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Marco Fontani
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Mariagrazia Costa

Chemistry and Chemists in Florence

From the Last of the Medici Family to the European Magnetic Resonance Center

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Preface

Florence, Italy, is known throughout the world as a center, and in fact, *the* center, of Western Renaissance art in every sense of the word. It was the birthplace, the cradle, the school, and now the custodian of about one-quarter of the world's great art. It is looked upon from afar as one of the poles of C.P. Snow's famous dichotomy of the two cultures.

Florence has never been thought of as a city with a rich scientific tradition, yet that tradition exists, with its roots in the former Grand Duchy of Tuscany down to our present day with three great centers of scientific research at the cutting edge of such pioneering fields as metabolomics and molecular magnetism.

We wrote this book to set the record straight—to lay out this scientific tradition as found in the lives and works of the first natural scientists to the most outstanding members of the chemistry department of what is now the University of Florence. Perhaps science has never been that romantic abode whose name is associated with the greatest opportunities and the highest ideals. Moreover, if one grants that the great discoveries have always nourished humanity's desire for power and immortality, it is also true that failure drives a great number of researchers to conceal or to disavow their own errors. Even in this case, and within the limited scope of research supporting this book, we have found exceptions: here we see scientists who, associated with a university lacking a long tradition and positioned at the periphery of the scientific center, rework their successes or failures, academic, political, personal or scientific, in a personal form with a view for either growth or emotional release.

The book's organization is chronological, and chapter headings reflect the evolution of the University of Florence from a museum of natural science through the various structural changes that brought it into the modern world as a full-fledged institution of higher learning.

Acknowledgments

Even in a small but complex book such as this present one, it is impossible to adequately remember the contributions of many persons who, in conversations or with specific responses to questions, have provided us with information, have criticized baseless beliefs, and as an old saying has it, have helped us to "follow the trail of the hidden treasure." With this in mind, we would like to express our personal thanks to the following: Francesca Salvianti, to whom we dedicate this volume. Thanks also to Alessandra Beni, Barbara Nardi, Renata Bertini, Agnese and Roberto Di Camillo, Alessandro Ciandella, Gioiosa Brogi-Bindi, Antonella Capperucci, Cecilia Bartoli, Damiano Tanini, Silvia and Francesco Michelazzo, Silvia Selleri, Laura Colli, Camilla Cyriax, Rosaria Parrini, and Lia Jovine-Mazza.

We are grateful for personal recollections about Luigi Rolla (1882–1960) from Gianluigi Calzetta, Enrico Franceschi, Aldo Iandelli (1912–2008) and Rocco Longo; about Angelo Angeli (1864–1931) from Natalina Angeli and Giovanni Battista di Giusto; about Giorgio Piccardi (1895–1972) from Anna, Maria Stella (1924–2012), Oretta (1923–2015) and Giovanni Piccardi, his daughters and nephew. The children of Giovanni Canneri (1897–1964) and of Lorenzo Fernandes (1902–77) have also illuminated the image of their fathers.

We are most grateful for the competence and enthusiasm of the science library staff at the University of Florence: Sabrina Albanese, Sabina Cavicchi, Marzia Fiorini, Laura Guarnieri, Serena Terzani, and Roberto Bongi. We also thank the Secretariat of the Department of Chemistry for their contributions, and specifically for that of Maria Luisa Amerise, Carla Anichini, Viviana Canto, Valeria Catelani, Fiorella Gherardeschi, Valentina Nardi, Beatrice Poggini, and Michele Carnemolla.

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Contents

Chapter 1
Introduction: A Brief Historic Outline

At Florence, Italy, the marriage between art and science leads to profound reflection and ongoing discovery. Florence has anticipated the present age: "the city of art" has always had a "scientific mind."

In the High Middle Ages, chemistry and the applied sciences had been the driving force for the striking economic growth of the city. For example, when it was discovered that urine was very useful as a mordant for dyeing textiles, the "Arte della Lana di Firenze" company, at the height of its economic development, directly employed 300 workers, and indirectly, about a third of the population of Florence, producing 100,000 pieces of dyed fabric annually. This lucrative enterprise enabled many Florentine families, in the course of just a few generations, to become very wealthy. Dynasties such as the Peruzzi, Bardi, and Medici families were richer than many sovereign kingdoms and were even able to support England in its eternal wars with France.

In more recent times, impressive scientific collections were amassed by the Medici family and continued during the reign of the House of Lorraine. When the Grand Duchy was joined with the newly established Kingdom of Italy, the duty of preserving and augmenting these collections fell to the University of Florence. Some museums, such as the Museum of Zoology, are historic; others, such as the museum "Chemical Heritage Hugo Schiff," are more recent institutions. Some of them, such as the Galileo Museum, have been completely renovated, but contain many original instruments and artifacts.

In the city that is the symbol of the European artistic Renaissance, it is possible to find scientific treasures that one might not expect. This book offers a new vision of the city; following the biographies of its most famous chemists, it will follow a pathway of scientific research that was not only (as it seems even up to now propounded in a monotonous din) the works of Galileo Galilei and of physics, but new disciplines, such as chemistry, pharmaceutical chemistry, and biochemistry.

