of α-(4-chlorophenylthio)-2-hydroxyacetophenone in methylene chloride with 3-chloroperoxybenzoic acid at 0° for 5 h (93%) [338].
-Also refer to: [1273].

m.p. 131-132° [338];
¹H NMR [338], IR [338], MS [338].

1-(2-Hydroxyphenyl)-2-(phenylthio)ethanone

[56307-98-3] $C_{14}H_{12}O_2S$ mol.wt. 244.31



Syntheses

-Preparation by adding an ethanolic solution of sodium benzenethiolate to a solution of 2-hydroxy-α-bromo-acetophenone in dioxane at r.t. and stirring for 1 h at the same temperature (77%) [1273] [1416].

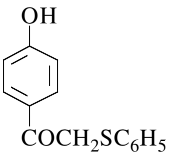
-Preparation by condensation of 2-hydroxy-α-bromoacetophenone (or 2-hydroxy-α-chloro-acetophenone) with thiophenol in the presence of sodium ethoxide in an ethanol/dioxane mixture (77%) [1421].

-Also refer to: [1113].

m.p. 55° [1416] [1421], 52-54° [1273];
^{1}H NMR [1273] [1416], IR [1273] [1416], UV [1416] [1421].

1-(4-Hydroxyphenyl)-2-(phenylthio)ethanone

[137524-65-3] $C_{14}H_{12}O_2S$ mol.wt. 244.31



Syntheses

-Preparation by adding thiophenol (0.1 ml) and rhodium (II) acetate dimer (2 mg) to a suspension of resin **6** (52 mg) in benzene and the mixture agitated at 50° for 2 h. Resin was filtered, successively washed with methylene chloride, THF and ethyl ether and dried *in vacuo*. A 50% (v/v) solution of TFA in methylene chloride was added to the above resin and the mixture was agitated at r.t. for 30 min. After, the resin was filtered and washed with methylene chloride, the combined filtrates were concentrated and purified by preparative TLC (ethyl acetate/toluene) to give the titled compound (64%) [682].

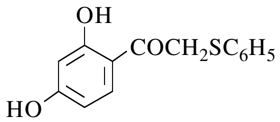
N.B.: Resin **6** (resin-bound α-TMS diazoketon 6) (preparation given).

-Also refer to: [1349].

^{1}H NMR [682], ^{13}C NMR [682], IR [682], MS [682].

1-(2,4-Dihydroxyphenyl)-2-(phenylthio)ethanone

[56307-99-4] $C_{14}H_{12}O_3S$ mol.wt. 260.31



Syntheses

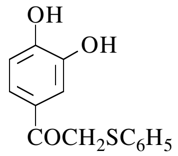
-Preparation by condensation of 2,4-dihydroxy-α-chloro-acetophenone with thiophenol in the presence of sodium ethoxide in a mixture of ethanol/dioxane (93%) [1421].

-Also obtained by condensation of phenylthioacetonitrile with resorcinol (Hoesch reaction) (54%) [1421].

m.p. 152-153° [1421]; UV [1421].

1-(3,4-Dihydroxyphenyl)-2-(phenylthio)ethanone

[131985-77-8] $C_{14}H_{12}O_3S$ mol.wt. 260.31

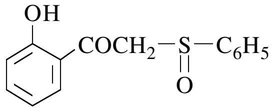


Synthesis

-Refer to: [538] (Japanese patent).

1-(2-Hydroxyphenyl)-2-(phenylsulfinyl)ethanone

[131137-70-7] $C_{14}H_{12}O_3S$ mol.wt. 260.31



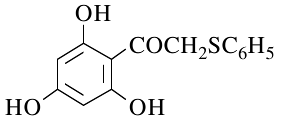
Synthesis

-Preparation by oxidation of 1-(2-hydroxyphenyl)-2-(phenylthio)ethanone with *m*-CPBA in methylene chloride at 0° for 5 h and water then added (90%) [1273].

m.p. 117-118° [1273];
^{1}H NMR [1273], IR [1273], MS [1273].

2-(Phenylthio)-1-(2,4,6-trihydroxyphenyl)ethanone

[56308-00-0] $C_{14}H_{12}O_4S$ mol.wt. 276.31



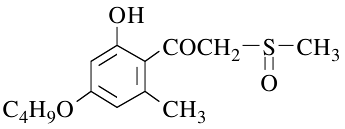
Syntheses

-Preparation by condensation of phenylthioacetonitrile with phloroglucinol (Hoesch reaction) (85%) [1421].
-Also obtained by condensation of 2,4,6-trihydroxy-α-chloroacetophenone with thiophenol in the presence of sodium ethoxide in an ethanol/dioxane mixture (20%) [1421].

m.p. 173-174° [1421]; UV [1421].

1-(4-Butoxy-2-hydroxy-6-methylphenyl)-2-(methylsulfinyl)ethanone

[478795-98-1] $C_{14}H_{20}O_4S$ mol.wt. 284.38



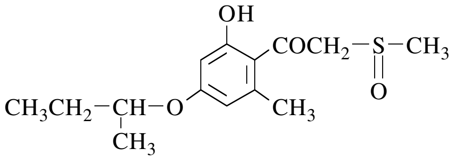
Synthesis

-Obtained by reaction of ethyl 4-butoxy-2-hydroxy-6-methylbenzoate with sodium methylsulfinylmethide [1178] according to [587].

oil [1178].

1-[2-Hydroxy-6-methyl-4-(1-methylpropoxy)phenyl]-2-(methylsulfinyl)ethanone

[478795-97-0] $C_{14}H_{20}O_4S$ mol.wt. 284.38



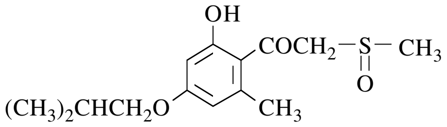
Synthesis

-Obtained by reaction of ethyl 4-sec-butoxy-2-hydroxy-6-methylbenzoate with sodium methylsulfinylmethide [1178] according to [587].

oil [1178].

1-[2-Hydroxy-6-methyl-4-(2-methylpropoxy)phenyl]-2-(methylsulfinyl)ethanone

[478795-96-9] $C_{14}H_{20}O_4S$ mol.wt. 284.38



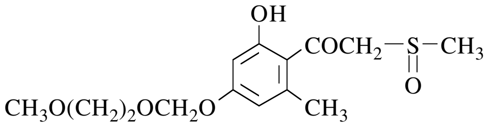
Synthesis

-Obtained by reaction of ethyl 4-isobutoxy-2-hydroxy-6-methylbenzoate with sodium methylsulfinylmethide [1178] according to [587].

oil [1178].

1-[2-Hydroxy-4-[(2-methoxyethoxy)methoxy]-6-methylphenyl]-2-(methylsulfinyl)-ethanone

$C_{14}H_{20}O_6S$ mol.wt. 316.38



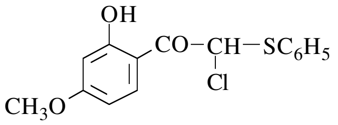
Synthesis

-Preparation by reaction of ethyl 2-hydroxy-4-(2-methoxyethoxy)-methoxy-6-methylbenzoate with methylsulfinyl carbanion, itself obtained from DMSO and sodium hydride (86%) [587].

m.p. 106-107° [587]; ^1H NMR [587], IR [587].

2-Chloro-1-(2-hydroxy-4-methoxyphenyl)-2-(phenylthio)ethanone

[153432-53-2] $C_{15}H_{13}ClO_3S$ mol.wt. 308.79



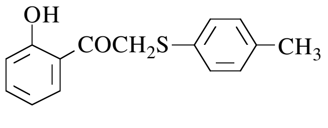
Synthesis

-Preparation by reaction of N-chlorosuccinimide with 2'-hydroxy-4'-methoxy-2-(phenylthio)acetophenone in carbon tetrachloride under argon at r.t. for 2 h (83%) [411].

m.p. 49-50°5 [411]; ^1H NMR [411], ^{13}C NMR [411], IR [411], MS [411].

1-(2-Hydroxyphenyl)-2-[(4-methylphenyl)thio]ethanone

[108378-94-5] $C_{15}H_{14}O_2S$ mol.wt. 258.34



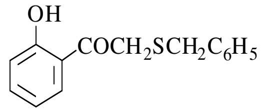
Synthesis

-Preparation by adding an ethanolic solution of sodium 4-methylbenzenethiolate to a solution of 2-hydroxy-α-bromoacetophenone in dioxane at r.t. and stirring for 1 h at the same temperature (83%) [1272] [1273].

m.p. 66-67° [1273]; ^{1}H NMR [1273], IR [1273].

1-(2-Hydroxyphenyl)-2-[(phenylmethyl)thio]ethanone

[111809-47-3] $C_{15}H_{14}O_2S$ mol.wt. 258.34



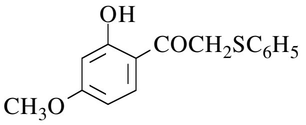
Synthesis

-Preparation by adding a solution of sodium phenylmethanethiolate in ethanol to a solution of o-hydroxy-α-chloroacetophenone in dioxane at 20° during 40 min and then stirring at the same temperature for 30 min more (84%) [162].

m.p. 64° [162]; ^{1}H NMR [162], IR [162].

1-(2-Hydroxy-4-methoxyphenyl)-2-(phenylthio)ethanone

[56308-01-1] $C_{15}H_{14}O_3S$ mol.wt. 274.34



Syntheses

-Preparation by reaction of sodium thiophenolate with 2-hydroxy-4-methoxy-α-chloroacetophenone in tetrahydrofuran under argon, at r.t. for 10 min (73%) [411].

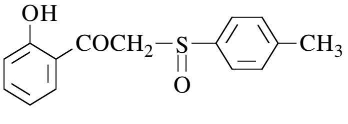
-Also obtained by partial methylation of 2,4-dihydroxy-α-phenylthioacetophenone with dimethyl sulfate in the presence of potassium carbonate in acetone for 3 h (64%) [1421].

-Also obtained by alkaline degradation of 3-(phenylthio)-7-methoxychromone (m.p. 101-102°) with N-sodium hydroxide in dilute methanol for 3 h (96%) [1421].

m.p. 42-44° [411], 42-43° [1421]; ^{1}H NMR [411], ^{13}C NMR [411], UV [1421].

1-(2-Hydroxyphenyl)-2-[(4-methylphenyl)sulfinyl]ethanone

[108378-95-6](±)
[108448-95-9](R) $C_{15}H_{14}O_3S$ mol.wt. 274.34



Syntheses

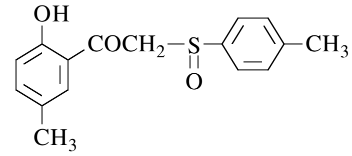
-Preparation by oxidation of 1-(2-hydroxyphenyl)-2-[(4-methylphenyl)thio]ethanone with *m*-CPBA in methylene chloride at 0° for 5 h and water then added (95%) [1273].

-Also refer to: [1272].

m.p. 118-119° [1273]; ^{1}H NMR [1273], IR [1273].

1-(2-Hydroxy-5-methylphenyl)-2-[(R)-(4-methylphenyl)sulfinyl]ethanone

[371258-74-1] $C_{16}H_{16}O_3S$ mol.wt. 288.37



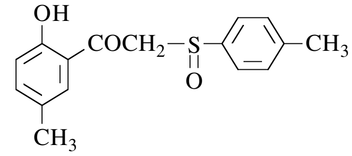
Synthesis

-Preparation at -78° by reaction between methyl 2-hydroxy-5-methylbenzoate and (R)-(+)-methyl p-tolyl sulfoxide in the presence of lithium diisopropylamide (LDA) in THF (91%) [642].

m.p. 128° [642]; $(\alpha)_D^{22}$ = +134 to +148° (c = 1 in chloroform) [642];
^{1}H NMR [642], IR [642], MS [642].

1-(2-Hydroxy-5-methylphenyl)-2-[(S)-(4-methylphenyl)sulfinyl]ethanone

[371258-72-9] $C_{16}H_{16}O_3S$ mol.wt. 288.37

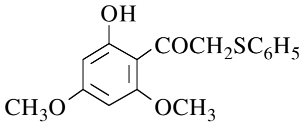


Synthesis

-Refer to: [642].

1-(2-Hydroxy-4,6-dimethoxyphenyl)-2-(phenylthio)ethanone

[56308-02-2] $C_{16}H_{16}O_4S$ mol.wt. 304.37



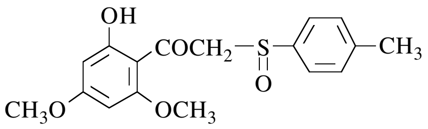
Synthesis

-Preparation by partial methylation of 2-(phenylthio)-2',4',6'-trihydroxyacetophenone with dimethyl sulfate in the presence of potassium carbonate in acetone for 2 h (88%) [1421].

m.p. 75° [1421]; UV [1421].

1-(2-Hydroxy-4,6-dimethoxyphenyl)-2-[(R)-(4-methylphenyl)sulfinyl]ethanone

[371258-80-9] $C_{17}H_{18}O_5S$ mol.wt. 334.39



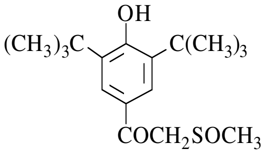
Synthesis

-Preparation at -78° by reaction between methyl 2-hydroxy-4,6-dimethoxybenzoate and (R)-(+)-methyl p-tolyl sulfoxide in the presence of lithium diisopropylamide (LDA) in THF (58%) [642].

m.p. 107-109° [642]; $(\alpha)_D^{20}$ = -28 to -32° (c = 1 in chloroform) [642];
^{1}H NMR [642], IR [642], MS [642]; TLC [642].

1-[3,5-Bis(1,1-dimethylethyl)-4-hydroxyphenyl]-2-(methylsulfinyl)ethanone

[115207-18-6] $C_{17}H_{26}O_3S$ mol.wt. 310.46



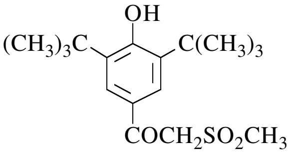
Syntheses

-Obtained by reaction of 3,5-di-tert-butyl-4-hydroxybenzoyl chloride with excess DMSO at r.t. (16-18%) [1453].
-Obtained by acylation of 2,6-di-tert-butylphenol with 2-(methylthio)acetic acid and the intermediate oxidized with m-CPBA [978].

m.p. 143°6-144°9 [978], 61-62° [1453].
One of the reported melting points is obviously wrong.
^1H NMR [1453], IR [1453].

1-[3,5-Bis(1,1-dimethylethyl)-4-hydroxyphenyl]-2-(methylsulfonyl)ethanone

[191157-34-3] $C_{17}H_{26}O_4S$ mol.wt. 326.46

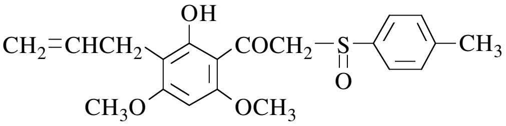


Synthesis

-Refer to: [978].

1-[2-Hydroxy-4,6-dimethoxy-3-(2-propenyl)phenyl]-2-[(S)-(4-methylphenyl)sulfinyl]-ethanone

[371258-84-3] $C_{20}H_{22}O_5S$ mol.wt. 374.46



Synthesis

-Obtained at -78° in THF using lithium diisopropylamide (LDA), either by reaction between methyl 2-hydroxy-4,6-dimethoxy-3-(2-propenyl)-benzoate and (R)-(+)-methyl p-tolyl sulfoxide in the presence of 1,3-dimethyl-3,4,5,6-tetrahydro-2[1*H*]-pyrimidinone (DMPU) (this method yields only a trace of the desired compound), or by reaction between 2-hydroxy-4,6-dimethoxy-3-(2-propenyl)benzaldehyde and (R)-(+)-methyl p-tolyl sulfoxide *via* the subsequent oxidation at r.t. by MnO_2 of the intermediate 1-[2-hydroxy-4,6-dimethoxy-3-(2-propenyl)phenyl]-2-(4-methylsulfinyl)ethanol (57%) [642].

m.p. 150-151° [642]; $(\alpha)_D^{30}$ = +52 to +56° (c = 1.5 in chloroform) [642];
^1H NMR [642], ^{13}C NMR [642], IR [642], MS [642];
TLC [642].

DI- AND POLYKETONES

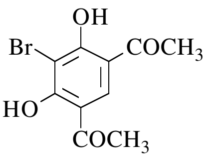
Chapter 11. Aromatic ketones containing only acetyl groups

11.1. *Acetyl groups located on one ring*

11.1.1. Unsubstituted acetyl groups and homologues

1,1'-(5-Bromo-4,6-dihydroxy-1,3-phenylene)bis-ethanone

[117156-78-2] $C_{10}H_9BrO_4$ mol.wt. 273.08



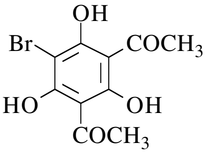
Syntheses

-Preparation by bromination of resodiacetophenone,
*with NBS in refluxing dioxane for 10 h (97%) [55];
*with bromine, for 6 h at r.t. [1463], in cooled acetic acid [6].
-Also refer to: [669].

m.p. 205° [6], 202-203° [1463]; ^{1}H NMR [55], IR [55], UV [55].

1,1'-(5-Bromo-2,4,6-trihydroxy-1,3-phenylene)bis-ethanone

[98149-38-3] $C_{10}H_9BrO_5$ mol.wt. 289.08



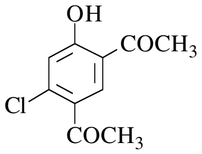
Synthesis

-Preparation by Friedel-Crafts acylation of 2-bromophloroglucinol with acetyl chloride or acetic anhydride in the presence of boron trifluoride (72-78%) [1561].

m.p. 150-152° [1561].

1,1'-(4-Chloro-6-hydroxy-1,3-phenylene)bis-ethanone

[30335-99-0] $C_{10}H_9ClO_3$ mol.wt. 212.63



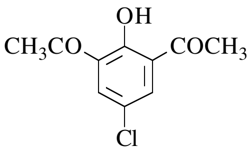
Syntheses

-Obtained by Fries rearrangement,
*of 4-acetyl-3-chlorophenyl acetate with aluminium chloride at 120° for 20 min (35%) [1260];
*of 3-chlorophenyl acetate with aluminium chloride at 175-180° for 3 h (by-product) [1452].
-Also obtained from 5-acetyl-6-chloro-2,3-dimethylbenzofuran by oxidation with chromium trioxide in dilute acetic acid at 50° for 30 min, followed by hydrolysis of the resulting keto ester (18%) [1260].

m.p. 84° [1452], 75° [1260]; b.p.$_9$ 167° [1260]; ^{1}H NMR [1452], MS [1452].

1,1'-(5-Chloro-2-hydroxy-1,3-phenylene)bis-ethanone

[71643-62-4] $C_{10}H_9ClO_3$ mol.wt. 212.63



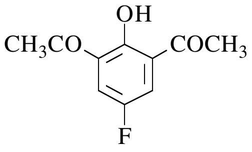
Syntheses

-Preparation by Fries rearrangement of 2-(acetyloxy)-5-chloroacetophenone with aluminium chloride for 1 h at 130°, then 1 h at 140° (80%) [1312].
-Also refer to: [671] [984].

b.p.$_6$ 120° [1312].

1,1'-(5-Fluoro-2-hydroxy-1,3-phenylene)bis-ethanone

[106823-62-5] $C_{10}H_9FO_3$ mol.wt. 196.18



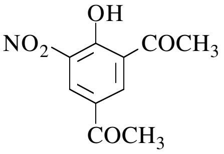
Synthesis

-Preparation by Fries rearrangement of 2-acetyl-4-fluorophenyl acetate (b.p. 124-126°) with aluminium chloride at 130-140° for 3 h (71%) [1268].

b.p. 130-135° [1268]; IR [1268].

1,1'-(4-Hydroxy-5-nitro-1,3-phenylene)bis-ethanone

[100245-07-6] $C_{10}H_9NO_5$ mol.wt. 223.19



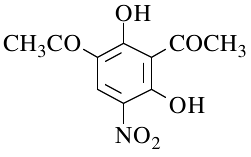
Synthesis

-Preparation by nitration of 5-acetyl-2-hydroxyacetophenone at -20° using standard reagents (51%) [506].

m.p. 104-105° [506].

1,1'-(2,4-Dihydroxy-5-nitro-1,3-phenylene)bis-ethanone

[103264-32-0] $C_{10}H_9NO_6$ mol.wt. 239.18



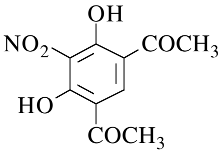
Syntheses

-Preparation by reaction of 1,3-dinitroquinolizin-4-one with sodio-2,4,6-heptanetrione in DMF for 1.5 h between -15 to -10° (57%) [69].
-Also obtained by nitration of 2,4-diacetylresorcinol with a nitric acid (d = 1.42)/sulfuric acid (d = 1.84) mixture in acetic acid at 0° for 1 h (41%) [41].
-Also obtained by Fries rearrangement of 4-nitroresorcinol diacetate in nitrobenzene with aluminium chloride at 95-100° for 2 h or at r.t. for 72 h (38%) [41].

m.p. 142-143° [69], 139-140° [41]; ^{1}H NMR [69], IR [69].

1,1'-(4,6-Dihydroxy-5-nitro-1,3-phenylene)bis-ethanone

[103262-48-2] $C_{10}H_9NO_6$ mol.wt. 239.18



Syntheses

-Preparation by Fries rearrangement of 2-nitroresorcinol diacetate with aluminium chloride,
*without solvent, at 140° [39], at 100-110° (30%) [42];
*in nitrobenzene, at 140° [39], at 100-110° for 3 h (60%) [42] and at 25-28° for 70 h (73%) [42].

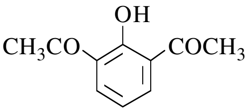
-Preparation by Friedel-Crafts acetylation of 2-nitroresorcinol with acetic anhydride in the presence of aluminium chloride in nitrobenzene at 120-130° for 3 h (76%) [42].

-Preparation by nitration of 4,6-diacetylresorcinol,
*with nitric acid (d = 1.42) at 80° (84%) [55], or first at 80°, then at r.t. for 2 h [116];
*with nitric acid in sulfuric acid at 0° [39];
*with concentrated nitric acid in a concentrated sulfuric acid/acetic acid mixture at 0° for 1 h [42];
*with cooled fuming nitric acid, then at r.t. for 30 min [6];
*with fuming nitric acid in acetic acid, first at 0°, then at r.t. for a few min [6].

m.p. 235° [55], 235°(d) [116], 234° [39] [42], 231° [6];
^{1}H NMR [55], IR [55], UV [55].

1,1'-(2-Hydroxy-1,3-phenylene)bis-ethanone

[103867-89-6] $C_{10}H_{10}O_3$ mol.wt. 178.19



Syntheses

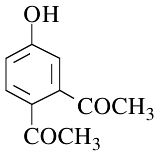
-Obtained by hydrolysis of 2-(3-acetyl-2-hydroxyphenyl)-2-methyl-1,3-dioxolane with a 5% aqueous hydrochloric acid/ethanol mixture at r.t. for 5 min (almost quantitative yield) [544].

-Also obtained by UV light irradiation of 2-(2-acetoxyphenyl)-2-methyl-1,3-dioxolane in hexane (7%) [542] or in hexane in the presence of potassium carbonate for 6 h (7%) [544].

m.p. 71-73° [542]; ^{1}H NMR [542], IR [542], UV [542].

1,1'-(4-Hydroxy-1,2-phenylene)bis-ethanone

[90464-79-2] $C_{10}H_{10}O_3$ mol.wt. 178.19

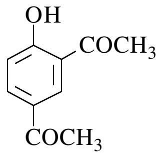


Synthesis

-Refer to: [1465] (Japanese patent).

1,1'-(4-Hydroxy-1,3-phenylene)bis-ethanone

[30186-16-4] $C_{10}H_{10}O_3$ mol.wt. 178.19



Syntheses

-Preparation by reaction of acetyl chloride (2 mol) with o-methoxyacetophenone (1 mol) in the presence of aluminium chloride (2 mol) in boiling carbon disulfide for 12 h (87%) [213].

-Preparation by Fries rearrangement of various substituted phenyl esters (1 mol) in the presence of aluminium chloride,

*of p-acetylphenyl acetate,

-at 150° for 3 h: ($AlCl_3$ 3.5 mol) (80%) [1281] [1282] or ($AlCl_3$ 4 mol) (60%) [633];

-at 140-150° for 2 h ($AlCl_3$ 3.4 mol) (78%) [196] or for 1 h ($AlCl_3$ 3.3 mol) (40%) [178];

-first at 130-140°, then at 160° for 10 min ($AlCl_3$ 2.7 mol) (poor yields) [213] [1540];

*of o-acetylphenyl acetate,

-first at 50°, then at 80° for 15 min ($AlCl_3$ 2.7 mol) (46%) [213] [1540];

-in nitrobenzene at r.t. overnight ($AlCl_3$ 3.3 mol) (43%) [178];

*of o-bromophenyl acetate at 180° for 5 h ($AlCl_3$ 3.2 mol) (by-product) (18%) [413].