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In 1321, the year that Dante Alighieri (1265–1321) died, thanks to a decision of the Republic of Florence, the *Studium Generale*, the true and proper nucleus of the University of Florence, was founded. Initially, among subjects taught at the *Studium*, Civil and Canon Law, Letters, and Medicine were represented. However, its very existence, right from the beginning, was difficult: it was often held hostage by Popes, Emperors, or petty local princes. Suppressed many times, and many times reborn, the university that we know today emerged at the end of the 18th century.

Up until the reign of the Medici the princes who governed Tuscany possessed, in addition to their collections of paintings, statues, and archaeological finds, holdings as well in the area of natural history. These were hidden from the eyes of the public at large since they were the special treasures of the Grand Dukes and were shown more than anything else to please and to impress courtiers and illustrious guests. It was only on rare occasions that they were used for public education. These collections were not arranged according to any scientific criteria [1]. A similar state of affairs endured until the death of the last Medici Grand Duke, Gian Gastone (1671–1737).

In 1763 the new Grand Duke of Tuscany, Francis II of Lorraine (1708–1765), asked the scientist Giovanni Targioni Tozzetti[1] (1712–1783) to reorder and classify "the natural objects of the Galleria of Florence." This work, neither short nor easy, was completed before the end of the following year. Targioni had wished that the Medici collection be used for public education; he proposed this idea to the Grand Duke, but for a variety of reasons, nothing was done. It was only in 1775 that Targioni was able to realize his desire when the Grand Duke Peter Leopold I of Lorraine (1747–1792) inaugurated the Museum of Physics and Natural History, naming Felice Fontana (1730–1805) as Director. The Grand Duke himself, a very cultivated man, was engaged in chemistry at a far higher level than that of a simple amateur; he used the well–equipped laboratory at the museum for his experiments (Fig. 1.1). In 1790, Peter Leopold I left the Duchy of Tuscany for Austria where he became the Emperor, succeeding his brother Joseph II (1741–1790). On account of these changed political conditions, including the French Revolution, the Museum was never opened for public education.

On the contrary, Pisa, with the decree of 10 October 1757, established the first Chair of chemistry in Tuscany (the third in all of Italy) to which the Florentine, Antonio Niccola Branchi (1723–1810), was appointed. This lectureship in chemistry came with a salary of 100 scudi annually, provided that he leave to the university his own dedicated (scientific) instruments [2]. Branchi not only observed this condition to the letter, but at the time of his retirement in 1807, he also "bequeathed" to the university his own son, Giuseppe Branchi (1766–1847), as his successor to the Chair of chemistry: "there is nothing new under the sun."

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[1] With him the true dynasty of naturalists began: his son Ottaviano (1755–1826) was a botanist; his nephew (1785–1856) was also a botanist, and finally, his great−nephew, Adolfo (1823–1902), was a zoologist.

Fig. 1.1 The Grand Duke Peter Leopold's "Chemistry Cabinet" (Museo Galileo Galilei, Florence). This self-contained mini-laboratory was actually only a part of a larger private laboratory. It was left to the Museum of Physics and Natural History when the Duke departed Florence in 1790. Photograph by M.V. Orna

Meanwhile back in Florence, in 1807 the King of Etruria,[2] Carlo Ludovico of Bourbon (1799–1883), under the guardianship of his mother, Queen Maria Luisa of Bourbon (1782–1824), established the Lyceum of Physical and Natural Studies. From this date forward the true and proper history of the Science Campus of the University of Florence begins.

The year prior to Florence's annexation to the Kingdom of Italy, in 1859, the Faculty of Physical and Natural Sciences of the Royal Institute of Higher Practical Studies and Specialization was established. This was a semi–public institution: it was partially supported by the city of Florence, and by other entities, both public and private. At the end of World War I, following serious financial difficulties due

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[2] The Kingdom of Etruria had a territorial extension somewhat similar to today's Tuscany and to Tuscany Romagna. The latter, in 1923 after six centuries as part of Tuscany and not without regret, was partially ceded to the region of Emilia (thereafter called Emilia—Romagna). Etruria was created as a consequence of the Treaty of Aranjuez made between the Kingdom of Spain and Napoleonic France on March 21, 1801. Therefore, the new kingdom had an ephemeral existence; six years later it was annexed to the French Empire.

to currency devaluation, the Institute's head, Marquis Filippo Torrigiani (1851–1924), requested the government's help. The fascist regime flatly refused.

The Institute ceased to exist on 30 September 1924, and a day later, it was reborn as the University. Torrigiani, embittered, never lived to see that day: he had passed away on the previous 17 February.

The first academic year was solemnly inaugurated on 20 January 1925 in the presence of the Minister of Public Education Pietro Fedele (1873–1943), of the Archbishop of Florence, Cardinal Alfonso Maria Mistrangelo (1852–1930) and of all relevant authorities. However, not everyone was in accord with this development, particularly men of influence like the poet and writer Angiolo Orvieto (1869–1967), who strongly opposed the creation of the University. The last head of the Royal Institute of Higher Studies, the honorable Cesare Merci (1853–1943), and the new Rector Giulio Chiarugi (1859–1944), fully recognized that it was due to the decisive personal will of Benito Mussolini (1883–1945). Mussolini wanted the University to be erected in what he called the "intellectual capital of the world." But this was not just a show of gratitude: it was a full self-identification with fascism and the new political reality. The fact that the city of Florence had obtained the University thanks to the "Duce" made it seem almost like a private estate of fascism.

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Chapter 2
Natural Scientists from the Last of the Medici (1694) to the Period of the Museum of Physics and Natural History (1775–1807)

By the end of the 17th century in Europe the new experimental method that eventually became central to the discipline of chemistry was in its infancy. Within a few decades, it passed with giant steps into the 18th century and became well-established thanks to the ideas, inventions, discoveries, intuition and theories of Antoine Laurent Lavoisier (1743–1794).

In documenting the roots of chemistry in Florence, it is essential to mention the patronage of the Medici and Lorraine, Lords of Florence, who supported it in many forms: costly chemical reagents (such as gems and diamonds) and fine scientific instruments built by skilled craftsmen. The most significant event in this period was the rise of the first great chemical industry in Italy—the manufacture of sulfuric acid. Other industries followed later such as sugar extraction from sugar beets, serving to tie chemistry irrevocably to industrial development.

But surely, one of the most auspicious events in Florentine scientific history was the burning-lens experiment by Giuseppe Averani and Cipriano Targioni that revealed the true nature of diamond. It also set the stage for Lavoisier's more famous demonstration a century later that demolished the phlogiston theory and replaced it with his theory of combustion.

In Tuscany, the area of pharmaceutical chemistry flourished, and in Florence, the Museum of Physics and Natural History was established. Opened in 1775 by decree of Peter Leopold of Tuscany (1747–1792) and under the direction of the abbot, Felice Fontana, it underwent substantial changes at the hands of the next director, chemist Giovanni Fabbroni, in 1805. In fact, Fabbroni took control of a situation in Florence that most would consider untenable. There were no analogous institutions in Tuscany similar to those in the great cities like London and Paris where scientific ferment gave rise to prestigious research publications and concomitant financial support. So Fabbroni undertook to transform the museum into a scientific institution that he hoped would function as a "quasi-university." However, with a change in government in 1807, officials appointed by the former government, such as Fabbroni, were removed.

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Fig. 2.1 The Burning Lens used by Averani and Targioni. Donated by its maker, Benedikt Bregans of Dresden, to Grand Duke Cosimo III in 1690. *Courtesy* Museo Galileo, Florence; *Photography* Franca Principe

2.1 Giuseppe Averani (1662–1738) and His Experiment with Cipriano Targioni (1672–1748)

Giuseppe Averani was born on 20 March 1662 in Florence. He completed his degree in law at Pisa in 1684 and was appointed to the Chair of civil law there in 1687, where he remained until his death in 1738. Although he was renowned for his interpretation of Roman law, and was a member of many prestigious regional and international academies, his interests were very broad: theology, geology, astronomy, geometry, and, above all, experimental physics. In 1694 the Grand Duke Cosimo III Medici commissioned Averani, together with Cipriano Targioni (1672–1748), with the task of using a burning lens (Fig. 2.1)[1] to investigate whether diamond was, indeed, combustible.

Conventional wisdom, dating back to the opinion of Emperor Rudolf II's physician, Anselmus De Boodt (1550–1632), and affirmed by Isaac Newton (1642–1727), asserted that it was not. Their conclusion was a hypothesis unsupported by experiment. And so the great experiment of Averani and Targioni, the results of which reverberate to the present day, demonstrated that the nature of

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[1] Donated to the Grand Duke by its maker, Benedetto Bregans, the lens is now housed in the Galileo Museum.

diamond, that most precious and hardest of stones, was pure carbon. They reported their findings in the following words [1]:

> Diamond, thought by all…that no force could break it, resisted the power of this fire less ably than other gemstones. So where the others were hardly consumed, this [diamond] completely disappeared.

Averani and Targioni, in demonstrating the combustible nature of diamond, as well as determining its nature, debunked the belief that this gem was absolutely unassailable: diamond exists in a form that is thermodynamically unstable at ambient conditions. The chemistry laboratory of the Museum, with its advanced scientific tools, became a research center of considerable importance for the naturalists of the time. For example, the aforementioned burning lens was used again in 1814, by Humphry Davy (1778–1829), when he came to Florence with his valet and laboratory apprentice Michael Faraday (1791–1867), to complete further research on the chemical nature of diamond.

Averani was a friend of the most learned men of his time. King Victor Amedeus II of Savoy (1666–1732) invited him to the faculty of the University of Turin, but he refused. In his honor in 1721, his scholarly associates struck a medal with his effigy. At his death in Florence on 24 August 1738, he left his belongings to the poor and his library to the University of Pisa.