-Also obtained by photo-Fries rearrangement of two different esters in hexane for 6 h,

*of 2-(4-acetoxyphenyl)-2-methyl-1,3-dioxolane (12%) [542] [544];

*of 2-(2-acetoxyphenyl)-2-methyl-1,3-dioxolane (4%) [542] [544].

-Also obtained by Friedel-Crafts acylation of p-hydroxyacetophenone with acetyl chloride in tetrachloroethane in the presence of aluminium chloride (4 mol) at 130° for 4 h (49%) [633].

-Also obtained by treatment of two different substituted acetophenones with 5% aqueous hydrochloric acid/ethanol (30v/1v) at r.t. for 5 min,

*of 2-(5-acetyl-2-hydroxyphenyl)-2-methyl-1,3-dioxolane (almost quantitative yield) [544];

*of 2-(3-acetyl-4-hydroxyphenyl)-2-methyl-1,3-dioxolane (almost quantitative yield) [544].

-Also obtained by decarboxylation of 3,5,3',3'-tetraacetylxanthyrone in boiling water for 4 h (18%) [345].

-Also refer to: [295] [632] [1366] and also [134] (Fries rearrangement).

Isolation from natural sources

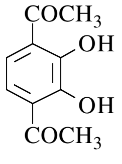
-From the aerial parts of *Ophryosporus floribundus* (Compositae, tribe Eupatorieae) [1570].

-From the *Artemisia campestris* L. subsp. *glutinosa* (Gay ex Besser) (Compositae) [373].

m.p. 95° [213], 93° [413], 92-93° [178], 92 [1281], 91-92° [633],
90-92° [542], 90-91° [1540], 72° [345], 64-65° [373].
One of the reported melting points is obviously wrong.
^1H NMR [196] [345] [373] [413] [542] [633],
IR [83] [196] [345] [373] [407] [633], UV [345] [373], MS [345] [373].

1,1'-(2,3-Dihydroxy-1,4-phenylene)bis-ethanone

[39126-03-9] $C_{10}H_{10}O_4$ mol.wt. 194.19



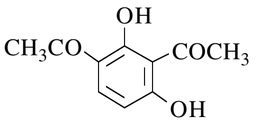
Synthesis

-Refer to: [4].

Hueckel MO calculations (compound XI) [845];
^1H NMR [4], ^{13}C NMR [4].

1,1'-(2,4-Dihydroxy-1,3-phenylene)bis-ethanone

[2163-12-4] $C_{10}H_{10}O_4$ mol.wt. 194.19



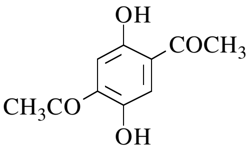
Syntheses

-Obtained from resorcinol by a typical Friedel-Crafts reaction (40%) [830],
*with acetic acid in the presence of boron trifluoride,
 -at 140° for 3 h in a sealed tube (30%) [1110];
 -at 125° for 6 h (20%) [962];
*with acetic anhydride,
 -in the presence of concentrated sulfuric acid at 130° for 15 min (15%) [684];
 -in the presence of zinc chloride at 145-150° (7%) [58] or at 150-160° for 20 min (6%) [1057];
*with acetyl chloride,
 -by heating in the presence of concentrated sulfuric acid (10%) [684];
 -in ethyl ether in the presence of aluminium chloride at r.t. for 3 days (7%) [601].
-Also obtained by acetylation of resacetophenone with acetic anhydride,
*in the presence of boron trifluoride in acetic acid at 80° for 1.5 h (31%) [374];
*in the presence of boron trifluoride at 70° for 2 h in a sealed tube (30%) [1110];
*in the presence of aluminium chloride in nitrobenzene at 105-110° for 2 h (15%) [381].
-Also obtained by acetylation of 2-acetylresorcinol with acetic acid in the presence of zinc chloride at reflux for 5 min [923].
-Also obtained by Fries rearrangement of resorcinol diacetate,
*on heating with concentrated sulfuric acid (45%) [684];
*with aluminium chloride,
 -at 180-185° for 1.5 h ($AlCl_3$ 3 mol) (60%) [384];
 -at 160-170° for 2 h ($AlCl_3$ 3 mol) [383];
 -at 130-135° for 4.5 h ($AlCl_3 > 2$ mol) (crude, 90%) [1249];
 -in nitrobenzene at 100° for 3 h ($AlCl_3$ 3.3 mol) [41].
-Also obtained by treatment of 4-acetoxy-2-hydroxyacetophenone with aluminium chloride in nitrobenzene at 115° [111] [1037], (26%) [116] (Fries rearrangement).
-Also obtained by heating 2,4-diacetoxyacetophenone with aluminium chloride for 3 h (26%) [760] (Fries rearrangement).
-Also obtained by decarboxylation of 3,5-diacetyl-2,4-dihydroxybenzoic acid,
*with refluxing very dilute hydrochloric acid in water for 12 to 18 h [40];
*with very dilute hydrochloric acid in acetic acid at 160-170° in a sealed tube for 7-8 h [385].
-Also obtained by degradation of 7,7'-diacetoxy-4,4'-dimethyl-3,4-dihydro-4,6'-bicoumarin with aluminium chloride between 135 to 170° for 2 h (19%) [760].
-Also obtained by Claisen rearrangement of 3-acetyl-2,4-bis(3-methyl-2-butenyloxy)acetophenone, resulting from deprenylation,
*in trifluoroacetic acid at 0° for 3 h (95%) [53];
*in the presence of palladium chloride-bis(acetonitrile) in refluxing dioxane for 45 min (31%) [53];
*by heating neat at 185° for 2 h (22%) [53].
-Also refer to: [57] [453] [920] [1023] [1390] [1394] [1467].
N.B.: Mono Na salt [921]; di Na salt [920].

m.p. 96-97° [830], 95-96° [385], 92° [111] [684], 91-92° [760], 90° [58] [1057], 89° [923], 88-89° [1249], 88° [1110], 86-87° [40], 86° [601], 85-87° [116], 85-86° [381], 85° [374] [962].
b.p.$_{26}$ 170-172° [1249];
^{1}H NMR [4] [830] [1057], ^{13}C NMR [4] [830], IR [1057], UV [1037].

1,1'-(2,5-Dihydroxy-1,4-phenylene)bis-ethanone

[20129-52-6] $C_{10}H_{10}O_4$ mol.wt. 194.19



Syntheses

-Obtained by reaction of acetyl chloride (7.6 mol) with hydroquinone dimethyl ether (1.8 mol) in nitrobenzene in the presence of aluminium chloride (5 mol), first at r.t. for 67 h, then at 95° for 40 h (10%) [745].

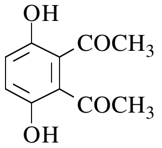
-Also obtained by photo-Fries rearrangement of hydroquinone diacetate in methanol under nitrogen for 12 h (10%) [1337].

-Also refer to: [837].

m.p. 192° [745], 155° [1337]. One of the reported melting points is obviously wrong.
^{1}H NMR [4] [1337], ^{13}C NMR [4], IR [1337], MS [837];
Crystals data [1517] [1518] [1576]; Hueckel MO calculations (compound VIII) [845].

1,1'-(3,6-Dihydroxy-1,2-phenylene)bis-ethanone

[39125-99-0] $C_{10}H_{10}O_4$ mol.wt. 194.19



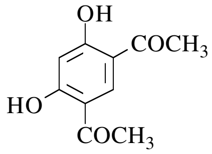
Synthesis

-Preparation by oxidative cyclization of 1,3-bis(trimethylsilyloxy)-1-methyl-1,3-butadiene: to a acetonitrile solution of sodium bicarbonate (12 equiv.) and CAN (6 equiv.) was slowly added an acetonitrile solution of 1,3-bis(trimethylsilyloxy)-1-methyl-1,3-butadiene (2 equiv.) at -45°. The temperature of the reaction mixture was allowed to rise to 20° during 2 h. After stirring for 1 h at 20°, a saturated aqueous solution of brine was added, the organic layer was separated and the aqueous layer was extracted with ethyl ether. The combined organic extracts were dried, filtered and the solvent was removed *in vacuo*. The residue was purified by column chromatography (compound 4 h) (28%) [875].

Hueckel MO calculations (compound VII) [845].

1,1'-(4,6-Dihydroxy-1,3-phenylene)bis-ethanone

[2161-85-5] $C_{10}H_{10}O_4$ mol.wt. 194.19



Syntheses

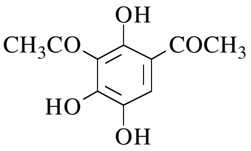
-Preparation by Friedel-Crafts acylation of resorcinol,
*with acetic anhydride,
-in the presence of zinc chloride [629] [824] [896], (80%) [872], at 142-150° for 15 min (96%) [59], (90%) [58] or at 150-160° for 20 min (68%) [1057];
-in the presence of ferric chloride [1082].
-in the presence of concentrated sulfuric acid at 130° for 15 min (15%) [684];
-in the presence of 70% perchloric acid at 125-135° for 15-20 min (42%) [417].
*with acetyl chloride,
-in the presence of zinc chloride [449] [456], at 120° [448];
-in the presence of ferric chloride [1081] [1082], at 150° for 15 min (60%) [127] or at reflux for 30 min [629];

-in the presence of concentrated sulfuric acid (18%) [684].
*by a typical Friedel-Crafts reaction (24%) [830].
-Also obtained by acylation of resorcinol with acetic acid,
*in the presence of polyphosphoric acid for 15 min in a boiling water bath (9%) [1069];
*in the presence of boron trifluoride at 125° for 6 h (20%) [962].
-Also obtained by Friedel-Crafts acylation of paeonol with acetic anhydride in nitrobenzene in the presence of aluminium chloride [734].
-Also obtained by Fries rearrangement of resorcinol diacetate,
*with hot concentrated sulfuric acid (31%) [684];
*with polyphosphoric acid at 70° for 2 h (19%) [547];
*with aluminium chloride,
-in nitrobenzene in a boiling water bath (70%) [1541];
-without solvent (15%) [1542], at 205-210° for 1.5 h (14%) [384].
*with fused zinc chloride [29] [449] [457] [629] [1463], at 120° [448] or at 130° (40-50%) [817];
*with ferric chloride at 180° for 3 h [943], (32%) [114], under nitrogen (16%) [1103] [1164] or under carbon dioxide [629], (15%) [598].
-Also obtained by photo-Fries rearrangement of resorcinol diacetate in methanol at 25° under nitrogen [1155].
-Also obtained by acylation of resacetophenone,
*with acetic acid,
-in the presence of zinc chloride (Nencki reaction) [42];
-in the presence of zinc chloride and phosphorous oxychloride at 140-150° for 30 min [339] [629] [1463].
-in the presence of polyphosphoric acid (14%) [1070], in a boiling water bath for 10 min (21%) [1069].
*with acetic anhydride,
-in the presence of boron trifluoride in acetic acid at 80° for 1.5 h (35%) [374].
-in the presence of aluminium chloride in nitrobenzene at 105-110° for 2 h (15%) [381].
-Also obtained by Friedel-Crafts acylation of resorcinol dimethyl ether with acetyl chloride in carbon disulfide at 10° for 1 h (9%) [374].
-Also obtained by Fries rearrangement of 2-acetoxy-4-hydroxyacetophenone with ferric chloride at 180° for 3 h (12%) [598].
-Also obtained by Fries rearrangement of 2,4-diacetoxyacetophenone with aluminium chloride (9%) [1435].
-Also obtained (poor yield) by treatment of 7,7'-diacetoxy-4,4'-dimethyl-3,4-dihydro-4,6'-bicoumarin with aluminium chloride between 135 and 170° for 2 h (< 3%) [1435].
-Also obtained by total dealkylation,
*of resodiacetophenone diallyl ether with trifluoroacetic acid at 60° for 1 h (85%) [55];
*of resodiacetophenone dimethyl ether with 48% aqueous hydrobromic acid in refluxing acetic acid for 2 h (34%) [201] [635].
*of resodiacetophenone diprenyl ether,
-with trifluoroacetic acid at 0° for 24 h (95%) [53];
-with boron trifluoride etherate in refluxing carbon tetrachloride (98%) [53].
-Also refer to: [57] [116] [288] [631] [669] [934] [940] [1023] [1037] [1086] [1229] [1231] [1249] [1284] [1389].
N.B.: Mono Na salt [52597-47-4] [192], di Na salt [52814-43-4] [378].

m.p. 185° [381] [734], 183° [448], 182-184° [201], 182-183° [42],
182° [114] [116] [374] [417] [598] [684] [817] [962] [1069],
181-184° [635], 181-182° [547], 180-180°5 [1435], 180° [339] [1070],
179°5 [457], 179-181° [1164], 178-180° [59],
178-179° [58] [127] [1057], 178° [313], 177-178° [1541], 176-177° [830];
^{1}H NMR [4] [830] [1057] [1103] [1164], ^{13}C NMR [4] [830],
IR [127] [1057], UV [298] [1037], MS [1103] [1164];
Crystal data [824]; Conductimetry [298]; Polarography [298].

1,1'-(2,4,5-Trihydroxy-1,3-phenylene)bis-ethanone

[2999-24-8] $C_{10}H_{10}O_5$ mol.wt. 210.19



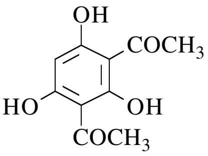
Syntheses

-Preparation by Fries rearrangement of 1,2,4-triacetoxybenzene with aluminium chloride,
*at 140° for 35 min [130], 64% [1297], 30% [625];
*at 160-170° for 2 h (60%) [383].
-Also obtained by oxidation of 2,4-diacetylresorcinol with potassium persulfate (Elbs reaction) [130].

m.p. 186-187° [130], 186° [625], 185° [383], 183° [1297].

1,1'-(2,4,6-Trihydroxy-1,3-phenylene)bis-ethanone

[2161-86-6] $C_{10}H_{10}O_5$ mol.wt. 210.19



Syntheses

-Preparation by Friedel-Crafts acylation of phloroglucinol,
*with acetic acid,
-by using boron trifluoride-acetic acid complex at 28-30° for 18 h (85%) [962];
-without cooling (71%) [263];
-or by heating on a steam bath for 2 h (60%) [991];
*with acetic anhydride,
-in the presence of boron trifluoride-ethyl ether complex at 20° for 1 h (80%) [374];
-in the presence of zinc chloride at 145-150° for 15 min (25%) [58];
-in the presence of concentrated sulfuric acid (24%) [684];
*with acetyl chloride,
-(4 equiv.) in the presence of ferric chloride [576] [629], (3%) [1082];
-in ethyl ether in the presence of aluminium chloride at r.t. for 5 days (8%) [601].
-Also obtained by Fries rearrangement of phloroglucinol triacetate with aluminium chloride at 160-170° for 2 h (10%) [383].
-Also obtained by monodecarbonylation of 2,4,6-triacetylphloroglucinol in 73% sulfuric acid at r.t. for 72 h [383].
-Also obtained by hydrolysis of 5-acetoxy-2,4-diacetyl-1,3-dihydroxybenzene [1337], in the presence of 70% sulfuric acid [1082].
-Also refer to: [25] [1456] [1547].

Isolation from natural sources

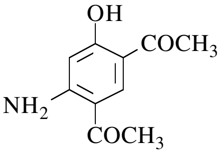
-This compound is one of the antifungal metabolites produced by *Pseudomonas fluorescens* [1] [2] [132] [203] [235] [349] [350] [422] [423] [424] [919] [1067] [1088] [1104] [1205] [1206] [1241] [1333] [1455].
-Production in the rhizosphere by strains of fluorescent *Pseudomonas* spp. [546].
-Also produced by a bacterial symbiot of the white-backed planthopper (insect), *Sogatella furcifera* [510] [781].
-Also produced by a fungal ectosymbiot of an ambrosia beetle (insect), *Scolytoplatypus mikado* [781].
N.B.: An hemihydrate was obtained by crystallisation of ketone in aqueous ethanol [235] and a monohydrate in 20% aqueous acetic acid [576]. The melting points are determined after solvents elimination.

m.p. 173° [58], 172-173° [1337], 171° [601], 170° [576], 168-170° [235] [991],
168° [263] [374] [383] [599] [962], 153° [684].

One of the reported melting points is obviously wrong.
^{1}H NMR [991], IR [235] [991], UV [235] [263]; TLC [235].

1,1'-(4-Amino-6-hydroxy-1,3-phenylene)bis-ethanone

[79324-45-1] $C_{10}H_{11}NO_3$ mol.wt. 193.20



Syntheses

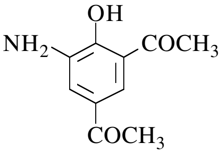
-Preparation by hydrolysis of 3-acetamido-4,6-diacetylphenol (m.p. 201-202°) with concentrated hydrochloric acid in refluxing ethanol for 5 h (91%) [1227] or for 3.5 h (60%) [458].

-Preparation by hydrolysis of 2-amino-5-(1-iminoethyl)-4-hydroxyacetophenone (SM) on heating with aqueous hydrochloric acid. SM was obtained by heating a mixture of resodiacetophenone, aqueous ammonia and concentrated hydrochloric acid as a catalyst in an autoclave during 8 to 72 h [60].

m.p. 227-230° [1227].

1,1'-(5-Amino-4-hydroxy-1,3-phenylene)bis-ethanone

[100245-11-2] $C_{10}H_{11}NO_3$ mol.wt. 193.20



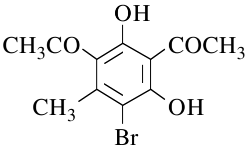
Synthesis

-Preparation by hydrogenation of 5-acetyl-2-hydroxy-3-nitroacetophenone using 5% Pd/C as a catalyst in ethanol (49%) [506].

m.p. 156-160° (d) [506].

1,1'-(5-Bromo-2,4-dihydroxy-6-methyl-1,3-phenylene)bis-ethanone

$C_{11}H_{11}BrO_4$ mol.wt. 287.11



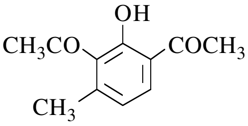
Synthesis

-Obtained by reaction of bromine with 2,4-diacetyl-3,5-dihydroxytoluene (diacetylorcinol) in acetic acid [318].

m.p. 79° [318].

1,1'-(2-Hydroxy-4-methyl-1,3-phenylene)bis-ethanone

[131941-97-4] $C_{11}H_{12}O_3$ mol.wt. 192.21



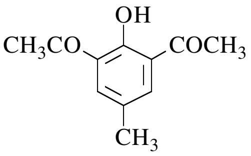
Synthesis

-Obtained by Fries rearrangement of m-cresyl acetate with aluminium chloride [783] [784].

^{13}C NMR [783].

1,1'-(2-Hydroxy-5-methyl-1,3-phenylene)bis-ethanone

[55108-28-6] $C_{11}H_{12}O_3$ mol.wt. 192.21



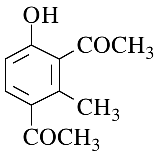
Syntheses

-Preparation by Friedel-Crafts acylation of p-cresol with excess acetyl chloride in nitrobenzene in the presence of aluminium chloride [107] [108], at 60° for 6 h (42%) [959], (20%) [1248].
-Also obtained by Friedel-Crafts acylation of p-cresol methyl ether with excess acetyl chloride in the presence of aluminium chloride [95].
Also obtained by Fries rearrangement of p-cresyl acetate with aluminium chloride [10] [783].
-Preparation by Fries rearrangement of 2-(acetyloxy)-5-methylacetophenone with aluminium chloride,
*at 100-120° for 10 min (76%) [1247];
*at 130° for 1 h, then at 140° for 1 h (70%) [1312].
-Also refer to: [7] [66] [138] [265] [266] [363] [364] [432] [958] [1014] [1072].
N.B.: Metal complexes of binucleating ligands: Cu (II) [107] [265] [266] [958], Ni (II) [265] and UO_2 (VI) [265]; Li salt (compound 2) [785].
Dioxime [188].

m.p. 83° [1247], 82-83° [95], 82° [959] [1248];
b.p.$_5$ 85-87° [1312], b.p.$_{18}$ 194° [1247];
^{1}H NMR [568] [783] [959], ^{13}C NMR [783], IR [959],
UV [364] [957] [959]; emission spectra [1014].

1,1'-(4-Hydroxy-2-methyl-1,3-phenylene)bis-ethanone

[170802-46-7] $C_{11}H_{12}O_3$ mol.wt. 192.21



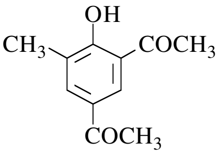
Synthesis

-Obtained by Fries rearrangement of m-cresyl acetate with aluminium chloride [783].

^{1}H NMR [783], ^{13}C NMR [783].

1,1'-(4-Hydroxy-5-methyl-1,3-phenylene)bis-ethanone

[23133-81-5] $C_{11}H_{12}O_3$ mol.wt. 192.21



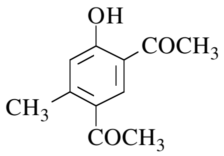
Syntheses

-Obtained by Fries rearrangement of o-cresyl acetate with aluminium chloride [783].
-Also refer to: [1077].

^{13}C NMR [783].

1,1'-(4-Hydroxy-6-methyl-1,3-phenylene)bis-ethanone

[16475-85-7] $C_{11}H_{12}O_3$ mol.wt. 192.21



Syntheses

-Preparation by cyclization of 1,1,3,3-tetraacetylpropene (formerly so called methenylbisacetylacetone) (SM) (m.p. 117-118°) [309],

*by adding a solution of SM (1 mol) in benzene to a sodium methoxide (4 mol) or magnesium methoxide (4 mol) solution in methanol and set aside for 24 h (quantitative yields) [346];

*on heating of its potassium salt in alcoholic solution for 6-8 h at reflux. SM was prepared by treatment of ethoxymethyleneacetylacetone (m.p. 140-142°) with the potassium salt of acetylacetone in ethanol [309].

-Also obtained directly by heating together sodioacetylacetone and ethoxymethyleneacetylacetone at 100° for 30 min [347].

-Also obtained by Fries rearrangement of m-cresyl acetate with aluminium chloride [134] [783] [784].

-Also obtained by heating a mixture of 3,5-diacetyl-2,4-heptanedione (m.p. 33-35°) and triethylammonium formate (TEAF) at 145-150° for 5 h with stirring in a constant stream of air (28%) [1306].

-Also obtained by heating a mixture of 4,6-diacetyl-3-methyl-2-cyclohexen-1-one and TEAF at 145-150° for 4 h with stirring in a stream of oxygen (33%) [1306].

-Also obtained from 1,1,3,3-tetraacetylpropane (formerly so called methylenebisacetylacetone) (SM1) (m.p. 87-88°),

*by reaction with concentrated sulfuric acid under oxygen of the air during short-lived — *via* the formation of 4,6-diacetyl-3-methyl-2-cyclohexen-1-one — (m.p. 75°) [822];

*in chloroformic solution with hydrogen chloride under oxygen of the air [822];

*SM1 (1 vol) in solution of 20% hydrochloric acid (3-4 vol) during 5 to 8 days at r.t. (44%). SM1 was obtained by condensation of formaldehyde with acetylacetone [822].

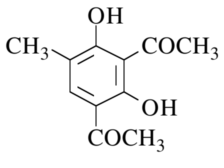
-Also refer to: [342] [343] [348] [1247].

N.B.: Ba [309] and K salts [309] [822].

m.p. 112° [309], 108° [346], 106° [822], 105° [347], 104-105° [1306];
b.p. 310° (without decomposition) [309]; TLC [346];
^{1}H NMR [346] [347] [783] [1306], ^{13}C NMR [783],
IR [346] [347] [1306], UV [346] [347] [1306], MS [346].

1,1'-(2,4-Dihydroxy-5-methyl-1,3-phenylene)bis-ethanone

$C_{11}H_{12}O_4$ mol.wt. 208.21



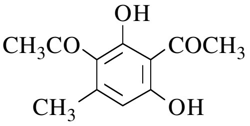
Synthesis

-Obtained by Fries rearrangement of 4,6-dimethylresorcinol diacetate (m.p. 44°) with aluminium chloride by heating, first at 120° and then raising the temperature to 180° over a period of an hour (19%) [337]. **N.B.**: One of the methyl groups was displaced during the reaction.

m.p. 83-84° [337].

1,1'-(2,4-Dihydroxy-6-methyl-1,3-phenylene)bis-ethanone

[13444-19-4] $C_{11}H_{12}O_4$ mol.wt. 208.21



Syntheses

-Preparation by Fries rearrangement of orcinol diacetate (m.p. 25°) [370] with aluminium chloride, at 140-150° for 1.5 h (80%) [384], at 150° for 2 h (42%) [1285].

-Also obtained by acylation of γ-orcacetophenone or β-orcacetophenone with acetic anhydride in nitrobenzene in the presence of aluminium chloride in a water bath for 6 h (15-20%) [386].

-Also obtained by reaction of acetyl chloride with an anhydrous disodium salt (SM) in chloroform (major product). SM was prepared by action of sodium ethoxide with diacetylacetone or dimethylpyrone in ethanol [318].

-Also obtained (small amount) during an attempt to acylate 2-acetylfuran with a 3-fold excess acetyl chloride in the presence of aluminium chloride, first between 20 to 45°, then at 115° for 3 h. This diketone was formed by self-condensation of acetyl chloride in these conditions [154].