2.2 Giovanni Targioni Tozzetti (1712–1783) and His Family

The Targioni Tozzetti family has been, for more than two centuries, an important point of reference in Tuscany's scientific and cultural life. The history of this family and of its familial relationships allow us also to understand the social climb of a complex familial nucleus motivated to maintain intact a patrimony consisting of a rich collection of manuscripts, books, herbaria, and other natural collections amassed over the course of decades by various family members.

The most well-known naturalist in the family is certainly Giovanni Targioni Tozzetti (1712–1783), physician, botanist, and naturalist, who probably inherited his passion for science from his paternal uncle, Cipriano Antonino Targioni (1672–1748). In 1747, he married Brigida Dandini, descendant of the famous family of painters. Their son, Ottaviano (1755–1829) followed in the footsteps of his father, becoming a physician, botanist, and professor at the University of Pisa and director of the Medicinal Plant Garden. Ottaviano in his turn married Vittoria Campana; they had two sons: Antonio (1785–1856) and Giovanni (1791–1863). Antonio continued the family tradition, studying medicine and becoming famous for his chemical discoveries and his botanical work. Giovanni, Ottaviano's other son, did not become a scientist, but one of his sons, Adolfo (1823–1902), completed his degree in medicine and later became professor of botany, zoology,

Fig. 2.2 Portrait of Giovanni Targioni Tozzetti. *Courtesy* Museo Galileo, Florence

comparative anatomy, and entomology at the Institution of Higher Studies at Florence. He was the last scientist in the family.

Son of Benedetto Targioni and Cecilia Tozzetti, Giovanni Targioni-Tozzetti (Fig. 2.2) was born in Florence on 11 September 1712. His childhood was dominated by a passion for all things natural, and above all for plants and fossils. The great botanist Pier Antonio Micheli was a frequent visitor to his home and with Micheli he explored the mountains and plains of Tuscany. In 1730 he went to study at Pisa and received his degree in medicine and philosophy in 1734.

The year 1737 marked a turning point in the history of Florence and also in Giovanni's personal life. On 2 January, Pier Antonio Micheli (1679–1737) died. On 7 January, Targioni was immediately appointed his successor as Director of the Garden and Reader in Botany at the Studio Fiorentino. On 12 March, he participated in the translation of the remains of Galileo to the church of Santa Croce; on 12 July, Francis Stephen of Lorraine (1708–1765) became the new Grand Duke of Tuscany starting the Lorraine dynasty, which reigned for more than 120 years. Subsequently, numerous studies on Tuscany's natural resources, needed to improve the living conditions of the people and to advance the economy, were undertaken.

Commissioned by the Lorraine Government and by the Botanical Society, between 1742 and 1745, Giovanni conducted scientific expeditions all over Tuscany, observing and cataloguing the natural resources in each area. Between 1751 and 1754, he published the first edition, entitled "*Viaggi fatti in diverse parti della Toscana per osservare le produzioni naturali e gli antichi monumenti di essa,*" in six volumes, and the second edition in 12 volumes, with much more information, including the report of Micheli's 1732 expedition, appeared between 1768 and 1779.

In 1763, Giovanni compiled a 12-volume manuscript catalog of the natural-products collection in his private museum. The catalog and the greater part of the samples described therein are presently held by the Museum of Natural History of Florence. It contains descriptions of animals, fossils, rocks, and minerals. The basis and details of the mineral collection are fully described in the 2007 work, "A Contribution to the Mineralogy of the 18th Century" [2].

Targioni's work was a milestone in the advancement of Tuscan science and its economy. For example, his publications contained the first scientific description of the borax-bearing zone, destined to become world-famous for the production of boric acid and the utilization of the subterranean steam arising from the famous boric acid fumaroles, used for production of electrical energy.

In 1754 he published his "Prodromo," an encyclopedic work describing Tuscany's physical topography and explanations of all aspects of its natural history, something he never could have accomplished without making use of his close relationships and friendships with scholars and intellectuals of the area. This monumental work has never been published as a single work. It is collected in 17 hand-written volumes under the title "Collected information pertaining to the origin of progress and improvement of the physical sciences in Tuscany (for the use of Doctor Ottaviano, his son)."

In addition to his scientific studies, throughout his life, Giovanni continued to practice medicine. In 1750 he worked at the Santa Maria Nuova hospital for incurables (syphilitics). In 1756, he administered smallpox vaccinations, the first in Italy, at the Spedale degli Innocenti (Foundling Hospital); the gratifying results were published by the press in 1757. His successes earned him great esteem as well as an appointment to the medical staff of the court, but this left him with little time to do scientific research and exploration.

After great famines that afflicted Tuscany in 1764 and 1766, the problem of agriculture became ever more serious and research for solutions involved all the great brains of the country, with Targioni Tozzetti always at the front line, thanks to his profound knowledge of the territory. In 1767 he published "*l'Alimurgia*," an enormous volume on how to minimize famine's effects. Of its 367 pages, almost 200 are devoted to weather-related causes of famine. The last part, based on his microscopic observations, addressed grain rust, a fungal infection that affected the nutrient quality of wheat.

Also in 1767 he published a prescient volume on the Arno River, calling it a vital element for the city's life, and, at the same time, a very dangerous one. According to Giovanni, the frequent and ruinous flooding was not due to natural causes, but to human activity: excessive deforestation, urbanization all along the river, and factories that choked up the river bed with detritus. He actually proposed that the course of the Arno be diverted and that its trench be filled in and used for streets, businesses, and markets.

Targioni devoted the latter years of his life to getting his private museum in order—finds and samples coming from his own explorations and those of Micheli. The entire collection was bequeathed to his son Ottavio, who reclassified it on the basis of new scientific discoveries. In 1829, Baron Bettino Ricasoli acquired the mineral and fossil sections, but when he married in 1838, these sections went to the Museum of Natural History [3]. The botanical section remained with the Targioni family until 1845. It consisted of about 19,000 plant samples coming in large part from Tuscany and other parts of Italy.

Giovanni Targioni Tozzetti, member of numerous domestic and international scholarly academies, died on 7 January 1783, and his renown earned him a well-deserved burial place in the church of Santa Croce.

2.3 Felice Fontana (1730–1805)

Felice Fontana was born at Pomarolo, Trent, on 15 April 1730. Anatomist, physiologist, chemist, and naturalist, he was one of the most famous Italian scientists of the 18th century [4–7]. Beginning his studies in mathematics, he studied histology and physiology at Padua and then Bologna. Among Fontana's earliest physiological experiments were those in which he used static electricity to examine the behavior of nerve and muscle tissue [8]. The stimuli that he produced using the electrical instruments of the time gave small quantities of electricity at very high voltages (about 10,000 volts or more). Fontana claimed that the way in which an organism reacted to external stimuli was an expression of its internal force and organization, independent of the external force and nature of the stimulant, an idea that was initially attributable to the Swiss physiologist Albrecht von Haller (1708–1777) [9]. He and his colleagues frequently borrowed the laboratory facilities of Laura Bassi (1711–1778) [10] and her husband for their work, which preceded the experiments of Galvani by several decades.

In 1766 he was appointed court physicist by Grand Duke Peter Leopold and was a driving force in establishing the Royal Museum of Physics and Natural History (founded in 1775) and which he directed until 1805. He also collaborated with Clemente Susini (1754–1814) in the preparation of the renowned anatomical wax figures presently held at the Museum of the Observatory.

From 1775 to 1780, Fontana traveled in different parts of Europe to cultivate relationships with major scientists of the day, e.g., Lavoisier and Joseph Priestley (1733–1804), accompanied by his student and future successor, Giovanni Fabroni. During this period, he studied the chemistry of poisons and also pneumatic chemistry. He published two papers with the Royal Society of Chemistry on the latter topic. He also became, in studying the anatomy of venomous reptiles, one of the world's foremost microscopists. In these studies, he did tissue staining to facilitate his work: he was a true precursor of modern histological techniques. One result of his work was the discovery of a new canal in the eye and hitherto unknown spaces near the anterior chamber of the eye, now called respectively Canal of Fontana and Fontana Spaces.

His other chemical research was directed at what was then called nitrous air (nitric oxide) and dephlogisticated air (oxygen). In 1779 he observed that oxygen's solubility in water is greater than that of air, and in 1780 he determined the nature of water gas (a mixture of hydrogen and carbon monoxide). In 1777 he discovered carbon's ability to absorb gases.

Felice Fontana died in Florence on 20 March 1805.

2.4 Giovanni Fabbroni (1752–1822)

Giovanni Valentino Mattia Fabbroni, born in Florence 13 February 1752, was a naturalist, economist, agronomist, chemist, and Italian politician with a wide cultural background. As Felice Fontana's assistant, he helped found the Museum of Physics and Natural History and was its provisional director from 1805 to 1807. He wrote works on soil fertility, the use of fertilizers, and coal.

During the reign of Ferdinand III of Tuscany (1769–1824) he became a member of the International Commission for the Reform of Weights and Measures and, in 1800, he became not only Director of the Florence Mint, but also a member of the Commission for the Institution of the Metric System during the Napoleonic occupation. After the Restoration, he became responsible for the mines of the Grand Duchy of Tuscany.

Although he was a polymath, his major scientific contributions were in the area of chemistry. He adopted Lavoisier's theory of combustion and had it broadly disseminated in Tuscany. He used Alessandro Volta's newly-invented "pile" to conduct important electrochemical research. But perhaps what made him famous in his time was his intervention of 1801 at the Academy of Georgofili, when he entered into the debate that took place years earlier between Alessandro Volta (1745–1827) and Luigi Galvani (1737–1798) relating to so-called "animal electricity." Fabbroni expounded the theory according to which the muscle contraction of a skinned frog connected to the conductors is due to the interplay of the two metals placed in contact in the presence of a solution. From this memory sprang the chemical theory that would explain the generation of electromotive force in Volta's "pile."

Fabbroni died at age 70 on 17 December 1822.