-Also obtained by decarboxylation of 3,5-diacetyl-o-orsellinic acid [1285].

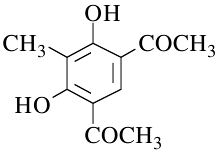
-Also obtained in two steps: first, reaction of acetyl chloride with diacetyl acetone disodium salt in chloroform at 20° for 1 h., then, after elimination of solvent, treatment of the residue in refluxing 3 N sodium hydroxide for 30 min [446].

-Also obtained by reaction of acetic anhydride with orcinol in concentrated sulfuric acid at 130° for 15 min [446], according to the method [684].

m.p. 96° [1285], 95° [318] [386] [446], 94-95° [154];
^{1}H NMR [154] [446], IR [446], MS [154] [446].

1,1'-(4,6-Dihydroxy-5-methyl-1,3-phenylene)bis-ethanone

[22304-66-1] $C_{11}H_{12}O_4$ mol.wt. 208.21



Syntheses

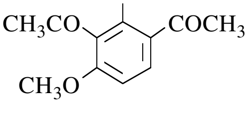
-Preparation by Fries rearrangement of 2,6-diacetoxytoluene with aluminium chloride in nitrobenzene,
*at 75° for 3 h, under nitrogen (63%) [1103] [1164];
*at 67° for 4 h (58%) [1542].

-Preparation by reaction of acetic anhydride with 2-methylresorcinol,
*in the presence of sodium acetate at reflux for 8 h (83%) [1542];
*in the presence of zinc chloride at 142° for 15 min (60%) [19].

m.p. 146-147° [19], 139-142° [1542], 137-139° [1103] [1164];
^{1}H NMR [19] [1103] [1164], IR [19], MS [1103] [1164].

1,1'-(2-Hydroxy-4-methoxy-1,3-phenylene)bis-ethanone

[64857-81-4] $C_{11}H_{12}O_4$ mol.wt. 208.21



Syntheses

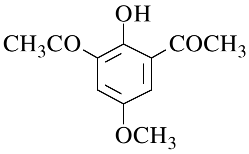
-Preparation by Friedel-Crafts acylation of paeonol with acetic anhydride,
*in acetic acid in the presence of boron trifluoride at 50° for 1 h [374];

*in nitrobenzene in the presence of aluminium chloride at r.t. for 72 h [734].
-Preparation by methylation of 2,4-diacetylresorcinol [734], with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 2 h (51%) [374] or for 8 h (50%) [111].
-Also obtained by hydrolysis of 2-(3-acetyl-2-hydroxy-4-methoxyphenyl)-2-methyl-1,3-dioxolane with a mixture of 5% aqueous hydrochloric acid and ethanol at r.t. for 5 min (almost quantitative yield) [111].

m.p. 104° [111] [374], 102° [734] [1063], 101-102° [544]; IR [544].

1,1'-(2-Hydroxy-5-methoxy-1,3-phenylene)bis-ethanone

[103867-90-9] $C_{11}H_{12}O_4$ mol.wt. 208.21



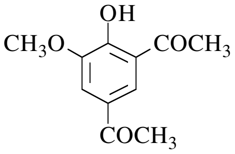
Synthesis

-Obtained by hydrolysis of 2-(3-acetyl-2-hydroxy-5-methoxyphenyl)-2-methyl-1,3-dioxolane with a mixture of 5% aqueous hydrochloric acid and ethanol at r.t. for 5 min (almost quantitative yield) [544].

m.p. 116-117° [544]; ^{1}H NMR [544], IR [544].

1,1'-(4-Hydroxy-5-methoxy-1,3-phenylene)bis-ethanone

[294888-77-0] $C_{11}H_{12}O_4$ mol.wt. 208.21

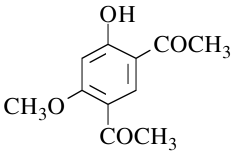


Synthesis

-Refer to: [1289].

1,1'-(4-Hydroxy-6-methoxy-1,3-phenylene)bis-ethanone

[99865-77-7] $C_{11}H_{12}O_4$ mol.wt. 208.21



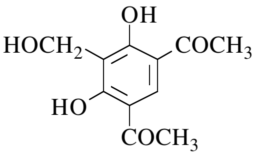
Syntheses

-Preparation by action of methyl iodide with the potassium salt of resodiacetophenone in ethanol [1463].
-Preparation by reaction of acetyl chloride (1 mol) with resorcinol dimethyl ether (0.15 mol) in the presence of aluminium chloride in carbon disulfide for 1 h (27%) [981].
-Preparation by reaction of acetic acid with resacetophenone monomethyl ether (m.p. 51°) in the presence of polyphosphoric acid for 10 min in a boiling water bath (36%) [1070].

m.p. 121-122° [981], 121°5 [448], 121° [1070], 120° [1463];
UV [298]; Conductimetry [298]; Polarography [298].

1,1'-[4,6-Dihydroxy-5-(hydroxymethyl)-1,3-phenylene]bis-ethanone

[58805-54-2] $C_{11}H_{12}O_5$ mol.wt. 224.21



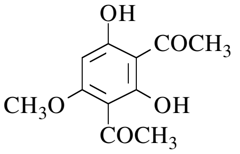
Synthesis

-Obtained by action of a 40% formaldehyde solution with resodiacetophenone in 1% aqueous sodium hydroxide at r.t. for 5 min (78%) [133].

m.p. 150-151° [133].

1,1'-(2,4-Dihydroxy-6-methoxy-1,3-phenylene)bis-ethanone

[3098-38-2] $C_{11}H_{12}O_5$ mol.wt. 224.21



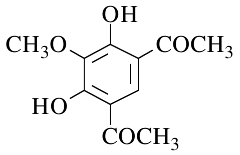
Syntheses

-Preparation by reaction of phloroglucinol monomethyl ether,
*with boron trifluoride-acetic acid complex at 100° for 4 h (80%) [962];
*with acetic anhydride and acetic acid in the presence of boron trifluoride at 20° for 1 h (81%) [374].
-Preparation by Fries rearrangement of phloroglucinol monomethyl ether diacetate in acetic acid in the presence of boron trifluoride at 75° for 15 min (66%) [619].
-Also obtained by partial demethylation,
*of 2,4-diacetylphloroglucinol trimethyl ether with boron trichloride, first at -70°, then at r.t. for 20 min (72%) [375];
*of 2,4-diacetyl-3,5-dimethoxyphenol with boron trifluoride in ethyl ether containing a small amount of acetic acid at r.t. for 24 h (10%) [374].
-Also obtained by monomethylation of 2,4-diacetylphloroglucinol [133] [259],
*with diazomethane in benzene [374];
*with methyl iodide in the presence of potassium carbonate in boiling acetone for 3 h [374].
-Also obtained by hydrogenolysis of 3-(benzyloxy)-2,6-diacetyl-5-methoxyphenol [374].
-Also obtained by treatment of 2,6-dihydroxy-4-methoxy-3-trichloroacetylacetophenone with zinc dust in acetic acid on a steam bath for 3 min (quantitative yield) [1535].
-Also refer to: [258].

m.p. 106° [374] [962], 105-106° [619], 105° [1535];
^{1}H NMR [202], ^{2}H NMR [202], ^{3}H NMR [202].

1,1'-(4,6-Dihydroxy-5-methoxy-1,3-phenylene)bis-ethanone

[144632-80-4] $C_{11}H_{12}O_5$ mol.wt. 224.21



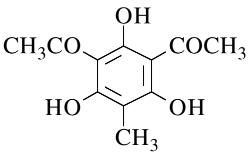
Synthesis

-Obtained by reaction of acetonitrile with pyrogallol 2-methyl ether in the presence of triflic acid, first at r.t. for 8 days, and at reflux for 30 min (20%) [1213].

m.p. 130-132° [1213];
^{1}H NMR [1213], IR [1213], MS [1213].

1,1'-(2,4,6-Trihydroxy-5-methyl-1,3-phenylene)bis-ethanone

[2999-42-0] $C_{11}H_{12}O_5$ mol.wt. 224.21



Syntheses

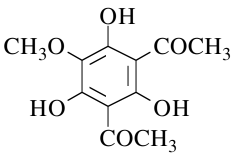
-Preparation by Friedel-Crafts acylation of 2-methylphloroglucinol with acetic anhydride/acetic acid in the presence of excess boron trifluoride,
*at r.t. for 20 h (56%) [374];
*first at r.t., then heating on a steam bath for 2 h [299], (21%) [991].

-Also obtained by UV irradiation of a d-usnic acid solution in THF for 12 h at -20° under oxygen (13%) [1429].
-Also obtained by UV irradiation of a decarbousnic acid solution in THF for 8 h at -20° under oxygen (6%) [1429].
-Also obtained by hydrolysis of 2,4-diacetyl-3,5-dihydroxy-6-methylphenyl acetate with concentrated sulfuric acid for 10 min in cold (78%) [1429].
-Also obtained by saponification of its diacetate (SM) —1,1'-[4,6-di(acetyloxy)-2-hydroxy-5-methyl-1,3-phenylene]bis-ethanone — with refluxing 2 N sodium carbonate for 10 min (69%). SM was prepared from the ozonid of diacetyldecarbousnic acid ($C_{21}H_{22}O_{11}$, m.p. 146°) by treatment with boiling 3% methanolic hydrogen chloride for 5 min (73%, m.p. 116°) [1300].
-Also refer to: [300] [1547].

m.p. 172° [1429], 169-170° [991], 168° [1300], 160° [374]; TLC [1429];
^{1}H NMR [991] [1429], IR [991], UV [1429], MS [1429].

1,1'-(2,4,6-Trihydroxy-5-methoxy-1,3-phenylene)bis-ethanone

[17678-03-4] $C_{11}H_{12}O_6$ mol.wt. 240.21



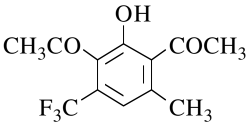
Synthesis

-Obtained by reaction of iretol with boron trifluoride-acetic acid complex at r.t. for 20 h (52%) [1175].

m.p. 140° [1175].

1,1'-[2-Hydroxy-4-methyl-6-(trifluoromethyl)-1,3-phenylene]bis-ethanone

[76716-15-9] $C_{12}H_{11}F_3O_3$ mol.wt. 260.21



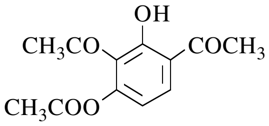
Synthesis

-Obtained (poor yield) by condensation of 2,4,6-heptanetrione (1 mol) and 1,1,1-trifluoro-2,4-pentanedione (1 mol) in the presence of sodium hydroxide in 50% aqueous methanol at 25° for 25 h (13%) [165].

m.p. 83-85° [165]; ^{1}H NMR [165], ^{19}F NMR [165].

1,1'-[4-(Acetyloxy)-2-hydroxy-1,3-phenylene]bis-ethanone

[116470-16-7] $C_{12}H_{12}O_5$ mol.wt. 236.22



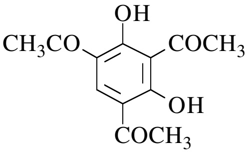
Synthesis

-Obtained by heating at reflux (180°) for 1 h a mixture of 2,4-diacetylresorcinol, sodium acetate and acetic anhydride (29%) [57].

m.p. 147-148° [57]; ^{1}H NMR [57], IR [57], UV [57].

1,1',1''-(2,4-Dihydroxy-1,3,5-benzenetriyl)tris-ethanone

[64857-82-5] $C_{12}H_{12}O_5$ mol.wt. 236.22



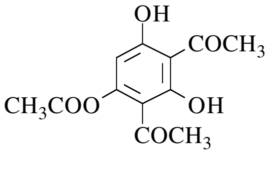
Syntheses

-Obtained by heating 2,4-diacetoxyacetophenone with aluminium chloride (29%) (Fries rearrangement) [760].
-Also obtained (by-product) by Friedel-Crafts acylation of resorcinol dimethyl ether with acetyl chloride in the presence of aluminium chloride in carbon disulfide at 10° for 1 h (5%) [374].
-Also obtained by Friedel-Crafts acylation of paeonol with acetic anhydride in the presence of aluminium chloride in nitrobenzene at 100° for 2 h [734].
-Also obtained by reaction of acetic anhydride (2 mol) with resacetophenone (1 mol) in the presence of aluminium chloride (3 mol) in nitrobenzene on a steam bath for 4 h (51%) [1467].
-Also obtained by reaction of acetyl chloride with 4,6-diacetylresorcinol in the presence of aluminium chloride, first at 110° for 15 min, then at 130° for 1 h (73%) [921].
-Also obtained by degradation of 7,7'-diacetoxy-4,4'-dimethyl-3,4-dihydro-4,6'-bicoumarin with aluminium chloride in dilute hydrochloric acid between 135-170° for 2 h (5%) [760].

m.p. 137-138° [1467], 137° [374], 136° [734] [921], 135-136°5 [760];
^{1}H NMR [760], MS [760].

1,1'-[4-(Acetyloxy)-2,6-dihydroxy-1,3-phenylene]bis-ethanone

[104654-31-1] $C_{12}H_{12}O_6$ mol.wt. 252.22



Synthesis

-Obtained by UV light irradiation of 1,3,5-triacetoxybenzene in methanol at r.t. for 12 h under nitrogen (25%) [1337].

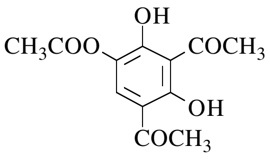
Isolation from natural sources

-From *Hypericum japonicum* Thunb. and *Agromonia pilosa* Ledb. [1547].

m.p. 150° [1337].

1,1'-[5-(Acetyloxy)-2,4-dihydroxy-1,3-phenylene]bis-ethanone

[55168-30-4] $C_{12}H_{12}O_6$ mol.wt. 252.22



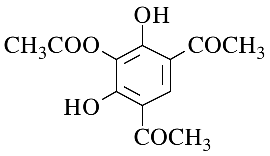
Synthesis

-Obtained by treatment of 1,2,4-triacetoxybenzene with acetic acid and zinc chloride at 130° for 1 h (24%) [1297] or at 140° for 30 min (9%) [1098].

m.p. 142-143° [1098], 142° [1297];
^1H NMR [1098] [1297], IR [1098] [1297], MS [1297].

1,1'-[5-(Acetyloxy)-4,6-dihydroxy-1,3-phenylene]bis-ethanone

[104654-32-2] $C_{12}H_{12}O_6$ mol.wt. 252.22



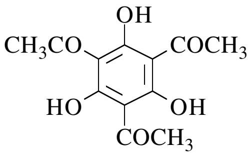
Syntheses

-Obtained by photolysis of 1,2,3-triacetoxybenzene in methanol at r.t. for 12 h under nitrogen (20%) [1337].
-Also obtained by reaction of acetic acid with gallacetophenone in the presence of zinc chloride and phosphorous oxychloride at 140-150° for 30 min [339], according to [630].

m.p. 209-210° [1337], 207-209° [339].

1,1',1"-(2,4,6-Trihydroxy-1,3,5-benzenetriyl)tris-ethanone

[2161-87-7] $C_{12}H_{12}O_6$ mol.wt. 252.22



Syntheses

-Obtained by Friedel-Crafts acylation of phloroglucinol,
*with acetic anhydride in the presence of boron trifluoride in acetic acid at r.t. (60%) [374];
*with acetyl chloride in the presence of aluminium chloride in ethyl ether at r.t. for 6 days (17%) [601];
*with acetyl chloride and acetic acid in the presence of ferric chloride in ethyl acetate [576].
-Also obtained by Fries rearrangement of phloroglucinol triacetate,
*in the presence of aluminium chloride,
  -without solvent [382], at 160-170° (40%) [383];
  -in nitrobenzene at r.t. for 4 h [383];
*in the presence of zinc chloride at 130°(40-50%) [817], for 3 h (60%) [628].
-Also refer to: [258] [319] [444] [599] [1547].
N.B.: Tri-Na salt [322] [323].

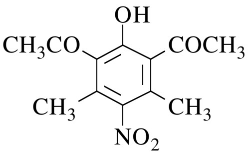
Isolation from natural sources

-From *Pseudomonas fluorescens* [235].

sublimation at 140°/15 mm [601]; TLC [235] [601];
m.p. 158-159° [383], 156° [374] [576] [628], 152-153° [601];
^1H NMR [4] [202] [601], ^2H NMR [202], ^3H NMR [202], ^{13}C NMR [4], MS [235].

1,1'-(2-Hydroxy-4,6-dimethyl-5-nitro-1,3-phenylene)bis-ethanone

[85450-67-5] $C_{12}H_{13}NO_5$ mol.wt. 251.24



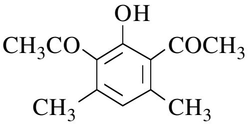
Synthesis

-Obtained by reaction of nitromethane with 3,5-diacetyl-2,6-dimethyl-4-pyrone in the presence of potassium tert-butoxide in tert-butanol at 30-40° for 75 min (74%) [447].

m.p. 117-119° [447].

1,1'-(2-Hydroxy-4,6-dimethyl-1,3-phenylene)bis-ethanone

[66634-65-9] $C_{12}H_{14}O_3$ mol.wt. 206.24



Syntheses

-Obtained by Friedel-Crafts acylation of 3,5-dimethylphenol with acetyl chloride in the presence of aluminium chloride in boiling carbon disulfide for some hours [97], (40%) [92], (36%) [103].

-Also obtained by acylation of 3,5-dimethylanisole with acetyl chloride (6 mol) in the presence of a large excess of aluminium chloride in boiling carbon disulfide for 2 h, then, after solvent elimination, heating in a water bath for 4 h (33%) [92].

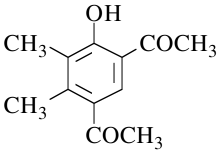
-Also obtained by Fries rearrangement of 3,5-dimethylphenyl acetate with aluminium chloride (2 mol) in a water bath for 2 h [97].

-Also obtained by condensation of 2,4,6-heptanetrione (1 mol) and 2,4-pentanedione (1 mol) in the presence of sodium hydroxide in 50% aqueous methanol at 25° for 25 h (50%) [165].

m.p. 109-110° [92] [97] [103], 102-105° [165]; ^{1}H NMR [165].

1,1'-(4-Hydroxy-5,6-dimethyl-1,3-phenylene)bis-ethanone

[51233-76-2] $C_{12}H_{14}O_3$ mol.wt. 206.24



Syntheses

-Obtained (by-product) by Fries rearrangement of 2,3-dimethylphenyl acetate with aluminium chloride at 135° for 30 min (< 10%) [821].

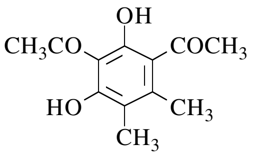
-A sample of pure 4-hydroxy-2,3-dimethylacetophenone (m.p. 144°) [970], stored in a stoppered bottle, was analyzed ten years later. The melting point (144°) was lowered to 138°. By treatment of the mixture in boiling heptane, the pure insoluble 4-hydroxy-2,3-dimethylacetophenone was recovered by filtration and thoroughly washed with boiling heptane (50%). The solution was then concentrated and the residue chromatographied on silica gel with benzene-ethyl acetate-acetic acid mixture (90/5/5) as eluent. The 2,3-dimethylphenol (25%) and the pure entitled diketone (25%) were isolated [965].

m.p. 101° [965]; TLC [965];
IR [965] 1685 cm^{-1} (C=O para), 1640 cm^{-1} (C=O ortho), UV [965].

N.B.: This transformation was unexpectedly obtained by a simple storage in a dry dull place.

1,1'-(2,4-Dihydroxy-5,6-dimethyl-1,3-phenylene)bis-ethanone

[82817-51-4] $C_{12}H_{14}O_4$ mol.wt. 222.24



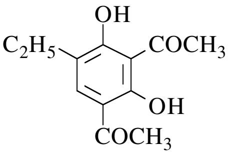
Synthesis

-Obtained by Fries rearrangement of 1,3-diacetoxy-4,5-dimethylbenzene with aluminium chloride at 115-120° for 30 min (54%) [278].

m.p. 78-80° [278]; IR [278], UV [278].

1,1'-(5-Ethyl-2,4-dihydroxy-1,3-phenylene)bis-ethanone

[63411-83-6] $C_{12}H_{14}O_4$ mol.wt. 222.24



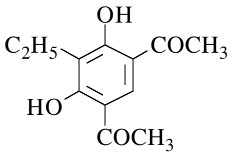
Synthesis

-Obtained by Fries rearrangement of 4,6-diethylresorcinol diacetate (1 mol) with aluminium chloride (2.2 mol) at 155° for 1 h (57%) [191].

m.p. 71-73° [191]; TLC [191].

1,1'-(5-Ethyl-4,6-dihydroxy-1,3-phenylene)bis-ethanone

$C_{12}H_{14}O_4$ mol.wt. 222.24



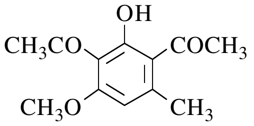
Synthesis

-Obtained by Fries rearrangement of 2-ethylresorcinol diacetate (m.p. 70-71°) with aluminium chloride at 150° for 30 min (84%) [921].

m.p. 110° [921].

1,1'-(2-Hydroxy-4-methoxy-6-methyl-1,3-phenylene)bis-ethanone

[78274-03-0] $C_{12}H_{14}O_4$ mol.wt. 222.24



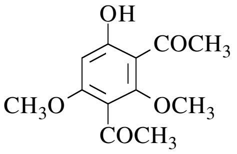
Synthesis

-Obtained by Friedel-Crafts acylation of 2-hydroxy-6-methoxy-4-methylacetophenone (yield 25%) or 2-hydroxy-4-methoxy-6-methylacetophenone with acetyl chloride in the presence of aluminium chloride [445].

m.p. 98° [445]; ^{1}H NMR [445], IR [445], MS [445].

1,1'-(4-Hydroxy-2,6-dimethoxy-1,3-phenylene)bis-ethanone

[72221-04-6] $C_{12}H_{14}O_5$ mol.wt. 238.24



Syntheses

-Obtained by debenzylation of 3-acetyl-6-(benzyloxy)-2,4-dimethoxyacetophenone (83%) [374].

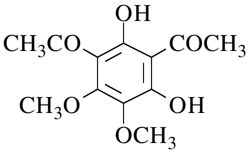
-Also obtained (by-product) by Friedel-Crafts acylation of phloroglucinol trimethyl ether with acetyl chloride in the presence of aluminium chloride in boiling carbon disulfide [1481]. **N.B.**: No direct proof of the constitution of the diketone was described, but it would appear most probable that it is 3-acetyl-6-hydroxy-2,4-dimethoxyacetophenone [1481].

-Also obtained by saponification of its veratric ester (m.p. 198°) in pyridine with powdered potassium hydroxide (pre-heated at 100°) at 50° for 1 h [922].

m.p. 192° [922], 127-128° [1481], 106° [374]. One note a very large dispersion of the various melting points.

1,1'-(2,4-Dihydroxy-5,6-dimethoxy-1,3-phenylene)bis-ethanone

[91498-04-3] $C_{12}H_{14}O_6$ mol.wt. 254.24



Synthesis

-Obtained from antiarol by reaction,

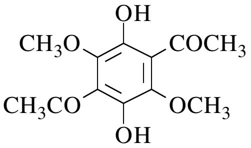
*with acetic anhydride in the presence of boron trifluoride in acetic acid at 30° (max.), followed by standing overnight (quantitative yield) [652];

*with acetyl chloride in the presence of aluminium chloride in nitrobenzene, during a short time on a steam bath (poor yield) [286].

m.p. 93°5-94°5 [652], 91-93° [286].

1,1'-(2,5-Dihydroxy-3,6-dimethoxy-1,4-phenylene)bis-ethanone

[34554-37-5] $C_{12}H_{14}O_6$ mol.wt. 254.24



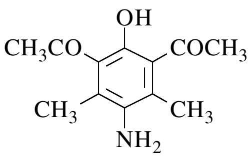
Synthesis

-Obtained (by-product) by metallation of 2,5-dimethoxyhydroquinonebis[tetrahydropyranyl (2) ether], followed by treatment of the intermediate aryllithium compound with acetic anhydride in THF at r.t. (3-5%) [1293].

m.p. 159° [1293].

1,1'-(5-Amino-2-hydroxy-4,6-dimethyl-1,3-phenylene)bis-ethanone

[85450-76-6] $C_{12}H_{15}NO_3$ mol.wt. 221.26



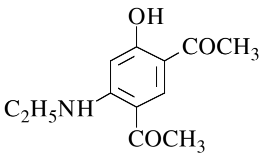
Synthesis

-Preparation by catalytic hydrogenation of 3-acetyl-2-hydroxy-4,6-dimethyl-5-nitroacetophenone in ethanol in the presence of 10% Pd/C at 40° for 3 days (61%) [447].

m.p. 111° [447].

1,1'-[4-(Ethylamino)-6-hydroxy-1,3-phenylene]bis-ethanone

[79324-49-5] $C_{12}H_{15}NO_3$ mol.wt. 221.26



Syntheses

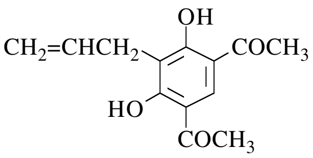
-Obtained by hydrolysis of 2-(ethylamino)-5-[1-(ethylimino)-ethyl]-4-hydroxyacetophenone on heating with aqueous hydrochloric acid [60].

-Also obtained first, by treatment of 3-acetamido-4,6-diacetylphenol with sodium hydride in N-methylpyrrolidone at < 5°. After 15 min, the mixture was treated with ethyl iodide at < 5° for 2 h, then acidified with concentrated hydrochloric acid/ethanol (1:1) and heated to reflux for 2.5 h (63%) [1227].

m.p. 103-104° [1227], 99° [60].

1,1'-[4,6-Dihydroxy-5-(2-propenyl)-1,3-phenylene]bis-ethanone

[75631-42-4] $C_{13}H_{14}O_4$ mol.wt. 234.25



Syntheses

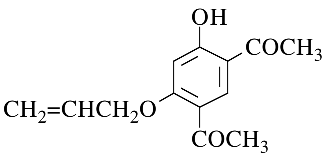
-Obtained (poor yield) by Claisen rearrangement of 4,6-diacetylresorcinol diallyl ether (m.p. 92°) in refluxing N,N-diethylaniline for 6 h (6%) [54].

-Also refer to: [60].

m.p. 93-94° [54]; MS [54].

1,1'-[4-Hydroxy-6-(2-propenyloxy)-1,3-phenylene]bis-ethanone

[117156-74-8] $C_{13}H_{14}O_4$ mol.wt. 234.25



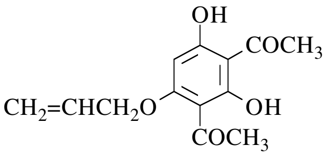
Synthesis

-Obtained by partial deallylation of 3-acetyl-4,6-di-(allyloxy)acetophenone (m.p. 92°) in trifluoroacetic acid, with stirring at 0°. Stirring was continued at r.t. for a further 24 h (70%) [55].

m.p. 95° [55]; TLC [55]; ^{1}H NMR [55], IR [55], UV [55].

1,1'-[2,4-Dihydroxy-6-(2-propenyloxy)-1,3-phenylene]bis-ethanone

[35075-32-2] $C_{13}H_{14}O_5$ mol.wt. 250.24



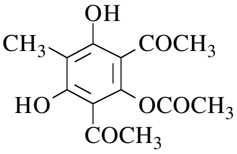
Synthesis

-Obtained by reaction of allyl bromide with 2,4-diacetylphloroglucinol in the presence of potassium carbonate in refluxing acetone for 48 h (27%) [133] [259].

m.p. 111-112° [133] [259].

1,1'-[2-(Acetyloxy)-4,6-dihydroxy-5-methyl-1,3-phenylene]bis-ethanone

$C_{13}H_{14}O_6$ mol.wt. 266.25



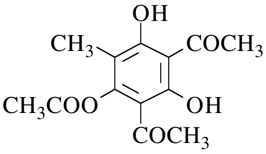
Synthesis

-Obtained by treatment of usnetol with ozone, in 20 parts of chloroform or acetic acid for 1 h [1300], (15-20%) [1299].

m.p. 172° [1299].

1,1'-[4-(Acetyloxy)-2,6-dihydroxy-5-methyl-1,3-phenylene]bis-ethanone

[69150-72-7] $C_{13}H_{14}O_6$ mol.wt. 266.25



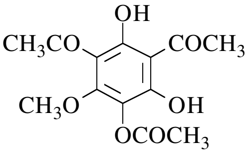
Synthesis

-Obtained by ozonolysis of diacetyldecarbousnic acid in carbon tetrachloride for 4 h at 15° [1429].

m.p. 120-121° [1429]; TLC [1429];
^{1}H NMR [1429], IR [1429], MS [1429].

1,1'-[5-(Acetyloxy)-2,4-dihydroxy-6-methoxy-1,3-phenylene]bis-ethanone

$C_{13}H_{14}O_7$ mol.wt. 282.25



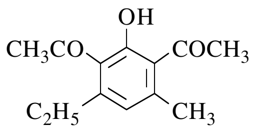
Synthesis

-Obtained by reaction of acetic anhydride with 2,6-dimethoxyhydroquinone diacetate in the presence of boron trifluoride in acetic acid at 30° (max), followed by standing overnight (60%) [652].

m.p. 98°5-100°2 [652].

1,1'-(4-Ethyl-2-hydroxy-6-methyl-1,3-phenylene)bis-ethanone

[76716-12-6] $C_{13}H_{16}O_3$ mol.wt. 220.27



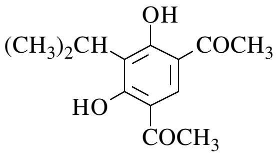
Synthesis

-Obtained by condensation of 2,4,6-heptanetrione (1 mol) and 2,4-hexanedione (1 mol) in the presence of sodium hydroxide in 50% aqueous methanol at 25° for 25 h (41%) [165].

m.p. 86-89° [165]; ^{1}H NMR [165].

1,1'-[4,6-Dihydroxy-5-(1-methylethyl)-1,3-phenylene]bis-ethanone

[75643-06-0] $C_{13}H_{16}O_4$ mol.wt. 236.27

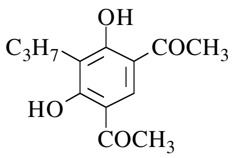


Synthesis

-Refer to: [498] (Japanese patent).

1,1'-(4,6-Dihydroxy-5-propyl-1,3-phenylene)bis-ethanone

[58805-52-0] $C_{13}H_{16}O_4$ mol.wt. 236.27

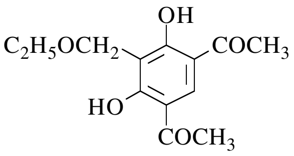


Syntheses

-Obtained by Fries rearrangement of 2-propylresorcinol diacetate with aluminium chloride for 1 h at 130-150° [133].
-Also refer to: [60] and [498] (Japanese patent).

1,1'-[5-(Ethoxymethyl)-4,6-dihydroxy-1,3-phenylene]bis-ethanone

[58805-51-9] $C_{13}H_{16}O_5$ mol.wt. 252.27



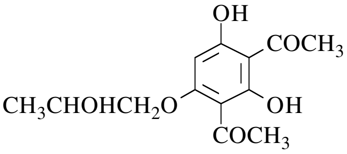
Synthesis

-Obtained by refluxing an ethanolic solution of 4,6-diacetyl-2-(hydroxymethyl)resorcinol in the presence of a small amount of concentrated sulfuric acid for 2 h (84%) [133].

m.p. 163-165° [133].

1,1'-[2,4-Dihydroxy-6-(2-hydroxypropoxy)-1,3-phenylene]bis-ethanone

[23937-51-1] $C_{13}H_{16}O_6$ mol.wt. 268.27



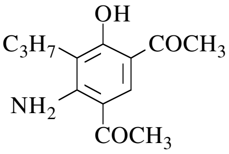
Synthesis

-Preparation by reaction of propylene oxide with 2,4-diacetylphloroglucinol in the presence of benzyl trimethyl ammonium hydroxide at 100° for 48 h (63%) [259].

m.p. 152-154° [259].

1,1'-(4-Amino-6-hydroxy-5-propyl-1,3-phenylene)bis-ethanone

[79324-47-3] $C_{13}H_{17}NO_3$ mol.wt. 235.28



Syntheses

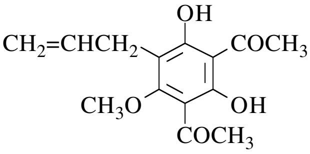
-Preparation by hydrogenation of 2-allyl-3-amino-4,6-diacetylphenol (SM) in ethanol in the presence of 5% Pd/C at atmospheric pressure and at r. t. (82%). SM was obtained by Claisen rearrangement of 3-(allyloxy)-4,6-diacetylaniline (m.p. 131-134°) in N-methylpyrrolidone under nitrogen at 200° for 3 h [1227].

-Also refer to: [321] [579] [1098].

m.p. 138-139° [1227].

1,1'-[2,4-Dihydroxy-6-methoxy-5-(2-propenyl)-1,3-phenylene]bis-ethanone

[37126-09-3] $C_{14}H_{16}O_5$ mol.wt. 264.28



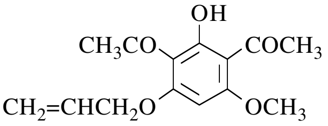
Synthesis

-Obtained by Claisen rearrangement of 2,6-diacetyl-3-(allyloxy)-5-methoxyphenol in refluxing tetralin for 3.5 h (25%) [133].

m.p. 84°5-85° [133].

1,1'-[2-Hydroxy-4-methoxy-6-(2-propenyloxy)-1,3-phenylene]bis-ethanone

[58805-53-1] $C_{14}H_{16}O_5$ mol.wt. 264.28



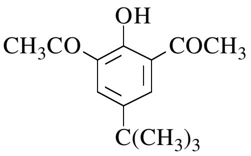
Synthesis

-Obtained by reaction of methyl iodide with 2,4-diacetyl-5-(allyloxy)resorcinol in the presence of potassium carbonate in refluxing acetone for 16 h (quantitative yield) [133].

red oil (crude product) [133]; b.p.$_{0.3}$ 148-162° [133].

1,1'-[5-(1,1-Dimethylethyl)-2-hydroxy-1,3-phenylene]bis-ethanone

[203004-96-0] $C_{14}H_{18}O_3$ mol.wt. 234.20



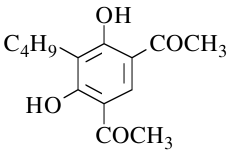
Synthesis

-Obtained by Friedel-Crafts acylation of p-tert-butylphenol with acetyl chloride (3 mol) in nitrobenzene in the presence of aluminium chloride at 65-70° overnight (45%) [1072].

m.p. 53-54° [1072]; ^{1}H NMR [1072], MS [1072].

1,1'-(5-Butyl-4,6-dihydroxy-1,3-phenylene)bis-ethanone

[40449-66-9] $C_{14}H_{18}O_4$ mol.wt. 250.29



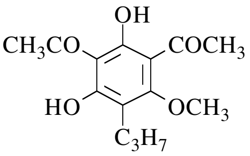
Syntheses

-Obtained by Fries rearrangement of 2-butylresorcinol diacetate with aluminium chloride for 1 h at 130-150° [133].
-Also refer to: [258] and [498] (Japanese patent).

m.p. 61-64° [133].

1,1'-(2,4-Dihydroxy-6-methoxy-5-propyl-1,3-phenylene)bis-ethanone

[37126-10-6] $C_{14}H_{18}O_5$ mol.wt. 266.29



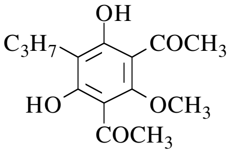
Synthesis

-Obtained by hydrogenation of 2,4-diacetyl-6-allyl-5-methoxyresorcinol in ethanol over 5% Pd/C at 3 atmospheres for 2 h (61%) [133].

m.p. 48-49° [133].

1,1'-(4,6-Dihydroxy-2-methoxy-5-propyl-1,3-phenylene)bis-ethanone

[37126-08-2] $C_{14}H_{18}O_5$ mol.wt. 266.29



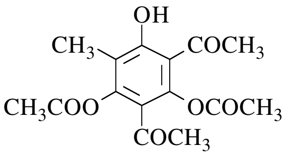
Syntheses

-Obtained by hydrogenation of 2,4-diacetyl-6-allyl-5-(benzyloxy)-3-methoxyphenol in ethanol containing hydrochloric acid at 3 atmospheres in the presence of 5% Pd/C for 1 h (61%) [133].
-Also refer to: [258] [500].

b.p.$_{0.6}$ 150-170° [133]; m.p. 80° [133].

1,1'-[2,4-(Diacetyloxy)-6-hydroxy-5-methyl-1,3-phenylene]bis-ethanone

$C_{15}H_{16}O_7$ mol.wt. 308.29



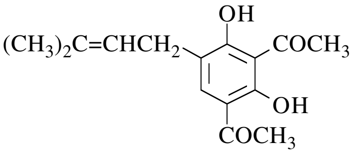
Synthesis

-Obtained from the ozonid of diacetyldecarbousnic acid ($C_{21}H_{22}O_{11}$, m.p. 146°) by treatment with boiling 3% methanolic hydrogen chloride for 5 min (73%) [1300].

m.p. 116° [1300]; sublimation without decomposition at 110°/12 mm [1300].

1,1'-[2,4-Dihydroxy-5-(3-methyl-2-butenyl)-1,3-phenylene]bis-ethanone

[117374-55-7] $C_{15}H_{18}O_4$ mol.wt. 262.31



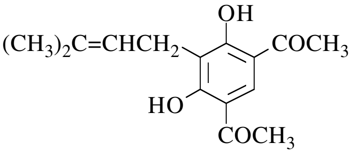
Syntheses

-Obtained by thermal rearrangement,
*of 3-acetyl-2,4-bis(3-methyl-2-butenyloxy)-acetophenone (m.p. 62°) in refluxing N,N-dimethylaniline for 1.5 h (11%) [697];
*of 5-acetyl-2,4-bis(3,3-dimethylallyloxy)-acetophenone (m.p. 103-104°), in refluxing N,N-dimethylaniline for 3 h (6%) [56], in refluxing n-decane for 18 h (6%) [56], in refluxing o-xylene for 90 h (10%) [56] or by heating in a sealed tube at 150° for 18 h (6%) or at 185° for 8 h (2%) [56].

m.p. 65-66° [56]; TLC [56]; ^{1}H NMR [56], IR [56], UV [56], MS [56].

1,1'-[4,6-Dihydroxy-5-(3-methyl-2-butenyl)-1,3-phenylene]bis-ethanone

[117374-56-8] $C_{15}H_{18}O_4$ mol.wt. 262.31



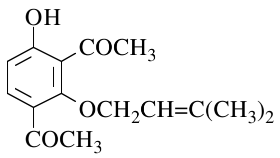
Syntheses

-Obtained (poor yields) by thermal rearangement of 5-acetyl-2,4-bis(3,3-dimethylallyloxy)acetophenone (m.p. 103-104°),
*in refluxing n-decane for 18 h (8%) [56];
*in refluxing o-xylene for 90 h (11%) [56];
*by heating in a sealed tube at 150° for 8 h (10%) [56].

m.p. 89-90° [56]; TLC [56]; ^{1}H NMR [56], IR [56], UV [56], MS [56].

1,1'-[4-Hydroxy-2-[(3-methyl-2-butenyl)oxy]-1,3-phenylene]bis-ethanone

[136811-82-0] $C_{15}H_{18}O_4$ mol.wt. 262.31



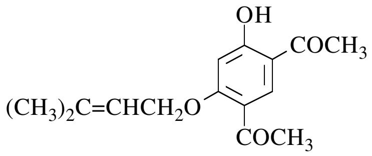
Syntheses

-Obtained by Claisen rearrangement of 3-acetyl-2,4-bis (3-methyl-2-butenyloxy)acetophenone with palladium chloride-bis(acetonitrile) in refluxing dioxane for 45 min (29%) [53].
-Also refer to: [52].

m.p. 51° [53]; ^{1}H NMR [53], IR [53], UV [53], MS [53].

1,1'-[4-Hydroxy-6-[(3-methyl-2-butenyl)oxy]-1,3-phenylene]bis-ethanone

[136811-83-1] $C_{15}H_{18}O_4$ mol.wt. 262.31



Syntheses

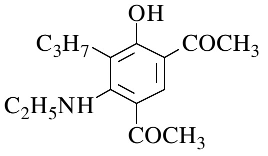
-Obtained by Claisen rearrangement of 5-acetyl-2,4-bis(3-methyl-2-butenyloxy)acetophenone,
*with palladium chloride-bis(acetonitrile) in refluxing dioxane for 4 h (95%) [53];
*with boron trifluoride etherate at r.t. for 7 days (48%) [53].

-Also refer to: [52].

m.p. 83-87° [53]; ^{1}H NMR [53], UV [53], MS [53].

1,1'-[4-(Ethylamino)-6-hydroxy-5-propyl-1,3-phenylene]bis-ethanone

[79324-51-9] $C_{15}H_{21}NO_3$ mol.wt. 263.34



Syntheses

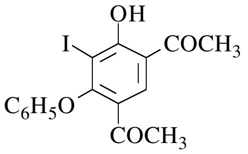
-Preparation by hydrogenation of 2-allyl-3-hydroxy-4,6-diacetyl-N-ethylaniline (SM) in ethanol in the presence of 5% Pd/C at 15-20 psi for 2.5 h (63%). SM was obtained by Claisen rearrangement of 3-(allyloxy)-4,6-diacetyl-N-ethylaniline (m.p. 82-83°) in refluxing N-methylpyrrolidone under nitrogen for 1 h [1227].

-Also refer to: [321].

m.p. 114-115° [1227].

1,1'-(4-Hydroxy-5-iodo-6-phenoxy-1,3-phenylene)bis-ethanone

[145489-92-5] $C_{16}H_{13}IO_4$ mol.wt. 396.18



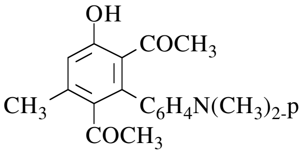
Synthesis

-Preparation by thermal rearrangement of 4,6-diacetyl-3-hydroxy-2-phenyliodoniophenolate (SM) in refluxing acetonitrile for 30 min (50%). SM was obtained by reaction of iodosobenzene diacetate with resodiacetophenone in methanol in the presence of potassium hydroxide, at 0° for 30 min (40%, m.p. 120-130°) [1389].

m.p. 132-136° [1389]; ^{1}H NMR [1389], IR [1389], MS [1389].

1,1'-[4'-(Dimethylamino)-3-hydroxy-5-methyl[1,1'-biphenyl]-2,6-diyl]bis-ethanone

[108909-50-8] $C_{19}H_{21}NO_3$ mol.wt. 311.38



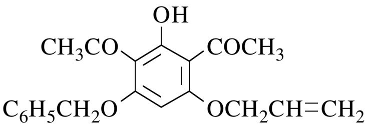
Synthesis

-Obtained by aromatization of 4,6-diacetyl-5-[4-(dimethylamino)phenyl]-3-methyl-2-cyclohexen-1-one (m.p. 117°) with bromine in chloroform (45%) or by heating at 170° for 3 h [605].

m.p. 153° [605]; IR [605].

1,1'-[2-Hydroxy-4-(phenylmethoxy)-6-(2-propenyloxy)-1,3-phenylene]bis-ethanone

[37126-05-9] $C_{20}H_{20}O_5$ mol.wt. 340.38



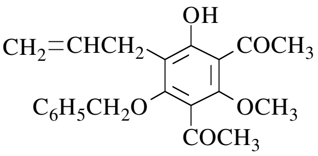
Synthesis

-Obtained by reaction of benzyl chloride with 2,4-diacetyl-5-(allyloxy)resorcinol in the presence of potassium carbonate and potassium iodide in refluxing acetone for 43 h (33%) [133].

m.p. 92° [133].

1,1'-[4-Hydroxy-2-methoxy-6-(phenylmethoxy)-5-(2-propenyl)-1,3-phenylene]bis-ethanone

$C_{21}H_{22}O_5$ mol.wt. 354.40



Syntheses

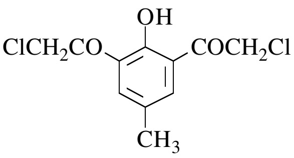
-Obtained by Claisen rearrangement of 3-acetyl-4-allyloxy-6-benzyloxy-2-methoxyacetophenone in refluxing tetralin under nitrogen for 4 h (36%) [133].
-Also refer to: [258] [500].

oil [133].

11.1.2. Diversely substituted acetyl groups

1,1'-(2-Hydroxy-5-methyl-1,3-phenylene)bis[2-chloroethanone

[99984-12-0] $C_{11}H_{10}Cl_2O_3$ mol.wt. 261.10



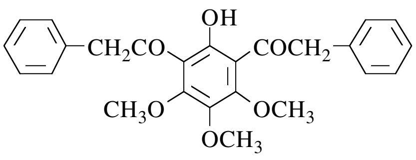
Syntheses

-Obtained (by-product) by Friedel-Crafts acylation of p-cresol methyl ether with chloroacetyl chloride in the presence of aluminium chloride in refluxing carbon disulfide for 4-5 h [95].
-Also obtained by Friedel-Crafts acylation of p-cresol with chloroacetyl chloride in the presence of aluminium chloride at 140° for 4 h [518].

m.p. 168° [518], 167-168° [95].

1,1'-(2-Hydroxy-4,5,6-trimethoxy-1,3-phenylene)bis[2-phenylethanone
3,4,5-Trimethoxy-2,6-bis(phenylacetyl)phenol

[22228-86-0] $C_{25}H_{24}O_6$ mol.wt. 420.46



Syntheses

-Obtained by Friedel-Crafts acylation of 6-hydroxy-2,3,4-trimethoxyphenyl benzyl ketone with phenylacetyl chloride in the presence of aluminium chloride [601].
-Also obtained (by-product) by Friedel-Crafts

acylation of antiarol with phenylacetyl chloride in the presence of aluminium chloride (< 3%) [601].

m.p. 106° [601]; ^{1}H NMR [601], IR [601].

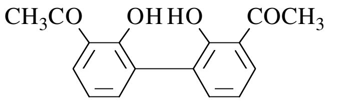
11.2. *Acetyl groups located on different rings*

11.2.1. Diphenyl derivatives

Symmetrical ketones

1,1'-(2,2'-Dihydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[60312-44-9] $C_{16}H_{14}O_4$ mol.wt. 270.28



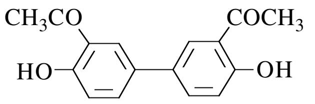
Synthesis

-Obtained by alkaline degradation of 8,8'-bichromonyl (m.p. 326°) with refluxing 10% sodium hydroxide for 20 min [1195].

m.p. 167-168° [1195]; IR [1195].

1,1'-(4,4'-Dihydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[13938-28-8] $C_{16}H_{14}O_4$ mol.wt. 270.28



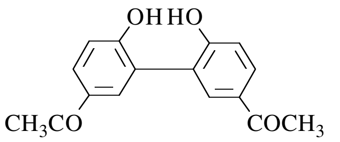
Syntheses

-Preparation by Fries rearrangement of 4,4'-diacetoxybiphenyl,
*with a mixture of aluminium chloride and sodium chloride (5:1, w/w), first at 140°, then at 200° for 2 min (melting) (70%) [1011];
*with a mixture of aluminium chloride and zinc chloride (5:1, w/w), first at 140°, then at 200° for 2 min (melting) (82%) [1011];
*with aluminium chloride at 120° [761], (75%) [205] [1405];
*with aluminium chloride in refluxing chlorobenzene for 24 h (19%) [1127].
-Also obtained by alkaline degradation of 6,6'-bichromonyl (m.p. 298-299°) with refluxing 10% sodium hydroxide for 20 min [1195].
-Also refer to: [90] [787].

m.p. 219-220° [205], 219-219°5 [1405], 215-216° [1127], 209-210° [1195]; IR [1127].

1,1'-(6,6'-Dihydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[23080-48-0] $C_{16}H_{14}O_4$ mol.wt. 270.28



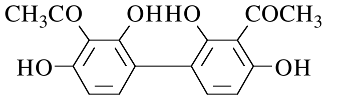
Syntheses

-Preparation by Fries rearrangement of 2,2'-diacetoxybiphenyl (1 mol) with aluminium chloride (1 mol) at 110-120° for 4 h (52%) [761].
-Also obtained by Friedel-Crafts acylation of 2,2'-dihydroxybiphenyl (1 mol) with acetyl chloride (4 mol) in the presence of aluminium chloride (4 mol) at 110-120° [761].

m.p. 275° [761].

1,1'-(2,2',4,4'-Tetrahydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[2551-44-2] $C_{16}H_{14}O_6$ mol.wt. 302.28



Syntheses

-Obtained by refluxing a solution of 9,9'-di-O-methylergoflavinone — m.p. 330° (d) — in 50% aqueous potassium hydroxide for 30 min (10%) [64].

-Also obtained (poor yield) by Fries rearrangement of 6,6'-bi-(7-acetoxy-4-methylcoumarin) (m.p. 327°) with aluminium chloride at 260° for 75 min, followed by heating the resulting 6,6'-bi-(8-acetyl-7-hydroxy-4-methylcoumarin) with 20% (w/v) aqueous sodium hydroxide on a steam bath for 5 h under nitrogen (< 3%) [65].

-Also obtained by Fries rearrangement of 2,2',4,4'-tetraacetoxybiphenyl (1 mol) with aluminium chloride (4 mol),

*without solvent at 130-140° for 4 h (27%) [761];

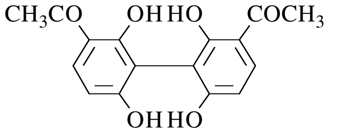
*in nitrobenzene at r.t. for 24 h [761].

-Also refer to: [509].

m.p. 249-250° [64], 248-249° [65], 245° [761]; IR [64].