His works were collected into one volume and published in 1848 under the title "Writings on Public Economy." Fabbroni was a versatile man of science and his scientific eclecticism was well recognized not only in Tuscany but abroad. When the Soviets, starting in 1959, succeeded in photographing the dark side of the moon, the International Astronomic Union decided to name one of its craters after him.

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Chapter 3
Chemists in the Period of the Lyceum of Physical and Natural Studies (1807–1859)

3.1 Girolamo de' Bardi (1777–1829)

Girolamo Arcangelo Antonio de' Bardi of Vernio was born on 25 August 1777. His parents were Eleanor Dainelli and Count Cosimo Gualterotto. As heir to a prestigious noble family, he was given a superb education, and then for a time, he served as a page to the Grand Duke Leopold. Later, backed by many leading scientists, on 17 February 1807, he managed to replace Giovanni Fabbroni as director of the Museum of Physics and Natural Sciences. As the new director, he hastened to place his own stamp on the Museum's restructuring, establishing four new chairs, including chemistry with pride of place. He encouraged these new instructors to hold lessons and demonstrations with the explicit objective of practical applications directed to economic development of the Grand Duchy [1]:

> That part of chemistry relative to manufacturing and like arts also will be given special treatment so as to benefit our economy such as establishing chemical factories, like those, for example, in France and England…

Bardi had in mind an ambitious project aimed at making the Museum the major driving force in the scientific and economic advancement of Tuscany. But, although he was a practical man, he nevertheless maintained contact with the hottest developments in Italian experimental science, interesting himself for example in the research on the calculus of infinitesimals by the mathematician Vincenzo Brunacci (1768–1818) [2].

Another fundamental plank in the plan for the Lyceum, as in all of Bardi's work, was his insistence on the practical application of knowledge and the social benefits that would accrue. By linking science with reform, Bardi reinvigorated Grand Duke Leopold's legacy of collaboration of the government with scientists. Also, to his great credit, he tried to confer on the "Etruscan State" a more modern and active role in public education. The early fall of the Kingdom of Etruria and its subsequent annexation to France prevented these projects from taking on a more concrete form.

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Bardi's activities as a man of science sees him occupied with confronting the exigencies dictated by changed political conditions: restructuring of weights and measures with the metric system, creation of borders for three new Tuscan "departments," and much else. He sought to align himself with the new Napoleonic government to accomplish his ends, but from the viewpoint of Tuscan science, French domination did not bring about perceptible changes. Due to further political upheavals, an increased budget for the Museum did not allay his fears for its survival. In addition, he realized that he was too compromised politically with the fall of Napoleon to be able to remain its director once the Grand Duke returned to power. His fears were confirmed on 1 July 1814 by official decree that the Lyceum be closed and that its professors be dismissed.

Ever attentive to practical matters, Bardi took his interest in public education into his own hands by opening a free school in 1818 for poor children. He also furthered hopes for the future of the Museum by continuing to enrich its mineral collections at his own expense.

The reopening of the Museum of Physics seemed more assured with the accession of Leopold II of Tuscany (1797–1870) to the throne. Thanks to Bardi's efforts, the Grand Duke reopened the Observatory located in via Romana, and where it remains to the present day (Fig. 3.1). In 1827, the Grand Duke's growing

Fig. 3.1 A fresco depicting Galileo's demonstration of Saturn's moons. Tribune of Galileo, located at the Museo "La Specola," the observatory reopened thanks to Bardi's efforts. The museum now houses the zoology collections and the collection of anatomic wax models. The original observatory can be visited by appointment only. *Photograph* M.V. Orna.

interest in science took the form of a higher budget for the Museum, and also his decision to send a group of Tuscan scientists on an expedition to Egypt with the Egyptologist J.-F. Champollion (1790–1832).

Bardi, stricken with tuberculosis several years previously, died on 28 February 1829, never having succeeded in returning the Museum to the public service. In his will, he left 50,000 scudi to establish a free school for working class education: the Pio Istituto de' Bardi. Along with the elementary school, two courses, one in mineralogy and geology applied to agriculture, and the other, chemistry and physics applied to the arts and manufacturing, were stipulated.

3.2 Giuseppe Gazzeri (1771–1847)

Giuseppe Gazzeri was born in Florence on 9 November 1771. He completed his law degree at the University of Pisa in 1795, and after a brief career in law, and inspired by the research activities of French chemists, he devoted himself entirely to scientific studies, eventually becoming an expert in agricultural chemistry [3].

Contrary to what one might think, chemical research in those years experienced great expansion. In particular, in Tuscany, there was considerable discussion about the "chemical revolution" begun by Lavoisier, and not surprisingly, the Royal and Imperial Museum of Physics and Natural History, was one of its centers. Gazzeri, however, identified in the Royal Academy of Georgofili an institutional reference point for his work as a scientist. At the Georgofili he presented, over a number of years, papers on the most disparate areas of chemistry and agronomy. In 1802 he read to Georgofili members a paper entitled "The need and usefulness of the study of chemistry as a driver in perfecting the arts" [4]. In this paper he emphasized chemistry's "regeneration," which had acquired the status of exact science, and it claimed importance for development of manufacturing and agriculture. Gazzeri did not fail to note that despite the scientific and social importance of chemistry, it lacked in Florence a public teaching institution; he proposed educational reform to ensure the dissemination of chemical knowledge.