1,1'-(2,2',6,6'-Tetrahydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[93107-98-3] $C_{16}H_{14}O_6$ mol.wt. 302.28



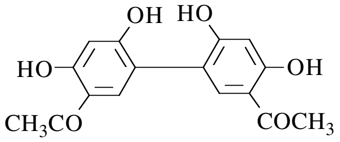
Synthesis

-Obtained by oxidative coupling of resacetophenone using silica-bound ferric chloride, first in methylene chloride, then, after solvent elimination, the residue left at r.t. for a week (13%) [1149].

m.p. 286-287° [1149]; TLC [1149]; IR [1149].

1,1'-(4,4',6,6'-Tetrahydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[23080-53-7] $C_{16}H_{14}O_6$ mol.wt. 302.28



Syntheses

-Obtained by Fries rearrangement of 2,2',4,4'-tetra-acetoxybiphenyl (1 mol) with aluminium chloride (4 mol),

*without solvent at 130-140° for 4 h (30%) [761];

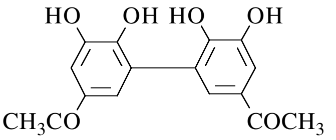
*in nitrobenzene at r.t. for 24 h [761].

-Also obtained by oxidative coupling of resacetophenone using silica-bound ferric chloride, first in methylene chloride, then, after solvent elimination, the residue left at r.t. for a week (10%) [1149].

m.p. 236° [761], 197-198° [1149]. One of the reported melting points is obviously wrong.
^{1}H NMR [1149], IR [1149]; TLC [1149].

1,1'-(5,5',6,6'-Tetrahydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[224030-70-0] $C_{16}H_{14}O_6$ mol.wt. 302.28

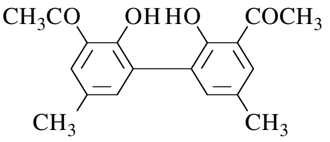


Synthesis

-Refer to: [644].

1,1'-(2,2'-Dihydroxy-5,5'-dimethyl[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[13938-30-2] $C_{18}H_{18}O_4$ mol.wt. 298.34



Syntheses

-Obtained by hydrolysis of [m,m'-bitolyl]-6,6'-diol-5,5'-bis(2-methyl-1,3-dioxolan-2-yl), its diketal, — [24046-06-8], $C_{22}H_{26}O_6$, m.p. 169°5-170° — with hydrogen chloride in methanol (almost quantitative yield) [1473].

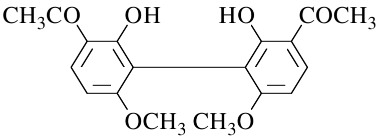
-Also obtained (poor yield) by Fries rearrangement of 2,2'-diacetoxy-5,5'-dimethylbiphenyl with aluminium chloride in nitrobenzene at 120° for 2 h (11%) [1473].

-Also refer to: [1433].

m.p. 189°5-190° [1473]; TLC [1473];
^{1}H NMR [1433] [1473], IR [1433] [1473].

1,1'-(2,2'-Dihydroxy-6,6'-dimethoxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[93107-89-2] $C_{18}H_{18}O_6$ mol.wt. 330.34



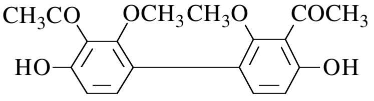
Synthesis

-Obtained by oxidative coupling of resacetophenone 4-methyl ether using silica-bound ferric chloride, first in methylene chloride, then, after solvent elimination, the residue left at r.t. for a week (10%) [1149].

m.p. 322° [1149]; TLC [1149]; IR [1149].

1,1'-(4,4'-Dihydroxy-2,2'-dimethoxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[2551-38-4] $C_{18}H_{18}O_6$ mol.wt. 330.34



Syntheses

-Obtained by degradation of 1,1',9,9'-tetra-O-methylergoflavinone in 10% sodium hydroxide solution at reflux for 2 h under nitrogen [646], (40%) [64].

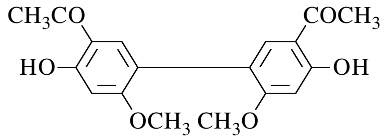
-Also obtained by degradation of 9,9'-di-O-ethyl-

1,1'-di-O-methylergoflavinone (m.p. 271°) in 1% sodium hydroxide solution on a steam bath for 2 h (31%) [64].
-Also obtained by degradation of 6,6'-bis(5-methoxy-2-methylchromone) in 80% (w/v) aqueous sodium hydroxide solution on a steam bath for 2.5 h under nitrogen (11%) [646].
-Also obtained by degradation of 1,1',9-tri-O-methylchrysinone A in 10% aqueous sodium hydroxide solution on a steam bath for 1.5 h under nitrogen (9%) [63].
-Also obtained by degradation of 1,1',9,9'-tetra-O-methylergoflavin (m.p. 282° (d)) with barium hydroxide octahydrate in boiling water for 5 h (5%) [442].
-Also obtained by degradation of 1,1'-di-O-methyl-9,9'-di-O-ethylergoflavin (m.p. 280° (d)) in a 50% (w/v) barium hydroxide octahydrate solution in boiling water for 5 h (< 2%) [64].

m.p. 168-169° [646], 168° [64] [442];
^{1}H NMR [646], IR [63] [64] [646], UV [64].

1,1'-(4,4'-Dihydroxy-6,6'-dimethoxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[93107-86-9] $C_{18}H_{18}O_6$ mol.wt. 330.34



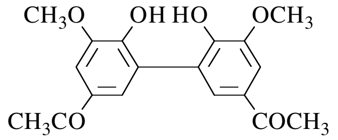
Synthesis

-Obtained by oxidative coupling of resacetophenone 4-methyl ether using silica-bound ferric chloride, first in methylene chloride, then, after solvent elimination, the residue left at r.t. for a week (10%) [1149].

m.p. 125° [1149]; TLC [1149]; ^{1}H NMR [1149], IR [1149].

1,1'-(6,6'-Dihydroxy-5,5'-dimethoxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[29799-22-2] $C_{18}H_{18}O_6$ mol.wt. 330.34



Syntheses

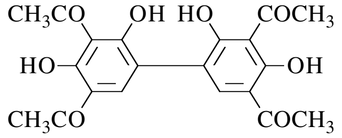
-Obtained by alkaline CuO oxidation of lignin (compound Vn-Vn) named dehydrodiacetovanillone [570].
-Also refer to: [675].

GC [570], GC-MS [570].

N.B.: Utilisation in the long-lasting perfume compositions [675].

1,1-(2,2',4,4'-Tetrahydroxy[1,1'-biphenyl]-3,3',5,5'-tetrayl)tetrakis-ethanone

[23080-58-2] $C_{20}H_{18}O_8$ mol.wt. 386.36



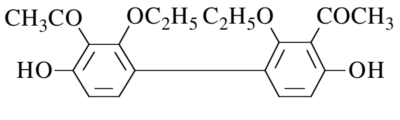
Syntheses

-Obtained by Fries rearrangement of 2,2',4,4'-tetra-acetoxybiphenyl (1 mol) with aluminium chloride (4 mol),
*without solvent at 130-140° for 4 h (20%) [761];
*in nitrobenzene at r.t. for 24 h [761].
-Also obtained by Friedel-Crafts acylation of 2,2',4,4'-tetrahydroxybiphenyl (1 mol) with acetyl chloride (4 mol) in the presence of aluminium chloride (7 mol) at 120° for 2 h [761].

m.p. 302° [761].

1,1'-(2,2'-Diethoxy-4,4'-dihydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[35292-40-1] $C_{20}H_{22}O_6$ mol.wt. 358.39



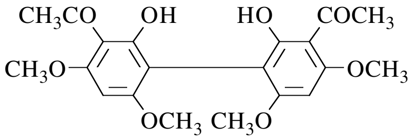
Synthesis

-Obtained by degradation of 1,1',9,9'-tetra-O-ethylergoflavinone (m.p. 303-306°) (SM) in 10% aqueous sodium hydroxide solution on a steam bath for 2 h under nitrogen (22%). SM was obtained by oxidation of 1,1',9,9'-tetra-O-ethylergoflavin with Jones reagent [646].

m.p. 99° [646]; ^{1}H NMR [646].

1,1'-(2,2'-Dihydroxy-4,4',6,6'-tetramethoxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[35134-71-5] $C_{20}H_{22}O_8$ mol.wt. 390.39



Syntheses

-Obtained by oxidative coupling of phloracetophenone 4,6-dimethyl ether *(Xanthoxylin)* using silica-bound ferric chloride, either at 43-45° for 6 days (81%) [912], or first in methylene chloride, then, after solvent elimination, the residue left at r.t. for a week (40%) [1149].

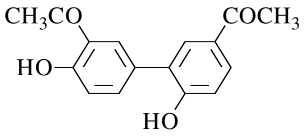
-Obtained by Friedel-Crafts acylation of 2,2',4,4',6,6'-hexamethoxybiphenyl,
*with acetic anhydride in the presence of aluminium chloride in nitrobenzene (20%) [1036];
*with acetyl chloride in the presence of aluminium chloride in ethyl ether (15%) [1036].

m.p. 262-264° [1149], 254-257° [1036], 211-212° [912]. One of the reported melting points is obviously wrong.
^{1}H NMR [912] [1036] [1149], ^{13}C NMR [912], IR [912] [1149], MS [912].

Asymmetrical ketones

1,1'-(4,6'-Dihydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[131844-78-5] $C_{16}H_{14}O_4$ mol.wt. 270.28

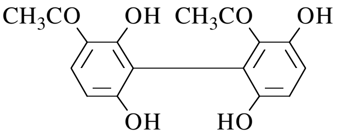


Synthesis

-Refer to: [1441] (European patent).

1,1'-(2',3,6,6'-Tetrahydroxy[1,1'-biphenyl]-2,3'-diyl)bis-ethanone *(Cynandione A)*
1,1'-(2,2',3',6,-Tetrahydroxy[1,1'-biphenyl]-3,4'-diyl)bis-ethanone
(Present name attributed by CAS Registry Handbook Number Section-1995 Supplement).

[168706-29-4] $C_{16}H_{14}O_6$ mol.wt. 302.28



Isolation from natural sources

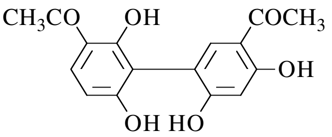
-From the *Cynanchum taiwanianum* (Asclepiadaceae) [660] [661] [924] [925] [928].
-From the *Cynanchum wilfordii* Hemsley (Asclepiadaceae) [668] [894] [895] [1563].

N.B.: The structure of *Cynandione A*, previously designated as 3',4-diacetyl-2,2',3,6'-tetrahydroxybiphenyl [660], has been revised as 2,3'-diacetyl-2',3,6,6'-tetrahydroxybiphenyl [928] in 1997.

m.p. 203-206° [660]; ^{1}H NMR [660] [924] [928], ^{1}H NMR-NOE [928], ^{13}C NMR [660], IR [660] [928], UV [660], MS [660] [924].

1,1'-(2,4',6,6'-Tetrahydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[93108-00-0] $C_{16}H_{14}O_6$ mol.wt. 302.28



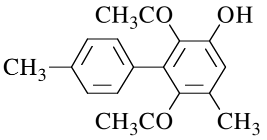
Synthesis

-Obtained by oxidative coupling of resacetophenone using silica-bound ferric chloride, first in methylene chloride, then, after solvent elimination, the residue left at r.t. for a week (15%) [1149].

m.p. 130° [1149]; TLC [1149]; IR [1149].

1,1'-(3-Hydroxy-4',5-dimethyl[1,1'-biphenyl]-2,6-diyl)bis-ethanone

[108909-49-5] $C_{18}H_{18}O_3$ mol.wt. 282.34



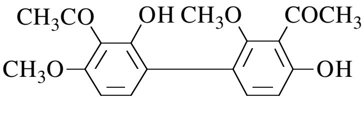
Synthesis

-Obtained by aromatization of 4,6-diacetyl-3-methyl-5-(4-methylphenyl)-2-cyclohexen-1-one (m.p. 140°) with bromine in chloroform (40%) or by heating at 170° for 3 h [605].

m.p. 165° [605].

1,1'-(2,4'-Dihydroxy-2',4-dimethoxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[35287-64-0] $C_{18}H_{18}O_6$ mol.wt. 330.34



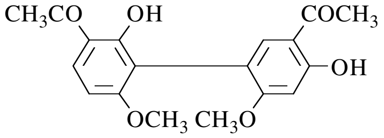
Synthesis

-Obtained by degradation of 6,8'-bis(5-methoxy-2-methylchromone) (m.p. 250-252°) in 80% (w/v) aqueous sodium hydroxide solution on a steam bath for 2 h (13%) [646].

m.p. 130-132° [646]; ^{1}H NMR [646].

1,1'-(2,4'-Dihydroxy-6,6'-dimethoxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[93107-87-0] $C_{18}H_{18}O_6$ mol.wt. 330.34



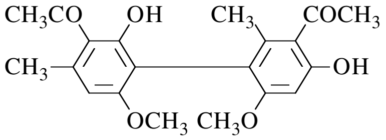
Synthesis

-Obtained by oxidative coupling of resacetophenone 4-methyl ether using silica-bound ferric chloride, first in methylene chloride, then, after solvent elimination, the residue left at r.t. for a week (20%) [1149].

m.p. 194-195° [1149]; TLC [1149]; ^{1}H NMR [1149], IR [1149].

1,1'-(2,4'-Dihydroxy-6,6'-dimethoxy-2',4-dimethyl[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[110325-66-1] $C_{20}H_{22}O_6$ mol.wt. 358.40



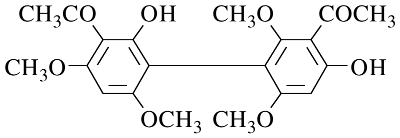
Synthesis

-Obtained by alkaline hydrolysis of *desertorin* C (m.p. 235-237°) (SM) in a mixture of 10% aqueous potassium hydroxide and dioxane (1:1) at reflux for 2 h (54%). SM was isolated from *Emericella desertorum* Samson & Mouchacca strain CBS 653.73. [1107].

m.p. 149-150° [1107];
^{1}H NMR [1107], ^{13}C NMR [1107], IR [1107], UV [1107], MS [1107].

1,1'-(2,4'-Dihydroxy-2',4,6,6'-tetramethoxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[37879-22-4] $C_{20}H_{22}O_8$ mol.wt. 390.39



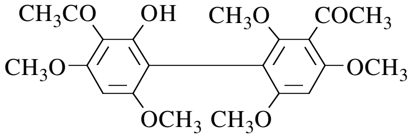
Synthesis

-Obtained by Friedel-Crafts acylation of 2,2',4,4',6,6'-hexamethoxybiphenyl with acetyl chloride in the presence of aluminium chloride in ethyl ether (23%) [1036].

m.p. 185-186° [1036]; ^{1}H NMR [1036].

1,1'-(2-Hydroxy-2',4,4',6,6'-pentamethoxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[37879-23-5] $C_{21}H_{24}O_8$ mol.wt. 404.42



Synthesis

-Obtained by Friedel-Crafts acylation of 2,2',4,4',6,6'-hexamethoxybiphenyl with acetyl chloride in the presence of aluminium chloride in ethyl ether (16%) [1036].

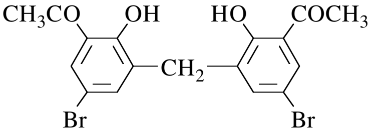
m.p. 213-215° [1036]; ^{1}H NMR [1036].

11.2.2. Diphenylmethane derivatives

11.2.2.1. Unsubstituted acetyl groups

1,1-[Methylenebis(5-bromo-2-hydroxy-3,1-phenylene)]bis-ethanone

[83143-04-8] $C_{17}H_{14}Br_2O_4$ mol.wt. 442.10



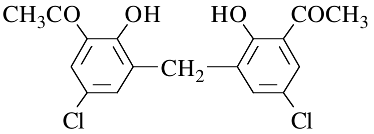
Synthesis

-Preparation by Fries rearrangement of 2,2'-diacetoxy-5,5'-dibromodiphenylmethane with aluminium chloride at 160-180° for 20 min (60%) [1040].

m.p. 232-235° [1040].

1,1'-[Methylenebis(5-chloro-2-hydroxy-3,1-phenylene)]bis-ethanone

[60011-06-5] $C_{17}H_{14}Cl_2O_4$ mol.wt. 353.20



Syntheses

-Preparation by Fries rearrangement of 2,2'-diacetoxy-5,5'-dichlorodiphenylmethane with aluminium chloride at 150-155° for 20 min (80-85%) [604], at 160-180° for 20 min (70%) [1040] or at 170-180° for 30 min (90%) [1041], (40%) [1265].

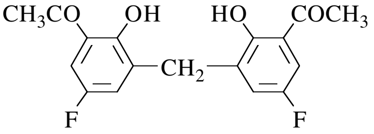
-Also obtained by adding 38% formaldehyde to a cooled solution of 2-acetyl-4-chlorophenol (SM) in concentrated sulfuric acid/methanol solution (2:1 v/v) and stirring for 1.5 h at 20°, then for 4 h at 60-70° (quantitative yield) [1041] or first at -10° under stirring for 2 h, then at r.t. overnight (60%) [1265]. SM was prepared by Fries rearrangement of p-chlorophenyl acetate with aluminium chloride at 160° for 20 min (98%, m.p. 54°) [1041].

N.B.: Mono- and binuclear complexes of Cu (II), Ni (II), Co (II), Fe (III) and V (V) [1265].

m.p. 202-203° [604] [1040] [1041] [1265]; sublimation 155-160°/0.01 mm [1041]; X-ray data [604] [1106] [1406].

1,1'-[Methylenebis(5-fluoro-2-hydroxy-3,1-phenylene)]bis-ethanone

[78563-09-4] $C_{17}H_{14}F_2O_4$ mol.wt. 310.78



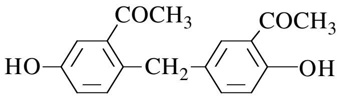
Synthesis

-Preparation by Fries rearrangement of 2,2'-diacetoxy-5,5'-difluorodiphenylmethane with aluminium chloride at 160-180° for 20 min (64%) [1040].

m.p. 155-156° [1040]; ^{13}C NMR [1040].

1-[2-[(3-Acetyl-4-hydroxyphenyl)methyl]-5-hydroxyphenyl]ethanone

[52977-39-6] $C_{17}H_{16}O_4$ mol.wt. 284.31

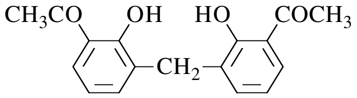


Synthesis

-Refer to: [849] (Russian patent).

1,1'-[Methylenebis(2-hydroxy-3,1-phenylene)]bis-ethanone

[60312-53-0] $C_{17}H_{16}O_4$ mol.wt. 284.31



Syntheses

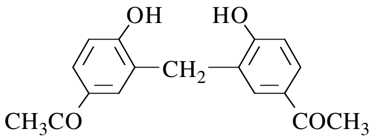
-Obtained by Fries rearrangement of 2,2'-diacetoxydiphenylmethane with aluminium chloride, first at 140° for 5 min, then at 160-180° for 20 min (70%) [1040].

-Also obtained by alkaline degradation of 8,8'-bichromonyl methane (m.p. 222-223°) with refluxing aqueous 10% sodium hydroxide for 20 min [1195].

m.p. 183-184° [1040], 108-109° [1195]. One of the reported melting points is obviously wrong. Sublimation at 220°/0.03 mm [1040];
IR [1195], MS [1040].

1,1'-[Methylenebis(4-hydroxy-3,1-phenylene)]bis-ethanone

[38782-68-2] $C_{17}H_{16}O_4$ mol.wt. 284.31



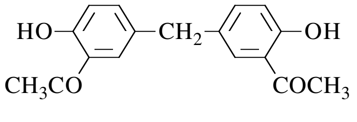
Syntheses

-Obtained by Fries rearrangement of 2,2'-diacetoxydiphenylmethane with aluminium chloride,
*in nitrobenzene at 45° for 3 h (30%) [1089];
*without solvent (by-product), first at 140° for 5 min, then at 160-180° for 20 min (20%) [1040].

m.p. 272-274° [1089], 271-274° [1040];
sublimation at 180-190°/0.035 mm [1040]; MS [1040].

1,1'-[Methylenebis(6-hydroxy-3,1-phenylene)]bis-ethanone

[28467-22-3] $C_{17}H_{16}O_4$ mol.wt. 284.31



Syntheses

-Obtained by Fries rearrangement of 4,4'-diacetoxydiphenylmethane,
*with aluminium chloride at 130-140° for 1 h (50%) [1194];
*with aluminium chloride and sodium chloride mixture at 140-150° for 4 h (28%) [257] [260].

-Also obtained by reaction of 1,3,5-trioxane with o-hydroxyacetophenone in acetic acid in the presence of 98% sulfuric acid under nitrogen at 95-100° for 24 h [787].

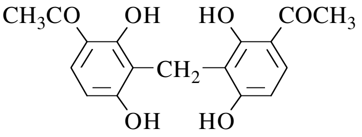
-Also obtained by alkaline degradation of 6,6'-bichromonyl methane (m.p. 193-194°) with refluxing

aqueous 10% sodium hydroxide for 20 min [1195].
-Also refer to: [256].

m.p. 156-157° [257] [260], 155-156° [1195], 155° [1194], 130° [787].
One of the reported melting points is obviously wrong.
IR [787], UV [787], MS [787].

1,1'-[Methylenebis(2,4-dihydroxy-3,1-phenylene)]bis-ethanone

[10508-84-6] $C_{17}H_{16}O_6$ mol.wt. 316.31



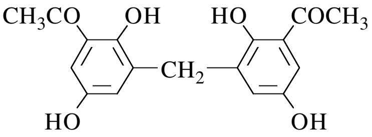
Syntheses

-Obtained by treatment of resacetophenone with methylene iodide in the presence of ethanolic sodium ethoxide for 18 h at r.t., then for 1 h at 60-70° [591] (19%) [595].
-Also refer to: [256].

m.p. 204-205° [595]; UV [595].

1,1'-[Methylenebis(2,5-dihydroxy-3,1-phenylene)]bis-ethanone

[78563-10-7] $C_{17}H_{16}O_6$ mol.wt. 316.31



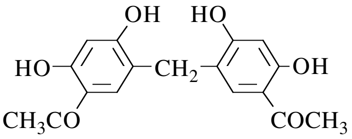
Synthesis

-Preparation by Fries rearrangement of 2,2',5,5'-tetra-acetoxydiphenylmethane with aluminium chloride at 150-155° for 20 min (50%) [604].

m.p. 227-228° [604]; IR [604], MS [604].

1,1'-[Methylenebis(4,6-dihydroxy-3,1-phenylene)]bis-ethanone

$C_{17}H_{16}O_6$ mol.wt. 316.31



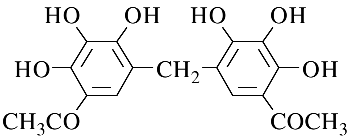
Synthesis

-Obtained by heating at reflux a mixture of resacetophenone, 40% formaldehyde and concentrated hydrochloric acid for 2 h [565].

m.p. > 250° [565].

1,1'-[Methylenebis(4,5,6-trihydroxy-3,1-phenylene)]bis-ethanone

$C_{17}H_{16}O_8$ mol.wt. 348.31



Synthesis

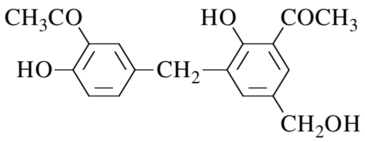
-Obtained by reaction of formaldehyde with gallacetophenone in the presence of hydrogen chloride [252] [565].

m.p. 265° [565].

1-[3-[(3-Acetyl-4-hydroxyphenyl)methyl]-2-hydroxy-5-(hydroxymethyl)phenyl]ethanone

2′,6‴-Dihydroxy-5′-(hydroxymethyl)-3′,3‴-methylenediacetophenone

[30787-44-1] $C_{18}H_{18}O_5$ mol.wt. 314.34

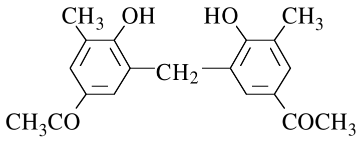


Synthesis

-Obtained by hydrolyzing 2-hydroxy-5-(chloromethyl)acetophenone [242] [243].

1,1'-[Methylenebis(4-hydroxy-5-methyl-3,1-phenylene)]bis-ethanone

[38782-67-1] $C_{19}H_{20}O_4$ mol.wt. 312.37



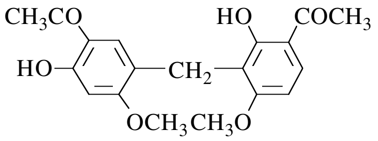
Synthesis

-Preparation by Fries rearrangement of 2,2'-diacetoxy-3,3'-dimethyldiphenylmethane in nitrobenzene with aluminium chloride at 60° for 3 h [455], (59%) [1089].

m.p. 257° [1089]; ^{1}H NMR [455], IR [455].

1-[3-[(5-Acetyl-4-hydroxy-2-methoxyphenyl)methyl]-2-hydroxy-4-methoxyphenyl]-ethanone

[71204-08-5] $C_{19}H_{20}O_6$ mol.wt. 344.36



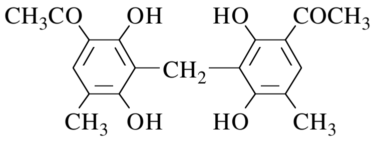
Synthesis

-Obtained by acid-catalyzed condensation of formaldehyde with 2-hydroxy-4-methoxyacetophenone in the presence of 35% aqueous sulfuric acid [1022].

m.p. 161-162° [1022]; ^{1}H NMR [1022].

1,1'-[Methylenebis(2,4-dihydroxy-5-methyl-3,1-phenylene)]bis-ethanone

$C_{19}H_{20}O_6$ mol.wt. 344.36



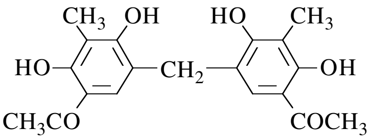
Synthesis

-Preparation by action of 40% aqueous formaldehyde with 2,4-dihydroxy-5-methylacetophenone in ethanol in the presence of concentrated sulfuric acid at 10° (77%) [985].

m.p. 258° (d) [985].

1,1'-[Methylenebis(4,6-dihydroxy-5-methyl-3,1-phenylene)]bis-ethanone

$C_{19}H_{20}O_6$ mol.wt. 344.36



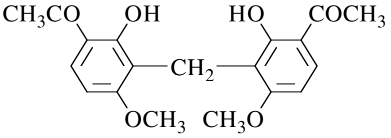
Synthesis

-Preparation by action of 40% aqueous formaldehyde with 2,4-dihydroxy-3-methylacetophenone in ethanol in the presence of concentrated sulfuric acid at r.t. for 3 days (68%) [985].

m.p. 263-264° [985].

1,1'-[Methylenebis(2-hydroxy-4-methoxy-3,1-phenylene)]bis-ethanone

[28466-42-4] $C_{19}H_{20}O_6$ mol.wt. 344.36



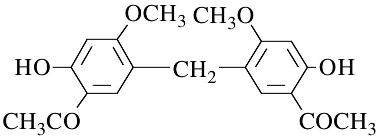
Synthesis

-Obtained by acid-catalyzed condensation of formaldehyde with 2-hydroxy-4-methoxy-acetophenone in the presence of 35% aqueous sulfuric acid [1022].

m.p. 255-256° [1022];
diacetate derivative: m.p. 161-162° [1022]; ^{1}H NMR [1022].

1,1'-[Methylenebis(6-hydroxy-4-methoxy-3,1-phenylene)]bis-ethanone

[71204-07-4] $C_{19}H_{20}O_6$ mol.wt. 344.36



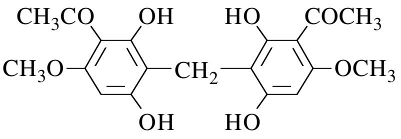
Synthesis

-Obtained by acid-catalyzed condensation of formaldehyde with 2-hydroxy-4-methoxy-acetophenone in the presence of 35% aqueous sulfuric acid [1022].

m.p. 204-205° [1022]; ^{1}H NMR [1022].

1,1'-[Methylenebis(2,4-dihydroxy-6-methoxy-3,1-phenylene)]bis-ethanone
(Didemethylpseudoaspidin)

[142382-28-3] $C_{19}H_{20}O_8$ mol.wt. 376.36



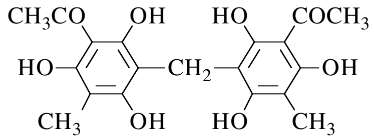
Isolation from natural sources

-From the roots of *Euphorbia ebracteolata Hayata* (Euphorbiaceae) [409].
-From the roots of *Euphorbia kansui* (Euphorbiaceae) [400].

m.p. 232-233° [400];
^{1}H NMR [400], ^{13}C NMR [400], IR [400], EIMS [400].

1,1'-[Methylenebis(2,4,6-trihydroxy-5-methyl-3,1-phenylene)]bis-ethanone

$C_{19}H_{20}O_8$ mol.wt. 376.36

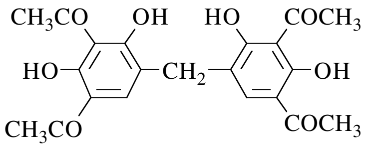


Synthesis

-Obtained by hydrolysis of 8-isobutyryl-5-methoxymethyleneoxy-2,2-dimethylchroman-7-ol (SM) in the presence of 2,4,6-trihydroxy-3-methylacetophenone. The hydrolysis of SM proceeds with the liberation of formaldehyde which condenses with phenol under these acidic conditions [991].

1,1',1",1'"-[Methylenebis(2,4-dihydroxy-5,1,3-benzenetriyl)]tetrakis-ethanone

[84422-46-8] $C_{21}H_{20}O_8$ mol.wt. 400.39



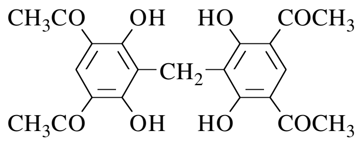
Synthesis

-Obtained by reaction of formaldehyde with 3-acetylresacetophenone in the presence of dilute sulfuric acid in refluxing ethanol for 16 h (42%) [1023].

m.p. 184° [1023]; ^{1}H NMR [1023].

1,1',1",1'"-[Methylenebis(4,6-dihydroxy-5,1,3-benzenetriyl)]tetrakis-ethanone

[84422-38-8] $C_{21}H_{20}O_8$ mol.wt. 400.39



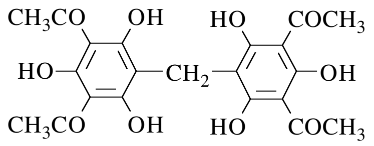
Synthesis

-Obtained by acid-catalysed condensation of formaldehyde with 5-acetylresacetophenone in the presence of dilute sulfuric acid in refluxing ethanol for 30 min [1023].

m.p. 345-346° [1023]; TLC [1023].

1,1',1",1'"-[Methylenebis(2,4,6-trihydroxy-5,1,3-benzenetriyl)]tetrakis-ethanone

[58316-48-6] $C_{21}H_{20}O_{10}$ mol.wt. 432.39



Synthesis

-Obtained by condensation of formaldehyde with 2,4-diacetylphloroglucinol (35%) [1561].

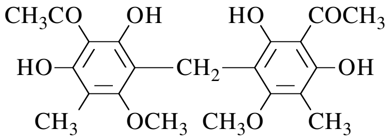
Isolation from natural sources

-From the culture fluid of *Pseudomonas aurantiaca* [452].
-Also refer to: [1547] (compound 28).

m.p. 284-286° [1561].

1,1'-[Methylenebis(2,6-dihydroxy-4-methoxy-5-methyl-3,1-phenylene)]bis-ethanone
(Mallotophenone)

[98569-63-2] $C_{21}H_{24}O_8$ mol.wt. 404.42



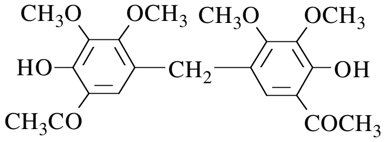
Isolation from natural sources

-From the pericarps of *Mallotus japonicus* Muell. Arg. (Euphorbiaceae) [71] [72] [73] [74] [75] [76] [77] [525] [1066].

m.p. 223-225° [77];
^{1}H NMR [73] [77], ^{13}C NMR [73] [77] [525], IR [77],
UV [77], MS [77]; Cytotoxicity [525].

1,1'-[Methylenebis(6-hydroxy-4,5-dimethoxy-3,1-phenylene)]bis-ethanone

[71204-14-3] $C_{21}H_{24}O_8$ mol.wt. 404.42



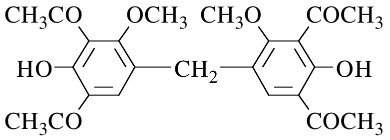
Synthesis

-Obtained from 2-hydroxy-3,4-dimethoxy-acetophenone with formaldehyde and 35% aqueous sulfuric acid [1022].

m.p. 141-142° [1022].

1,1',1'',1'''-[Methylenebis(2-hydroxy-4-methoxy-5,1,3-benzenetriyl)]tetrakis-ethanone

[84422-49-1] $C_{23}H_{24}O_8$ mol.wt. 428.44



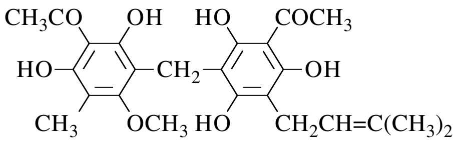
Synthesis

-Obtained by partial methylation of 3,3',5,5'-tetra-acetyl-2,2',4,4'-tetrahydroxydiphenylmethane with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 12 h (29%) [1023].

m.p. 132° [1023]; ^{1}H NMR [1023];
TLC [1023], column chromatography [1023].

1-[3-[(3-Acetyl-2,4-dihydroxy-6-methoxy-5-methylphenyl)methyl]-2,4,6-trihydroxy-5-(3-methyl-2-butenyl)phenyl]ethanone
*proposed name mallotojaponin**

[86828-07-1] $C_{24}H_{28}O_8$ mol.wt. 444.48



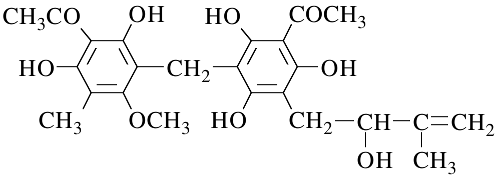
Isolation from natural sources

-From the pericarps of *Mallotus japonicus* Muell. Arg. (Euphorbiaceae) [70]* [71] [73] [74] [75] [76] [77] [525] [833] [1348].

m.p. 190-191° [77], 188-189° [1348];
^{1}H NMR [77] [1348], ^{13}C NMR [833] [1348], IR [77] [1348],
UV [77] [1348], MS [77] [1348]; Cytotoxicity [525].

1-[3-[(3-Acetyl-2,4-dihydroxy-6-methoxy-5-methylphenyl)methyl]-2,4,6-trihydroxy-5-(2-hydroxy-3-methyl-3-butenyl)phenyl]ethanone *(proposed name mallotolerin)**

[86828-08-2] $C_{24}H_{28}O_9$ mol.wt. 460.48



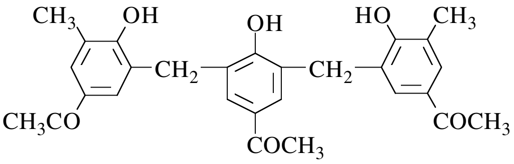
Isolation from natural sources

-From the pericarps of *Mallotus japonicus* Muell. Arg. (Euphorbiaceae) [70]* [73] [74] [75] [76] [525] [833] [1348].

m.p. 197-199° [1348];
^{1}H NMR [76] [1348], ^{13}C NMR [1348], IR [76] [1348],
UV [76] [1348] MS [76] [1348]; Cytotoxicity [525].

1-[3,5-Bis[(5-acetyl-2-hydroxy-3-methylphenyl)methyl]-4-hydroxyphenyl]ethanone

[38782-69-3] $C_{28}H_{28}O_6$ mol.wt. 460.53



Synthesis

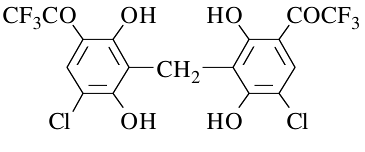
-Obtained by Fries rearrangement of 2,6-bis(2-acetoxy-3-methylbenzyl)-acetoxybenzene with aluminium chloride in nitrobenzene at 50° for 5 h (41%) [1089].

m.p. 242° [1089].

11.2.2.2. Halogenated acetyl groups

1,1'-[Methylenebis(5-chloro-2,4-dihydroxy-3,1-phenylene)]bis[2,2,2-trifluoroethanone

[65240-40-6] $C_{17}H_8Cl_2F_6O_6$ mol.wt. 493.14



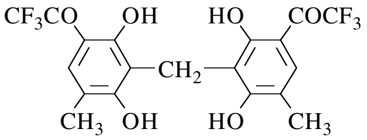
Synthesis

-Preparation by reaction of paraformaldehyde with 5-chloro-2,4-dihydroxy-α,α,α-trifluoro-acetophenone in methanol in the presence of concentrated sulfuric acid at 0° for 5 h (87%) [232].

m.p. 205° [232].

1,1'-[Methylenebis(2,4-dihydroxy-5-methyl-3,1-phenylene)]bis[2,2,2-trifluoroethanone

[65240-30-4] $C_{19}H_{14}F_6O_6$ mol.wt. 452.31



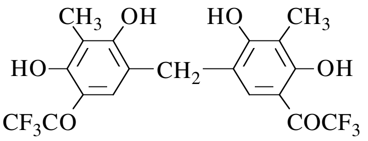
Synthesis

-Preparation by reaction of paraformaldehyde with 2,4-dihydroxy-5-methyl-α,α,α-trifluoroacetophenone at 140° (92%) [232].

m.p. 234° [232].

1,1'-[Methylenebis(4,6-dihydroxy-5-methyl-3,1-phenylene)]bis[2,2,2-trifluoroethanone

[65240-39-3] $C_{19}H_{14}F_6O_6$ mol.wt. 452.31



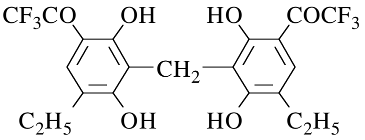
Synthesis

-Preparation by reaction of paraformaldehyde with 2,4-dihydroxy-3-methyl-α,α,α-trifluoroacetophenone in methanol in the presence of concentrated sulfuric acid at 0° for 5 h (87%) [232].

m.p. 195° [232].

1,1'-[Methylenebis(5-ethyl-2,4-dihydroxy-3,1-phenylene)]bis[2,2,2-trifluoroethanone

[65240-29-1] $C_{21}H_{18}F_6O_6$ mol.wt. 480.36



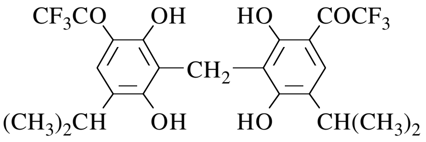
Synthesis

-Preparation by reaction of paraformaldehyde with 2,4-dihydroxy-5-ethyl-α,α,α-trifluoroacetophenone at 140° for 1 h (92%) [232].

m.p. 170° [232].

1,1'-[Methylenebis[2,4-dihydroxy-5-(1-methylethyl)-3,1-phenylene]]bis[2,2,2-trifluoroethanone

[65240-35-9] $C_{23}H_{22}F_6O_6$ mol.wt. 508.41



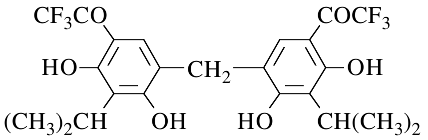
Synthesis

-Preparation by reaction of paraformaldehyde with 2,4-dihydroxy-5-isopropyl-α,α,α-trifluoroacetophenone at 140° (89%) [232].

m.p. 140° [232].

1,1'-[Methylenebis[4,6-dihydroxy-5-(1-methylethyl)-3,1-phenylene]]bis[2,2,2-trifluoroethanone

[65240-38-2] $C_{23}H_{22}F_6O_6$ mol.wt. 508.41



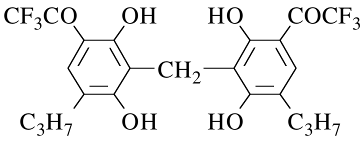
Synthesis

-Preparation by reaction of paraformaldehyde with 2,4-dihydroxy-3-isopropyl-α,α,α-trifluoroacetophenone at 140° (90%) [232].

m.p. 123° [232].

1,1'-[Methylenebis(2,4-dihydroxy-5-propyl-3,1-phenylene)]bis[2,2,2-trifluoroethanone

[65240-31-5] $C_{23}H_{22}F_6O_6$ mol.wt. 508.41



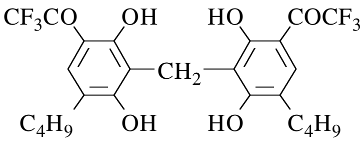
Synthesis

-Preparation by reaction of paraformaldehyde with 2,4-dihydroxy-5-propyl-α,α,α-trifluoroacetophenone at 140° (90%) [232].

m.p. 153° [232].

1,1'-[Methylenebis(5-butyl-2,4-dihydroxy-3,1-phenylene)]bis[2,2,2-trifluoroethanone

[65290-78-0] $C_{25}H_{26}F_6O_6$ mol.wt. 536.47



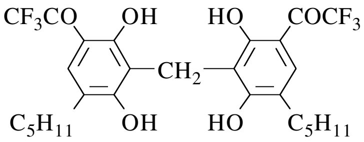
Synthesis

-Preparation by reaction of paraformaldehyde with 5-butyl-2,4-dihydroxy-α,α,α-trifluoroacetophenone at 140° (91%) [232].

m.p. 145° [232].

1,1'-[Methylenebis(2,4-dihydroxy-5-pentyl-3,1-phenylene)]bis[2,2,2-trifluoroethanone

[65240-32-6] $C_{27}H_{30}F_6O_6$ mol.wt. 564.52



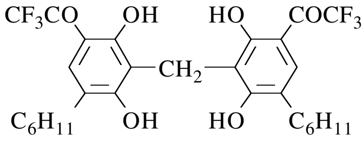
Synthesis

-Preparation by reaction of paraformaldehyde with 2,4-dihydroxy-5-pentyl-α,α,α-trifluoroacetophenone at 140° (90%) [232].

m.p. 131° [232].

1,1'-[Methylenebis(5-cyclohexyl-2,4-dihydroxy-3,1-phenylene)]bis[2,2,2-trifluoroethanone

[65240-37-1] $C_{29}H_{30}F_6O_6$ mol.wt. 588.54



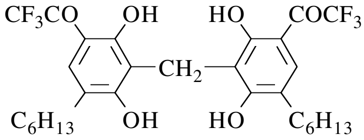
Synthesis

-Preparation by reaction of paraformaldehyde with 5-cyclohexyl-2,4-dihydroxy-α,α,α-trifluoroacetophenone at 140° (85%) [232].

m.p. 206° [232].

1,1'-[Methylenebis(5-hexyl-2,4-dihydroxy-3,1-phenylene)]bis[2,2,2-trifluoroethanone

[65240-33-7] $C_{29}H_{34}F_6O_6$ mol.wt. 592.58



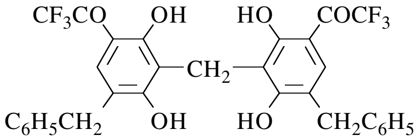
Synthesis

-Preparation by reaction of paraformaldehyde with 2,4-dihydroxy-5-hexyl-α,α,α-trifluoroacetophenone at 140° (93%) [232].

m.p. 120° [232].

1,1'-[Methylenebis[2,4-dihydroxy-5-(phenylmethyl)-3,1-phenylene]]bis[2,2,2-trifluoroethanone

[65240-36-0] $C_{31}H_{22}F_6O_6$ mol.wt. 604.50



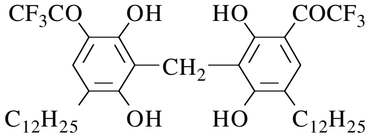
Synthesis

-Preparation by reaction of paraformaldehyde with 5-benzyl-2,4-dihydroxy-α,α,α-trifluoroacetophenone at 140° (90%) [232].

m.p. 183° [232].

1,1'-[Methylenebis(5-dodecyl-2,4-dihydroxy-3,1-phenylene)]bis[2,2,2-trifluoroethanone

[65240-34-8] $C_{41}H_{58}F_6O_6$ mol.wt. 760.90



Synthesis

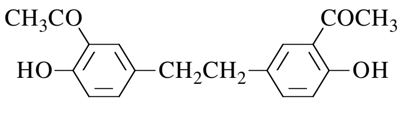
-Preparation by reaction of paraformaldehyde with 2,4-dihydroxy-5-dodecyl-α,α,α-trifluoroacetophenone at 140° (85%) [232].

m.p. 110° [232].

11.2.3. Diphenylalkanes derivatives and homologues

1,1'-[1,2-Ethanediylbis(6-hydroxy-3,1-phenylene)]bis-ethanone

[34036-53-8] $C_{18}H_{18}O_4$ mol.wt. 298.34



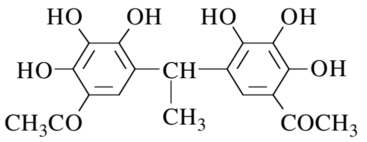
Synthesis

-Preparation by Friedel-Crafts acylation of 1,2-bis(p-methoxyphenyl)ethane (m.p. 127-129°) with acetyl chloride in the presence of aluminium chloride in ethylene dichloride at 65° for 2.5 h (86%) [831].

m.p. 194-195°5 [831].

1,1'-[Ethylidenebis(4,5,6-trihydroxy-3,1-phenylene)]bis-ethanone

[128197-51-3] $C_{18}H_{18}O_8$ mol.wt. 362.34

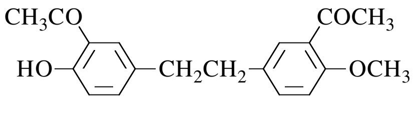


Syntheses

-Refer to: [774] and [773] [1060] [1485] (Japanese patents).

1-[5-[2-(3-Acetyl-4-hydroxyphenyl)ethyl]-2-methoxyphenyl]ethanone

[27171-77-3] $C_{19}H_{20}O_4$ mol.wt. 312.37



Syntheses

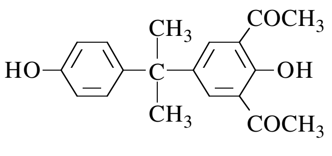
-Obtained by partial methylation of 1,2-bis-(3'-acetyl-4'-hydroxyphenyl)ethane with dimethyl sulfate in ethyl ether in the presence of 2 N aqueous potassium hydroxide at 100° for 8 h (29%) [831] or with methyl halide [1567].

-Also obtained by acetylation of 1,2-bis(4'-methoxyphenyl)ethane with acetyl chloride in the presence of aluminium chloride [1567].

m.p. 62-63°5 [831].

1,1'-[2-Hydroxy-5-[1-(4-hydroxyphenyl)-1-methylethyl]-1,3-phenylene]bis-ethanone

[104676-23-5] $C_{19}H_{20}O_4$ mol.wt. 312.37



Syntheses

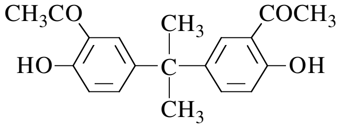
-Obtained by action of acetyl chloride with 2,2-bis (4-acetoxyphenyl)propane in ethylene dichloride in the presence of aluminium chloride at 50° for 5 h (38%) [477].

-Also refer to: [476].

m.p. 151-152° [477].

1,1'-[(1-Methylethylidene)bis(6-hydroxy-3,1-phenylene)]bis-ethanone

[3511-69-1] $C_{19}H_{20}O_4$ mol.wt. 312.37



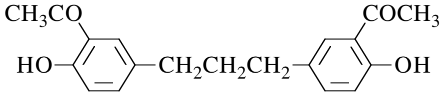
Syntheses

-Preparation by reaction of acetyl chloride,
*with 2,2-bis(4-ethoxyphenyl)propane (bisphenol A diethyl ether) in the presence of aluminium chloride in methylene chloride at 30° for 30 min (61%) [477] or in ethylene dichloride at 50° for 3 h (63-65%) [1376];
*with 2,2-bis(4-methoxyphenyl)propane (bisphenol A dimethyl ether) in the presence of aluminium chloride in ethylene dichloride at 70° for 2 h (45%) [832].
-Also obtained by Fries rearrangement of bisphenol A diacetate in nitrobenzene,
*in the presence of aluminium chloride, first at r.t., then at 120-130° for 3 h (28%) [340];
*in the presence of titanium tetrachloride, first at r.t. for 24 h, then at 55° for 6 h (11%) [1105].

m.p. 142-143° [1105], 141-142° [477] [832] [1376], 107-109° [340].
One of the reported melting points is obviously wrong.
^{1}H NMR [1105], ^{13}C NMR [1105], IR [1105].

1,1'-[1,3-Propanediylbis(6-hydroxy-3,1-phenylene)]bis-ethanone

[29668-20-0] $C_{19}H_{20}O_4$ mol.wt. 312.37



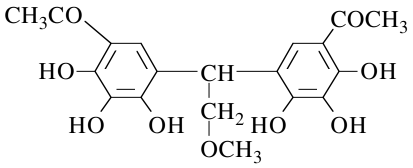
Syntheses

-Obtained by Friedel-Crafts acylation of 1,3-bis(4-methoxyphenyl)propane with acetyl chloride in tetrachloroethane in the presence of aluminium chloride, first at 0 to 5°, then below 15° overnight [260].
-Also refer to: [804] [805] [806].

m.p. 112° [260].

1,1'-[(2-Methoxyethylidene)bis(4,5,6-trihydroxy-3,1-phenylene)]bis-ethanone

[143868-77-3] $C_{19}H_{20}O_9$ mol.wt. 392.36

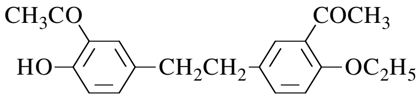


Synthesis

-Refer to: [1060] (Japanese patent).