When Maria Luisa of Bourbon re-established the Royal and Imperial Museum of Physics and Natural Science, she appointed as director Girolamo de' Bardi, as noted previously. Shortly thereafter, when Bardi began his Lyceum at the Museum, his appointee to the Chair of Chemistry was Gazzeri. Thus, Gazzeri became the architect of public education in chemistry at Florence.

Gazzeri's appointment to the chemistry chair was the first step in what became his outstanding career in science and service to the public. Among Gazzeri's papers, conspicuous are those related to the possibility of extraction of a blue dye that Gazzeri identified in the woad plant (*Isatis tinctoria*) growing in Tuscany. We now know this blue dye as indigo (see Fig. 3.2).

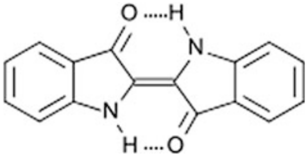

Fig. 3.2 Indigo. Indigo is a colorant extracted from a plant and was well-known in Asia 4000 years ago: its name, in fact, derives from "India," which was its principal source. The same name is used to identify the substance, derived from indole. Its IUPAC name is 2-(1,3-dihydro-3-oxo-2H-indol-2-ylidene)-1,2-dihydro-3H-indol-3-one

This was one of his first industrial applications. Another of his duties was evaluating the ore quality of the recently discovered lead mines in the area, which he found to be very good. He was not only current regarding the experimental discoveries by Lavoisier, Henry Cavendish (1731–1810), Priestley, and Volta, but Gazzeri espoused their theories and made them part of his chemistry curriculum. In his course content that he published in the first volume of the Annals of the Museum, it is clear that he supported state-of-the-art chemistry of his time, referring to the experimental methods and results by such luminaries as Humphry Davy, Joseph-Louis Gay Lussac (1778–1850), and Louis-Jacques Thénard (1777–1857), as well as those mentioned above.

In addition to Gazzeri's indigo research, he also applied his chemical knowledge to exploiting the mineralogical resources of the area, such as boric acid. He also developed cost-effective chemical processes for extracting sugar from grapes, beets, and chestnuts, and for obtaining potash from the ashes of swamp and bog plants growing in the Maremma area in southern part of Tuscany.

After the Restoration and consequent suppression of the Lyceum, Gazzeri (Fig. 3.3) taught pharmaceutical chemistry for many years. He also became Commissioner General of Mines and of the Foundry, vigorously pursued drilling in the steam-vent area of Tuscany to find new fumaroles, and was active in the field of agrarian chemistry.

From this experience, he wrote his most successful work, *The Compendium*, an elementary treatise on chemistry in two volumes that appeared in new editions in 1819, 1828, and 1833. The work consisted of 100 lessons modeled on the "*Traité élémentaire de chimie*" (1789) of Lavoisier and Antoine François Fourcroy (1755–1809) and Jöns Jacob Berzelius's (1779–1848) "*Lärbok i Kemien*" (1808–1818). Although the work was aimed at pharmacy-school students, it contained theoretical material such as the law of definite proportions and atomic theory, as well as practical chemistry.

In addition to fulfilling important official duties, Gazzeri never forgot the education of the poor, founding and presiding over kindergartens for poor children.