1-[5-[2-(3-Acetyl-4-hydroxyphenyl)ethyl]-2-ethoxyphenyl]ethanone

[27171-79-5] $C_{20}H_{22}O_4$ mol.wt. 326.39



Syntheses

-Obtained by partial ethylation of 1,2-bis-(3'-acetyl-4'-hydroxyphenyl)ethane with ethyl iodide in the presence of potassium carbonate

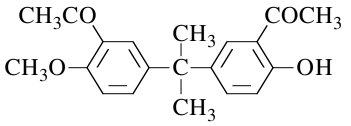
in refluxing acetone for 12 h (17%) [831] or with ethyl halide [1567].
-Also obtained by acetylation of 1,2-bis(4-ethoxyphenyl)ethane with acetyl chloride in the presence of aluminium chloride [1567].

m.p. 75°5-76° [831].

1-[5-[1-(3-Acetyl-4-hydroxyphenyl)-1-methylethyl]-2-methoxyphenyl]ethanone

6′-Hydroxy-6‴-methoxy-3′,3‴-isopropylidenediacetophenone

[27171-78-4] $C_{20}H_{22}O_4$ mol.wt. 326.39



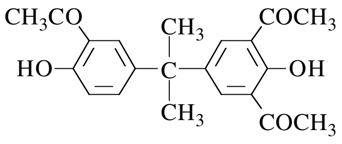
Synthesis

-Preparation by acetylation of bisphenol A dimethyl ether with acetyl chloride in the presence of aluminium chloride, and subsequent partial methylation with methyl bromide of the obtained 2,2-bis(3-acetyl-4-hydroxyphenyl)propane [1567].

^{1}H NMR [1567], IR [1567].

1,1'-[5-[1-(3-Acetyl-4-hydroxyphenyl)-1-methylethyl]-2-hydroxy-1,3-phenylene]bis-ethanone

[104676-24-6] $C_{21}H_{22}O_5$ mol.wt. 354.40



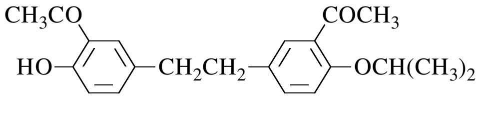
Synthesis

-Obtained by action of acetyl chloride with 2,2-bis (4-acetoxyphenyl)propane in ethylene dichloride in the presence of aluminium chloride at 50° for 30 h (15%) [477].

m.p. 111°5-112° [477].

1-[5-[2-(3-Acetyl-4-hydroxyphenyl)ethyl]-2-isopropoxyphenyl]ethanone

[34036-60-7] $C_{21}H_{24}O_4$ mol.wt. 340.42



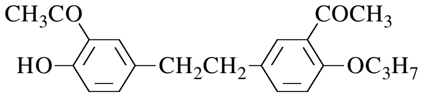
Synthesis

-Obtained by partial alkylation of 1,2-bis-(3-acetyl-4-hydroxyphenyl)ethane with isopropyl iodide in the presence of potassium hydroxide in ethanol at 80° for 14 h (25%) [831].

m.p. 70-71° [831].

1-[5-[2-(3-Acetyl-4-hydroxyphenyl)ethyl]-2-propoxyphenyl]ethanone

[27171-80-8] $C_{21}H_{24}O_4$ mol.wt. 340.42



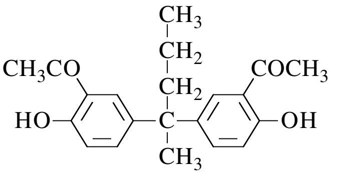
Synthesis

-Preparation by acetylation of 1,2-bis-(4-hydroxyphenyl)ethane diisopropyl ether with acetyl chloride in the presence of aluminium chloride and subsequent partial alkylation of the obtained 1,2-bis(3-acetyl-4-hydroxyphenyl)ethane with isopropyl bromide (or chloride) [1567].

^{1}H NMR [1567].

1,1'-[(1-Ethylpropylidene)bis(6-hydroxy-3,1-phenylene)]bis-ethanone

[20636-45-7] $C_{21}H_{24}O_4$ mol.wt. 340.42

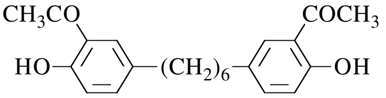


Syntheses

-Refer to: [1376] [1568].

1,1'-[1,6-Hexanediylbis(6-hydroxy-3,1-phenylene)]bis-ethanone

[29668-19-7] $C_{22}H_{26}O_4$ mol.wt. 354.45



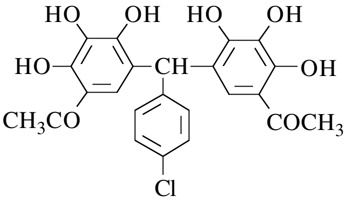
Synthesis

-Obtained by Friedel-Crafts acylation of 1,6-bis-(4-methoxyphenyl)hexane with acetyl chloride in the presence of aluminium chloride in tetrachloroethane, first at 0-5°, then below 15° overnight (65%) [260].

m.p. 97-98° [260].

1,1'-[[(4-Chlorophenyl)methylene]bis(4,5,6-trihydroxy-3,1-phenylene)]bis-ethanone

$C_{23}H_{19}ClO_8$ mol.wt. 458.85



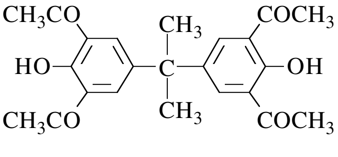
Synthesis

-Obtained by condensation of one mol of p-chlorobenzaldehyde (m.p. 47-50°) with two mol of gallacetophenone [252].

m.p. 230-231° [252].

1,1',1",1"'-[(1-Methylethylidene)bis(2-hydroxy-5,1,3-benzenetriyl)]tetrakis-ethanone

[104676-25-7] $C_{23}H_{24}O_6$ mol.wt. 396.44



Syntheses

-Preparation by Friedel-Crafts acylation of 2,2-bis (4-ethoxyphenyl)propane (bisphenol A diethyl ether) with acetyl chloride in ethylene dichloride in the presence of aluminium chloride at 60° for 7 h (52%) [477].

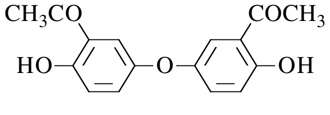
-Also obtained by Fries rearrangement of 2,2-bis(4-acetoxyphenyl)propane (bisphenol A diacetate) with aluminium chloride in an acetyl chloride/ethylene dichloride mixture at 50° for 30 h (10%) [477].

m.p. 204°5-205° [477].

11.2.4. Diphenyl ethers and related compounds

1,1'-[Oxybis(6-hydroxy-3,1-phenylene)]bis-ethanone

[28467-08-5] $C_{16}H_{14}O_5$ mol.wt. 286.28



Syntheses

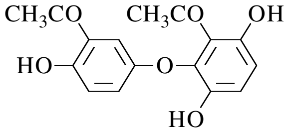
-Obtained by Fries rearrangement of 4,4'-diacetoxydiphenyl ether with aluminium chloride and sodium chloride at 140-150° for 4 h [260] or at 140° for 3 h (40%) [1196].

-Also refer to: [256] [257].

m.p. 185° [1196], 181-183° [260].

1-[5-(2-Acetyl-3,6-dihydroxyphenoxy)-2-hydroxyphenyl]ethanone

[72926-21-7] $C_{16}H_{14}O_6$ mol.wt. 302.28



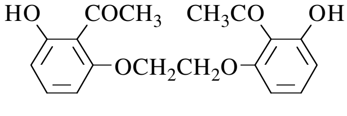
Synthesis

-Preparation by adding an aqueous solution of sodium hydrosulfite to an ethereal solution of 2-acetyl-3-(3-acetyl-4-hydroxyphenoxy)-1,4-benzoquinone (m.p. 120-121°) and stirring the mixture at r.t. for 30 min (80%) [973].

^{1}H NMR [973].

1,1'-[1,2-Ethanediylbis[oxy(6-hydroxy-2,1-phenylene)]]bis-ethanone

[16139-62-1] $C_{18}H_{18}O_6$ mol.wt. 330.34



Syntheses

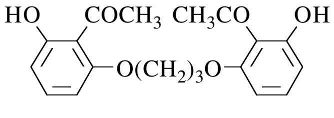
-Obtained by reaction of 1,2-dibromoethane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h [260] or for 72 h [499].

-Also refer to: [501].

m.p. 188-189° [260] [499].

1,1'-[1,3-Propanediylbis[oxy(6-hydroxy-2,1-phenylene)]]bis-ethanone

[16150-42-8] $C_{19}H_{20}O_6$ mol.wt. 344.36



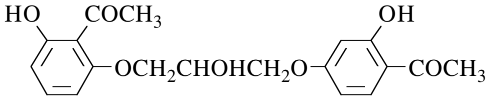
Synthesis

-Obtained by reaction of 1,3-dibromopropane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h [260].

m.p. 184-185° [260].

1-[4-[3-(2-Acetyl-3-hydroxyphenoxy)-2-hydroxypropoxy]-2-hydroxyphenyl]ethanone

[16130-16-8] $C_{19}H_{20}O_7$ mol.wt. 360.36



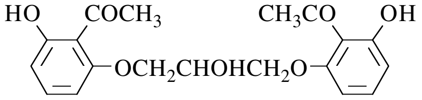
Synthesis

-Obtained by reaction of 2-(3-chloro-2-hydroxypropoxy)-6-hydroxyacetophenone (SM) with resacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h (31%). SM was prepared by reaction of epichlorohydrin with 2,6-dihydroxyacetophenone in the presence of benzyltrimethylammonium hydroxide in dioxane at 100° for 72 h (37%, oil) [260].

m.p. 182-185° [260].

1,1'-[(2-Hydroxy-1,3-propanediyl)bis[oxy(6-hydroxy-2,1-phenylene)]]bis-ethanone

[16150-44-0] $C_{19}H_{20}O_7$ mol.wt. 360.36



Syntheses

-Preparation by reaction of 2,6-hydroxyacetophenone,

*with 1,3-dichloro-2-propanol [179], in the presence of potassium carbonate in refluxing acetone for 72 h [499];

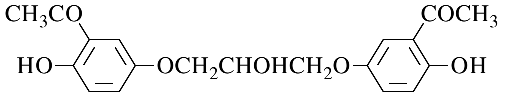
*with 1,3-dibromo-2-propanol in the presence of potassium carbonate in refluxing acetone for 48 h (21%) [260].

*with epichlorohydrin in the presence of potassium hydroxide in refluxing isopropanol for 48 h (59%) [260].

m.p. 165-166° [260] [499].

1,1'-[(2-Hydroxy-1,3-propanediyl)bis[oxy(6-hydroxy-3,1-phenylene)]]bis-ethanone

[16139-50-7] $C_{19}H_{20}O_7$ mol.wt. 360.36



Syntheses

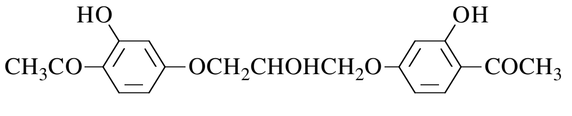
-Obtained by reaction of 1,3-dibromo-2-hydroxypropane with 2,5-dihydroxyacetophenone (quinacetophenone) in the presence of potassium carbonate in refluxing acetone for 48 h [260].

-Also obtained by reaction of epichlorohydrin with quinacetophenone in the presence of potassium hydroxide in boiling isopropanol for 48 h [260].

m.p. 127-129° [260].

1,1'-[(2-Hydroxy-1,3-propanediyl)bis[oxy(2-hydroxy-4,1-phenylene)]]bis-ethanone

[16139-45-0] $C_{19}H_{20}O_7$ mol.wt. 360.36



Syntheses

-Obtained by reaction of 1,3-dibromo-2-hydroxypropane with resacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h [260].

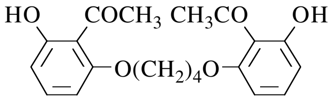
-Also obtained by reaction of epichlorohydrin with resacetophenone in the presence of potassium hydroxide, in boiling acetone for 48 h [260] or in boiling water for 3 h (20%) (by-product) [1059].

-Also obtained by heating a mixture of epichlorohydrin, sodium, ethanol and resacetophenone under reflux for 4 h [1059].

m.p. 178-180° [260], 161° [1059]. One of the reported melting points is obviously wrong.

1,1'-[1,4-Butanediylbis[oxy-(6-hydroxy-2,1-phenylene)]]bis-ethanone

[16129-95-6] $C_{20}H_{22}O_6$ mol.wt. 358.39



Synthesis

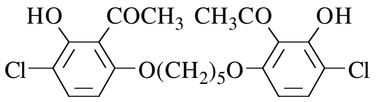
-Preparation by reaction of 1,4-dibromobutane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 72 h [499] or for 48 h [260].

m.p. 219-221° [260] [499].

1,1'-[1,5-Pentanediylbis[oxy(5-chloro-6-hydroxy-2,1-phenylene)]]bis-ethanone

2',2'''-(Pentamethylenedioxy)bis[5'-chloro-6'-hydroxyacetophenone

[16130-26-0] $C_{21}H_{22}Cl_2O_6$ mol.wt. 441.31



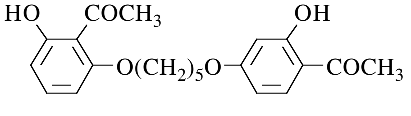
Synthesis

-Preparation by reaction of 1,5-dibromopentane with 3-chloro-2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 72 h [499].

m.p. 96° [499].

1-[4-[[5-(2-Acetyl-3-hydroxyphenoxy)pentyl]oxy]-2-hydroxyphenyl]ethanone

[16130-20-4] $C_{21}H_{24}O_6$ mol.wt. 372.42



Syntheses

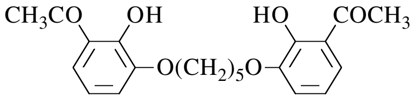
-Obtained by reaction of 2-(5-bromopentyloxy)-6-hydroxyacetophenone (SM) with resacetophenone in the presence of potassium carbonate in refluxing acetone for 18 h (60%). SM was formed by reaction of 1,5-dibromopentane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 20 h (oil, 50%) [260].

-Also refer to: [499].

m.p. 91-91°5 [260] [499].

1,1'-[1,5-Pentanediylbis[oxy(2-hydroxy-3,1-phenylene)]]bis-ethanone

[16139-26-7] $C_{21}H_{24}O_6$ mol.wt. 372.42



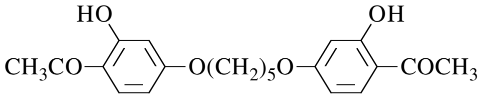
Synthesis

-Obtained by reaction of 1,5-dibromopentane with 2,3-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h [260] [499].

m.p. 103°5-104°5 [260] [499].

1,1'-[1,5-Pentanediylbis[oxy(2-hydroxy-4,1-phenylene)]]bis-ethanone

[37086-37-6] $C_{21}H_{24}O_6$ mol.wt. 372.42



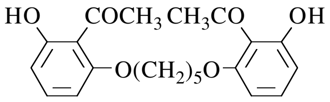
Synthesis

-Obtained by reaction of 1,5-dibromopentane with resacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h [260].

m.p. 119-121° [260].

1,1'-[1,5-Pentanediylbis[oxy(6-hydroxy-2,1-phenylene)]]bis-ethanone

[16130-01-1] $C_{21}H_{24}O_6$ mol.wt. 372.42



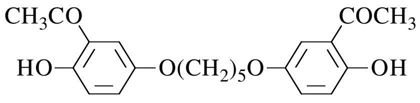
Synthesis

-Preparation by reaction of 1,5-dibromopentane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 72 h [499] or for 48 h [260].

m.p. 131-133° [260] [499].

1,1'-[1,5-Pentanediylbis[oxy(6-hydroxy-3,1-phenylene)]]bis-ethanone

[16139-42-7] $C_{21}H_{24}O_6$ mol.wt. 372.42



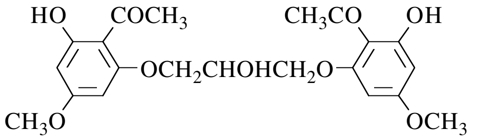
Synthesis

-Obtained by reaction of 1,5-dibromopentane with quinacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h [260] [499].

m.p. 107-109° [260] [499].

1,1'-[(2-Hydroxy-1,3-propanediyl)bis[oxy(6-hydroxy-4-methoxy-2,1-phenylene)]]bis-ethanone

[23937-88-4] $C_{21}H_{24}O_9$ mol.wt. 420.42



Syntheses

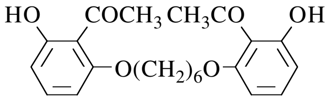
-Obtained by reaction of 1,3-dibromo-2-hydroxypropane with 2,6-dihydroxy-4-methoxyacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h [260].

-Also obtained by reaction of epichlorohydrin with 2,6-dihydroxy-4-methoxyacetophenone in the presence of potassium hydroxide in refluxing isopropanol for 48 h [260].

m.p. 108-182° [260]. A typing error probably occurred in the published data.

1,1'-[1,6-Hexanediylbis[oxy-(6-hydroxy-2,1-phenylene)]]bis-ethanone

[16130-02-2] $C_{22}H_{26}O_6$ mol.wt. 386.44



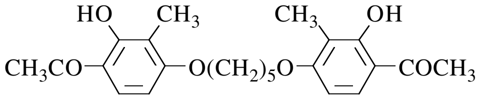
Synthesis

-Preparation by reaction of 1,6-dibromohexane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 72 h [499] or for 48 h [260].

m.p. 147°5-148°5 [260] [499].

1,1'-[1,5-Pentanediylbis[oxy(2-hydroxy-3-methyl-4,1-phenylene)]]bis-ethanone

$C_{23}H_{28}O_6$ mol.wt. 400.47



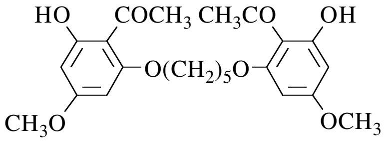
Synthesis

-Preparation by reaction of 1,5-dibromopentane with 2,4-dihydroxy-3-methylacetophenone in the presence of potassium carbonate in refluxing acetone for 72 h [499].

m.p. 116-117° [499].

1,1'-[1,5-Pentanediylbis[oxy(6-hydroxy-4-methoxy-2,1-phenylene)]]bis-ethanone

[23937-90-8] $C_{23}H_{28}O_8$ mol.wt. 432.47



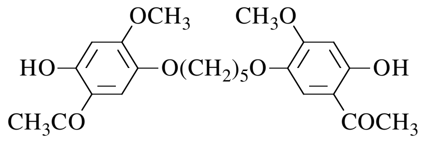
Synthesis

-Obtained by reaction of 1,5-dibromopentane with 2,6-dihydroxy-4-methoxyacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h [260].

m.p. 146-147° [260].

1,1'-[1,5-Pentanediylbis[oxy(6-hydroxy-4-methoxy-3,1-phenylene)]]bis-ethanone

[23937-59-9] $C_{23}H_{28}O_8$ mol.wt. 432.47



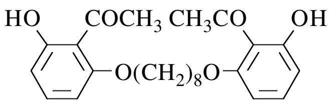
Synthesis

-Obtained by reaction of 1,5-dibromopentane with 2,5-dihydroxy-4-methoxyacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h [260].

m.p. 145-148° [260].

1,1'-[1,8-Octanediylbis[oxy-(6-hydroxy-2,1-phenylene)]]bis-ethanone

[16139-58-5] $C_{24}H_{30}O_6$ mol.wt. 414.50



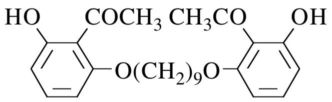
Synthesis

-Preparation by reaction of 1,8-dibromooctane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 72 h [499] or for 48 h [260].

m.p. 108-109° [260], 107-109° [499].

1,1'-[1,9-Nonanediylbis[oxy-(6-hydroxy-2,1-phenylene)]]bis-ethanone

[16139-60-9] $C_{25}H_{32}O_6$ mol.wt. 428.53



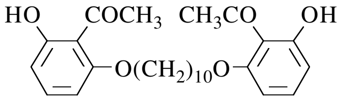
Synthesis

-Preparation by reaction of 1,9-dibromononane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 72 h [499] or for 48 h [260].

m.p. 55-59° [260] [499].

1,1'-[1,10-Decanediylbis[oxy-(6-hydroxy-2,1-phenylene)]]bis-ethanone

[16258-59-6] $C_{26}H_{34}O_6$ mol.wt. 442.55



Synthesis

-Preparation by reaction of 1,10-dibromodecane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 72 h [499] or for 48 h [260].

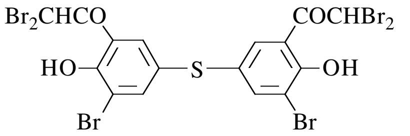
m.p. 102°5-104° [260] [499].

11.2.5. Diphenyl sulfide derivatives and related compounds

11.2.5.1. Diphenyl sulfide derivatives

1,1'-[Thiobis(5-bromo-6-hydroxy-3,1-phenylene)]bis[2,2-dibromoethanone

$C_{16}H_8Br_6O_4S$ mol.wt. 775.73



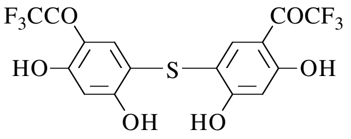
Synthesis

-Obtained by reaction of excess bromine with 3,3'-diacetyl-4,4'-dihydroxydiphenyl sulfide in acetic acid in a boiling water bath for 3 h [692].

m.p. 168-170° [692].

1,1'-[Thiobis(4,6-dihydroxy-3,1-phenylene)]bis[2,2,2-trifluoroethanone

[65239-96-5] $C_{16}H_8F_6O_6S$ mol.wt. 442.29



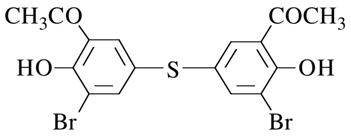
Synthesis

-Obtained by Friedel-Crafts acylation of 2,2',4,4'-tetrahydroxydiphenylsulfide with trifluoroacetic anhydride in the presence of aluminium chloride in ethylene dichloride at r.t. (10%) [232].

m.p. 172° [232].

1,1'-[Thiobis(5-Bromo-6-hydroxy-3,1-phenylene)]bis-ethanone

$C_{16}H_{12}Br_2O_4S$ mol.wt. 460.14



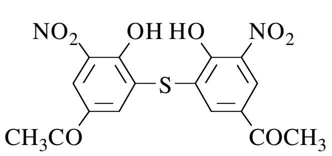
Synthesis

-Obtained by reaction of bromine with 3,3'-diacetyl-4,4'-dihydroxydiphenyl sulfide in acetic acid, first at 90°, then at r.t. for 6 h [692].

m.p. 218-219° [692].

1,1'-[Thiobis(4-hydroxy-5-nitro-3,1-phenylene)]bis-ethanone

$C_{16}H_{12}N_2O_8S$ mol.wt. 392.35



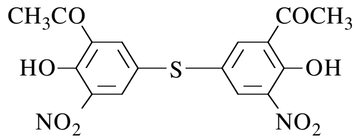
Synthesis

-Obtained by reaction of thionyl chloride with 4-hydroxy-3-nitroacetophenone in the presence of copper, first at r.t. overnight, then at reflux for 30 min [852].

m.p. > 300° [852].

1,1'-[Thiobis(6-hydroxy-5-nitro-3,1-phenylene)]bis-ethanone

$C_{16}H_{12}N_2O_8S$ mol.wt. 392.35



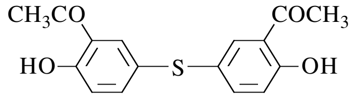
Synthesis

-Obtained by reaction of 3,3'-diacetyl-4,4'-dihydroxydiphenyl sulfide with dilute nitric acid at reflux for 2 h [692].

m.p. 206-208° [692].

1,1'-[Thiobis(6-hydroxy-3,1-phenylene)]bis-ethanone

$C_{16}H_{14}O_4S$ mol.wt. 302.35



Syntheses

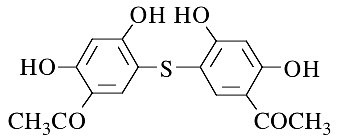
-Obtained by reaction of thionyl chloride or sulfur dichloride with o-hydroxyacetophenone in the presence of copper powder, first at r.t. overnight, then in a boiling water bath for 10 min [692].

-Also refer to: [998].

m.p. 196-197° [692].

1,1'-[Thiobis(4,6-dihydroxy-3,1-phenylene)]bis-ethanone

[56923-41-2] $C_{16}H_{14}O_6S$ mol.wt. 334.35



Syntheses

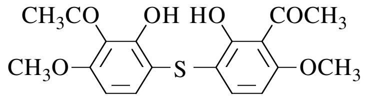
-Obtained by reaction of thionyl chloride with resacetophenone in chloroform in the presence of copper powder, first at 0°, then at r.t. overnight and, the next day, at reflux (60°) for 5 min (11%) [690].

-Also refer to: [998].

m.p. 209-210° [690].

1,1'-[Thiobis(2-hydroxy-6-methoxy-3,1-phenylene)]bis-ethanone

[103154-01-4] $C_{18}H_{18}O_6S$ mol.wt. 362.40



Syntheses

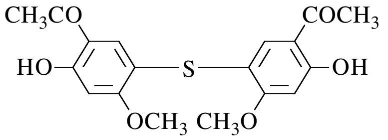
-Obtained by reaction of thionyl chloride with 2-hydroxy-6-methoxyacetophenone in chloroform in the presence of copper powder at r.t. overnight (23%) [358].

-Also obtained by reaction of sulfur monochloride or sulfur dichloride with 2-hydroxy-6-methoxyacetophenone in ethyl ether, first at 0° for 1 h and at r.t. overnight (<15%) [358].

m.p. 184-185° [358].

1,1'-[Thiobis(6-hydroxy-4-methoxy-3,1-phenylene)]bis-ethanone

[56923-42-3] $C_{18}H_{18}O_6S$ mol.wt. 362.40



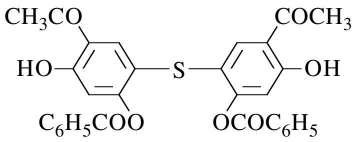
Syntheses

-Obtained by reaction of thionyl chloride with paeonol in chloroform in the presence of copper powder, first at r.t. overnight, then at 60° for 10 min (19%) [691].
-Also refer to: [998].

m.p. 223-224° [691].

1,1'-[Thiobis[4-(benzoyloxy)-6-hydroxy-3,1-phenylene]]bis-ethanone

[56923-50-3] $C_{30}H_{22}O_8S$ mol.wt. 542.57



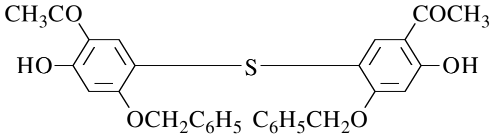
Syntheses

-Obtained by reaction of thionyl chloride or sulfur dichloride with 4-(benzoyloxy)-2-hydroxy-acetophenone in the presence of copper powder in chloroform at 60° for 10 min [693].
-Also refer to: [998].

m.p. 228-229° [693].

1,1'-[Thiobis[6-hydroxy-4-(phenylmethoxy)-3,1-phenylene]]bis-ethanone

[56923-49-0] $C_{30}H_{26}O_6S$ mol.wt. 514.60



Syntheses

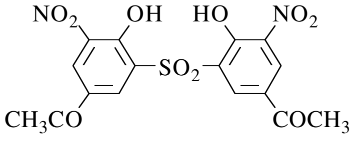
-Obtained by reaction of thionyl chloride or sulfur chloride with 4-(benzyloxy)-2-hydroxy-acetophenone in chloroform in the presence of copper powder, first at 0°, then at r.t. overnight and at 60° for 10 min [696].
-Also refer to: [998].

m.p. 202-203° [696].

11.2.5.2. Diphenyl sulfone derivatives

1,1'-[Sulfonylbis(4-hydroxy-5-nitro-3,1-phenylene)]bis-ethanone

$C_{16}H_{12}N_2O_{10}S$ mol.wt. 424.34



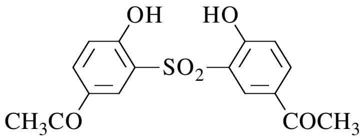
Synthesis

-Obtained by oxidation of 5,5'-diacetyl-2,2'-dihydroxy-3,3'-dinitrodiphenyl sulfide with hydrogen peroxide in acetone at r.t. overnight (74%) [852].

m.p. 135° [852].

1,1'-[Sulfonylbis(4-hydroxy-3,1-phenylene)]bis-ethanone

$C_{16}H_{14}O_6S$ mol.wt. 334.35



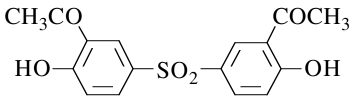
Synthesis

-Obtained by oxidation of 5,5'-diacetyl-2,2'-dihydroxydiphenyl sulfide with hydrogen peroxide in acetone at r.t. overnight (73%) [852].

m.p. > 300° [852].

1,1'-[Sulfonylbis(6-hydroxy-3,1-phenylene)]bis-ethanone

[56923-31-0] $C_{16}H_{14}O_6S$ mol.wt. 334.35



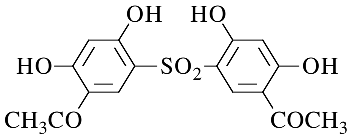
Syntheses

-Obtained by Fries rearrangement of bisphenol S diacetate with aluminium chloride (10 equiv.) at 160° (23%) [1392].
N.B.: The UV irradiation of a diester solution in 0.02 M acetonitrile does not lead to the above mentioned diketone.
-Also obtained by Fries rearrangement of 4,4'-diacetoxydiphenyl sulfone with aluminium chloride (5 equiv.) at 150-160° for 5 h (30%) [1196].
-Also obtained by oxidation of 3,3'-diacetyl-4,4'-dihydroxydiphenyl sulfide with hydrogen peroxide (73%) [1196] according to [852] or with 30% hydrogen peroxide in acetic acid at r.t. for 48 h (63%) [998].
-Also obtained by alkaline degradation of 6,6'-bichromonyl sulfone (m.p. 266-268°) with refluxing aqueous 10% sodium hydroxide for 20 min [1195].
-Also refer to: [1079].

m.p. 189-190° [1196], 189° [852] [998], 187-188° [1195], 186°6 [1392];
^{1}H NMR [1392], IR [998], UV [998].

1,1'-[Sulfonylbis(4,6-dihydroxy-3,1-phenylene)]bis-ethanone

[56923-32-1] $C_{16}H_{14}O_8S$ mol.wt. 366.35



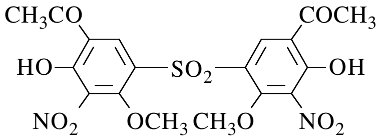
Synthesis

-Obtained by oxidation of 5,5'-diacetyl-2,2'-4,4'-tetrahydroxydiphenyl sulfide with 30% hydrogen peroxide in acetic acid at r.t. for 48 h (75%) [998] or in acetone at r.t. overnight (73%) [852].

m.p. 195° [852] [998]; IR [998], UV [998].

1,1'-[Sulfonylbis(6-hydroxy-4-methoxy-5-nitro-3,1-phenylene)]bis-ethanone

$C_{18}H_{16}N_2O_{12}S$ mol.wt. 484.40

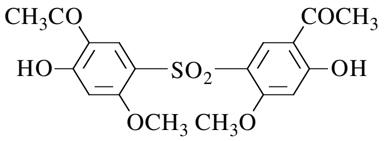


Synthesis

-Obtained by nitration of 3,3'-diacetyl-4,4'-dihydroxy-6,6'-dimethoxydiphenyl sulfone in concentrated sulfuric acid with concentrated nitric acid at 60° for 15 min [998].

1,1'-[Sulfonylbis(6-hydroxy-4-methoxy-3,1-phenylene)]bis-ethanone

[56923-33-2] $C_{18}H_{18}O_8S$ mol.wt. 394.40



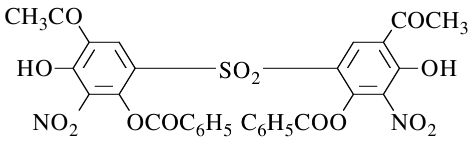
Synthesis

-Obtained by oxidation of 3,3'-diacetyl-4,4'-dihydroxy-6,6'-dimethoxydiphenyl sulfide with 30% hydrogen peroxide in acetic acid at r.t. for 48 h (68%) [998].

m.p. 281-282° [998]; IR [998], UV [998].

1,1'-[Sulfonylbis[4-(benzoyloxy)-6-hydroxy-5-nitro-3,1-phenylene]]bis-ethanone

$C_{30}H_{20}N_2O_{14}S$ mol.wt. 664.56

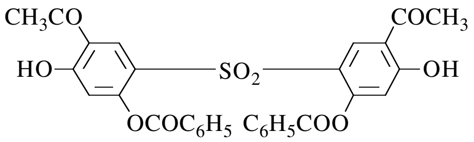


Synthesis

-Obtained by nitration of 5,5'-diacetyl-2,2'-bis(benzoyloxy)-4,4'-dihydroxydiphenyl sulfone in concentrated sulfuric acid with concentrated nitric acid at 50° for 15 min [998].

1,1'-[Sulfonylbis[4-(benzoyloxy)-6-hydroxy-3,1-phenylene]]bis-ethanone

[56923-35-4] $C_{30}H_{22}O_{10}S$ mol.wt. 574.56



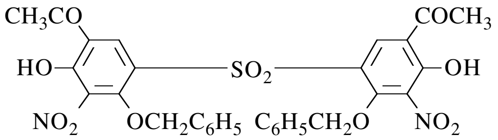
Synthesis

-Obtained by oxidation of 5,5'-diacetyl-2,2'-bis(benzoyloxy)-4,4'-dihydroxydiphenyl sulfide with 30% hydrogen peroxide in acetic acid at r.t. for 48 h (71%) [998].

m.p. 245-246° [998]; IR [998], UV [998].

1,1'-[Sulfonybis[6-hydroxy-5-nitro-4-(phenylmethoxy)-3,1-phenylene]]bis-ethanone

$C_{30}H_{24}N_2O_{12}S$ mol.wt. 636.59

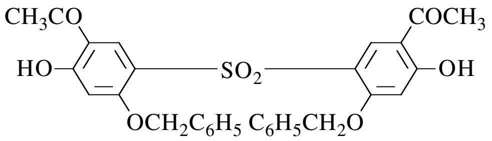


Synthesis

-Obtained by nitration of 5,5'-diacetyl-2,2'-bis(benzyloxy)-4,4'-dihydroxydiphenyl sulfone in concentrated sulfuric acid with concentrated nitric acid at 60° for 15 min [998].

1,1'-[Sulfonylbis[6-hydroxy-4-(phenylmethoxy)-3,1-phenylene]]bis-ethanone

[56923-34-3] $C_{30}H_{26}O_8S$ mol.wt. 546.60



Synthesis

-Obtained by oxidation of 5,5'-diacetyl-2,2'-bis(benzyloxy)-4,4'-dihydroxydiphenyl sulfide with 30% hydrogen peroxide in acetic acid at r.t. for 48 h (75%) [998].

m.p. 222-223° [998]; IR [998], UV [998].

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$C_8H_4Cl_3NO_4$

2,2-Dichloro-1-(3-chloro-4-hydroxy-5-nitrophenyl)ethanone, 59

$C_8H_4Cl_4O_2$

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$C_8H_5BrN_2O_6$

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$C_8H_5Br_2NO_4$

2,2-Dibromo-1-(4-hydroxy-3-nitrophenyl)ethanone, 28

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$C_8H_5ClINO_4$

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$C_9H_{11}NO_3$, HCl

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$C_{10}H_9BrO_5$

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$C_{10}H_9Br_3O_3$

2,2-Dibromo-1-(3-bromo-5-ethyl-2,4-dihydroxyphenyl)ethanone, 30

$C_{10}H_9Br_3O_4$

2,2-Dibromo-1-(3-bromo-2-hydroxy-4,6-dimethoxyphenyl)ethanone, 30

$C_{13}H_{20}O_2SSi$

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$C_{14}H_{10}BrFO_2$

1-(3-Bromo-5-fluoro-2-hydroxyphenyl)-2-phenylethanone, 193

$C_{14}H_{10}Br_2O_3$

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$C_{14}H_{11}BrO_2$

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$C_{14}H_{11}BrO_3$

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$C_{14}H_{11}BrO_5$

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$C_{14}H_{11}ClO_2$

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$C_{15}H_{13}NO_7$

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$C_{15}H_{14}O_2S$

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$C_{15}H_{14}O_3S$

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$C_{15}H_{15}NO_3$

1-(3,4-Dihydroxyphenyl)-2-[(phenylmethyl)amino]ethanone, 118

$C_{15}H_{15}NO_3$, HCl

1-(3,4-Dihydroxyphenyl)-2-[(phenylmethyl)amino]ethanone *(Hydrochloride)*, 119

$C_{15}H_{16}O_7$

1,1'-[2,4-(Diacetyloxy)-6-hydroxy-5-methyl-1,3-phenylene]bis-ethanone, 360

$C_{15}H_{17}F_3O_3$

1-(3-Cycloheptyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone, 88
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$C_{15}H_{18}O_4$

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$C_{15}H_{18}O_5$

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$C_{15}H_{19}F_3O_3$

2,2,2-Trifluoro-1-(5-heptyl-2,4-dihydroxyphenyl)ethanone, 89

$C_{15}H_{20}O_9$

2-(β-D-Glucopyranosyloxy)-1-(4-hydroxy-3-methoxyphenyl)ethanone, 150

$C_{15}H_{21}NO_3$

1,1'-[4-(Ethylamino)-6-hydroxy-5-propyl-1,3-phenylene]bis-ethanone, 361

$C_{15}H_{22}O_6$

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$C_{15}H_{23}NO_3$

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$C_{16}H_8Br_6O_4S$

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$C_{19}H_{22}ClF_3O_4$

1-[5-Chloro-2-hydroxy-4-(10-undecenoyloxy)phenyl]-2,2,2-trifluoroethanone, 91

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$C_{19}H_{22}O_6$

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$C_{19}H_{22}O_7$

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$C_{19}H_{26}O_6$

1-[6-[(3,7-Dimethyl-2,6-octadienyl)oxy]-2,4-dihydroxy-3-methoxyphenyl]-2-hydroxyethanone, 177

$C_{20}H_{15}NO_5$

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$C_{20}H_{16}O_2$

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1-[2-Hydroxy-6-methoxy-4-(phenylmethoxy)phenyl]-2-(2-hydroxy-4-methoxyphenyl)-ethanone, 314

$C_{23}H_{24}O_6$

1,1',1'',1'''-[(1-Methylethylidene)bis(2-hydroxy-5,1,3-benzenetriyl)]tetrakis-ethanone, 384

$C_{23}H_{24}O_8$

1,1',1'',1'''-[Methylenebis(2-hydroxy-4-methoxy-5,1,3-benzenetriyl)]tetrakis-ethanone, 376

$C_{23}H_{28}O_6$

1,1'-[1,5-Pentanediylbis[oxy(2-hydroxy-3-methyl-4,1-phenylene)]]bis-ethanone, 389

$C_{23}H_{28}O_8$

1,1'-[1,5-Pentanediylbis[oxy(6-hydroxy-4-methoxy-2,1-phenylene)]]bis-ethanone, 389
1,1'-[1,5-Pentanediylbis[oxy(6-hydroxy-4-methoxy-3,1-phenylene)]]bis-ethanone, 390

$C_{23}H_{28}O_{10}$

1,1'-[Methylenebis(2-hydroxy-4,6-dimethoxy-3,1-phenylene)]bis[2-methoxyethanone, 411

$C_{23}H_{30}O_2$

1-[3,5-Bis(1,1-dimethylethyl)-4-hydroxyphenyl]-2-(4-methylphenyl)ethanone, 314

$C_{23}H_{32}O_5$

1-[4-[(3,7-Dimethyl-2,6-octadienyl)oxy]-2,6-dihydroxy-3-(3-methyl-2-butenyl)phenyl]-2-hydroxyethanone *(E)*, 178

$C_{24}H_{22}O_6$

1-[3-[(5-Benzoyl-2,4-dihydroxy-3-methylphenyl)methyl]-2,4-dihydroxy-5-methyl-phenyl]ethanone, 411
1-[6-Hydroxy-2,4-dimethoxy-3-[(phenylacetyl)oxy]phenyl]-2-phenylethanone, 233

$C_{24}H_{22}O_7$

2-(Benzoyloxy)-1-[2-hydroxy-3,6-dimethoxy-4-(phenylmethoxy)phenyl]ethanone, 189

$C_{24}H_{22}O_8$

1,1'-[[(4-Hydroxy-3-methoxyphenyl)methylene]bis(4,6-dihydroxy-3,1-phenylene)]bis-ethanone, 412

$C_{24}H_{24}O_5$

1-[2-Hydroxy-6-methoxy-3-methyl-4-(phenylmethoxy)phenyl]-2-(4-methoxyphenyl)-ethanone, 314

1-(4-Hydroxyphenyl)-2,2,2-triphenylethanone, 319
1-(2'-Hydroxy[1,1':3',1''-terphenyl]-5'-yl)-2-phenylethanone, 233

$C_{26}H_{32}O_8$

1-[3-[(3-Acetyl-2,4-dihydroxy-6-methoxy-5-methylphenyl)methyl]-2,4,6-trihydroxy-5-(3-methyl-2-butenyl)phenyl]-1-butanone, 412
1-[3-[(3-Acetyl-2,4-dihydroxy-6-methoxy-5-methylphenyl)methyl]-2,4,6-trihydroxy-5-(3-methyl-2-butenyl)phenyl]-2-methyl-1-propanone, 413

$C_{26}H_{32}O_9$

1-[3-[(3-Acetyl-2,4-dihydroxy-6-methoxy-5-methylphenyl)methyl]-2,4,6-trihydroxy-5-(2-hydroxy-3-methyl-3-butenyl)phenyl]-1-butanone, 413
1-[3-[(3-Acetyl-2,4-dihydroxy-6-methoxy-5-methylphenyl)methyl]-2,4,6-trihydroxy-5-(2-hydroxy-3-methyl-3-butenyl)phenyl]-2-methyl-1-propanone, 413

$C_{26}H_{34}O_6$

1,1'-[1,10-Decanediylbis[oxy-(6-hydroxy-2,1-phenylene)]]bis-ethanone, 390

$C_{26}H_{36}O_3$

1-[4-(Dodecyloxy)-2-hydroxyphenyl]-2-phenylethanone, 234

$C_{26}H_{38}ClF_3O_4$

1-[5-Chloro-2-hydroxy-4-(octadecanoyloxy)phenyl]-2,2,2-trifluoroethanone, 92
1-[5-Chloro-4-hydroxy-2-(octadecanoyloxy)phenyl]-2,2,2-trifluoroethanone, 92

$C_{26}H_{41}F_3O_3$

1-[2,4-Dihydroxy-3-(1-methylheptadecyl)phenyl]-2,2,2-trifluoroethanone, 92

$C_{27}H_{22}O_3$

1-[3-(Diphenylmethyl)-2,4-dihydroxyphenyl]-2-phenylethanone, 234
1-[5-(Diphenylmethyl)-2,4-dihydroxyphenyl]-2-phenylethanone, 234

$C_{27}H_{22}O_4$

1-[3-(Diphenylmethyl)-2,4,6-trihydroxyphenyl]-2-phenylethanone, 234
1-[5-(Diphenylmethyl)-2,3,4-trihydroxyphenyl]-2-phenylethanone, 235

$C_{27}H_{28}O_6$

1,1'-[(Phenylmethylene)bis(4-ethoxy-6-hydroxy-3,1-phenylene)]bis-ethanone, 414

$C_{27}H_{30}F_6O_6$

1,1'-[Methylenebis(2,4-dihydroxy-5-pentyl-3,1-phenylene)]bis[2,2,2-trifluoroethanone, 379

$C_{28}H_{24}O_3$

1-[2,4-Dihydroxy-3,5-bis(phenylmethyl)phenyl]-2-phenylethanone, 235
1-[3-(Diphenylmethyl)-2-hydroxy-4-methoxyphenyl]-2-phenylethanone, 235

$C_{29}H_{32}O_{14}$

1-[2-Hydroxy-4-[(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)oxy]phenyl]-2-(4-methoxyphenoxy)ethanone, 166

$C_{29}H_{34}F_6O_6$

1,1'-[Methylenebis(5-hexyl-2,4-dihydroxy-3,1-phenylene)]bis[2,2,2-trifluoroethanone, 380

$C_{30}H_{20}N_2O_{14}S$

1,1'-[Sulfonylbis[4-(benzoyloxy)-6-hydroxy-5-nitro-3,1-phenylene]]bis-ethanone, 395

$C_{30}H_{22}O_8S$

1,1'-[Thiobis[4-(benzoyloxy)-6-hydroxy-3,1-phenylene]]bis-ethanone, 393

$C_{30}H_{22}O_{10}S$

1,1'-[Sulfonylbis[4-(benzoyloxy)-6-hydroxy-3,1-phenylene]]bis-ethanone, 395

$C_{30}H_{24}N_2O_{12}S$

1,1'-[Sulfonybis[6-hydroxy-5-nitro-4-(phenylmethoxy)-3,1-phenylene]]bis-ethanone, 396

$C_{30}H_{26}O_6S$

1,1'-[Thiobis[6-hydroxy-4-(phenylmethoxy)-3,1-phenylene]]bis-ethanone, 393

$C_{30}H_{26}O_8S$

1,1'-[Sulfonylbis[6-hydroxy-4-(phenylmethoxy)-3,1-phenylene]]bis-ethanone, 396

$C_{30}H_{28}O_5$

1-[2-Hydroxy-4,6-bis(phenylmethoxy)-3-(phenylmethyl)phenyl]-2-methoxyethanone, 143
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1-[2-Hydroxy-3-methyl-4,6-bis(phenylmethoxy)phenyl]-2-(4-methoxyphenyl)ethanone, 316

$C_{30}H_{28}O_6$

2-(2,4-Dimethoxyphenyl)-1-[2-hydroxy-4,6-bis(phenylmethoxy)phenyl]ethanone, 317

$C_{31}H_{22}F_6O_6$

1,1'-[Methylenebis[2,4-dihydroxy-5-(phenylmethyl)-3,1-phenylene]]bis[2,2,2-trifluoroethanone, 380

$C_{35}H_{28}O_8$

1,1'-[Methylenebis(5-acetyl-4,6-dihydroxy-3,1-phenylene)]bis-[3-phenyl-2-propen-1-one *(E,E)*, 414

$C_{35}H_{30}O_3$

1-[2-Hydroxy-4-(phenylmethoxy)-3,5-bis(phenylmethyl)phenyl]-2-phenylethanone, 237

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[65240-40-6]	1,1'-[Methylenebis(5-chloro-2,4-dihydroxy-3,1-phenylene)]bis[2,2,2-trifluoroethanone, 377
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[117421-24-6]	2-(Benzoyloxy)-1-(2,5-dihydroxyphenyl)ethanone, 185
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USUAL NAMES INDEX

COMMON ABBREVIATIONS

Å	Angström units
$(\alpha)_D^{20}$	Specific optical rotation at 20°C for D (sodium) line
ART	2-Amino-1-(3,4-dihydroxyphenyl)ethanone
b.p.	Boiling point (for example, $b.p._{0.1}$ 100° means boils at 100° if the pressure is 0.1 mm Hg)
CAN	Ceric ammonium nitrate
m-CPBA	m-Chloroperoxybenzoic acid
20°	20 degrees Celsius
d	Density (for example, d^{20} specific gravity at 20°C referred to water at 4°C)
(d)	with decomposition
DEAD	Diethyl azodicarboxylate
dl	Racemic
DME	1,2-Dimethoxyethane (glyme)
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DMPU	1,3-Dimethyl-3,4,5,6-tetrahydro-2-*[1H]*-pyrimidinone
DOPKET	1-(3,4-Dihydroxyphenyl)-2-hydroxyethanone
equiv	Equivalent
GC	Gas chromatography
HMPA	Hexamethylphosphoramide (hexamethylphosphoric triamide)
HMPT	Hexamethylphosphorous triamide
HPLC	High performance (pressure, power) liquid chromatography
^{13}C NMR	Nuclear magnetic resonance relative to carbon 13
(E)	Geometric stereodescriptor used for compounds having achiral elements resulting from double bonds where the groups of highest priority are on the opposite sides of the vertical reference plane
^{19}F NMR	Nuclear magnetic resonance relative to fluorine 19
h	Hour

HR-MS	High resolution mass spectra
^{1}H NMR	Nuclear magnetic resonance relative to proton
IR	Infrared spectra
iso-	Aliphatic hydrocarbon having two methyl groups on the terminal carbon atom of the chain (for example, isoamyl $(CH_3)_2CH-CH_2-CH_2-$)
LCEC	Liquid chromatography with electrochemical detection
LDA	Lithium diisopropylamide
m-	Meta-
M	Molar (concentration)
min	Minute
mol	Molecule
mol.wt.	Molecular weight
MOM-	Methoxymethyl-
m.p.	Melting point
MS	Mass spectra
n-	Normal (as n-butyl)
N	Normal (equivalents per litre, as applied to concentration)
N.B.	Nota bene
NBS	N-Bromosuccinimide
n_D^{20}	Index of refraction (n_D^{20} for 20°C and sodium light)
N,N'-MBA	N,N'-Methylenebisacrylamide
NPFA	Nitropentafluoroacetone
o-	Ortho-
p-	Para-
Pd/C	Palladium on charcoal
$PdCl_2/C$	Palladium chloride on charcoal
PdO/C	Palladium oxide on charcoal
pH	Log of reciprocal of hydrogen ion concentration
pK_A	Log of the reciprocal of the dissociation constant, 1/log K_A

pK_B	Log of the reciprocal of the dissociation constant, 1/log K_B
Ψ	pseudo
psi	per square inch
Pt/C	Platinum on charcoal
r.t.	Room temperature
sec-	Secondary (as sec-butyl)
SM	Starting material
TBAI	Tetrabutylammonium iodide
TEAF	Triethylammonium formate
tert-	Tertiary (as tert-butyl)
TFA	Trifluoroacetic acid
TFE	2,2,2-Trifluoroethanol
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TMS	Tetramethylsilane
UV	Ultraviolet spectra
w/w	per cent "weight in weight" expresses the number of grams of an active constituent in 100 grams of solution or mixture
(Z)	Opposite of *(E)*