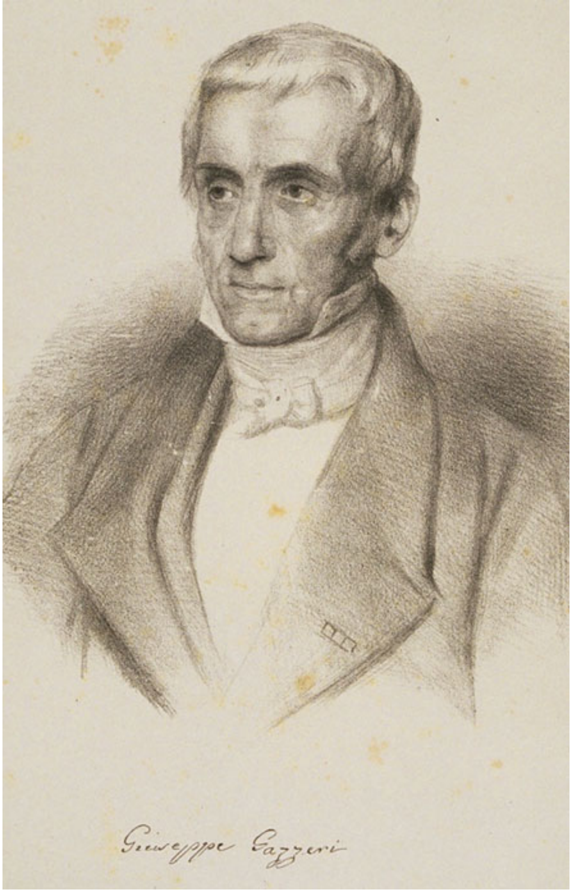

Fig. 3.3 Giuseppe Gazzeri (1771–1847). *Courtesy* Museo Galileo, Firenze

Furthermore, Gazzeri was interested in the development of physics, and in particular, of electromagnetism. He performed experiments with Bardi and Vincenzo Antinori (1792–1865), always approaching them with methods marked by strict empiricism, but at the theoretical level, he was convinced of the existence of a fluid he called "etereo" that filled the space of a finite universe and was responsible for the phenomena of light, heat, electricity and magnetism [5]. He never had a specific scientific discovery associated with his name, but his many investigations in pharmaceutical and applied chemistry (including problems of air and water quality), in physics, and agronomy testify to his undeniable brilliance in scientific and cultural contexts of the Grand Duchy.

But he was not a well man. He suffered from miliary tuberculosis that invaded his entire body, forcing him into retirement early in 1846. He died on 22 June 1847.

To commemorate his passing and his scientific contributions, the grieving community affixed this plaque, still visible, at his former residence in the Piazza del Carmine no. 7 [6]:

> IN QUESTA CASA DIMORÒ LUNGAMENTE GIUSEPPE GAZZERI PROFESSORE DI CHIMICA CHE ARRICCHÌ LE SCIENZE SPERIMENTALI DI NUOVI TROVATI E LI CONVERSE IN PUBBLICO BENEFIZIO ILLUSTRÒ CON LA DOTTRINA E LA PAROLA LA CATTEDRA CON GLI SCRITTI IL SUO NOME E QUI MORÌ IL XXII GIUG. DEL MDCCCXLVII COLMO D'ANNI E DI MERITI ONORATO DELLA STIMA UNIVERSALE

3.3 Gioacchino Taddei (1792–1860)

Gioacchino Taddei (Fig. 3.4) was born in San Miniato on 30 March 1792, but was orphaned at age 13. Thanks to a grant [7] he was able to study at the University of Pisa, from where he graduated in medicine in 1815. Due to a typhoid epidemic, he returned to practice medicine in his home town and remained there.

In addition to medicine, Taddei studied chemistry, particularly pharmaceutical and applied chemistry, with distinction, and published papers as early as 1816. He became a member of several learned societies, among which was the Academy of the Georgofili. In 1820 he won the competition for the Chair of Pharmacy at the Hospital of Santa Maria Nuova, succeeding Giuseppe Gazzeri. His excellent and numerous investigations in organic and toxicological chemistry were published in a valuable work entitled *Farmacopea generale* [8].

Thanks to his interest in the economy and to his friendship with the Marquis Cosimo Ridolfi (1794–1865), a philanthropist and champion of renewal of the physical sciences in Tuscany, Taddei had the opportunity to specialize in chemistry in the Marquis' laboratory and, later, of going on a grand scientific tour of the major European capitals (1821–1822). He studied for four months in Paris with Louis Nicolas Vauquelin (1763–1829), Thénard, Michel Eugène Chevreul (1786–1889), Gay Lussac, and Mathieu Orfila (1787–1853). In England, he established personal acquaintances with Humphry Davy, William Hyde Wollaston (1766–1828), and John Dalton (1766–1844). On the way back home, he visited Brussels, Strasbourg, the Piedmont, Lombardy, the Veneto, Bologna, Modena, and Parma, visiting hospitals, laboratories, factories, universities, and industrial sites.

Then in 1824 he published his "*System of Stoichiometric Chemistry: The Theory of Definite Proportions*," followed in 1826 by his four-volume "*General Pharmacopeia*." Nine years later, his "*List of Poisons and Their Antidotes*" appeared (1835).

Taddei was also interested in thermodynamics and its practical applications, as was the wont of many Italian chemists. In 1836 he invented a device, which he called a "calefattore," or heat-producer, designed to heat buildings with greater fuel

Fig. 3.4 Gioacchino Taddei (1792–1860). *Courtesy* Museo Galileo, Firenze

economy. He took pleasure in devising other gadgets of a practical and technical nature, but when a massive cholera outbreak occurred, he turned his attention to stopping its spread. He proposed making extensive use of chlorine in order to disinfect houses, clothes and people. He advised frequent change of clothes and disinfection of those removed and of those already disinfected [9]. Shortly afterward, he was appointed to the Chair of Organic Chemistry and Medical Physics at the Medical-Surgical School of Santa Maria Nuova.

In 1844, the indefatigable Taddei published his essay on examination of blood [10] and in the following year, his “Manual of Organic Chemistry and Medical Physics” [11]. The first was a profound study of hematology focusing on how to distinguish the blood of animals from human blood, a useful tool in forensic medicine. The second was aimed at educating his own students. It contained studies on blood, urine, and other biological materials, as well as analytical chemistry as applied to different illnesses [12]. He also did research on gluten, the water of the city of Florence, and mercury poisoning [13, 14].

By this time, he had become a member of 42 scholarly academies, both Italian and international. Versatile in many disciplines, he was particularly distinguished as a hematologist and a hydrologist.

He organized, attended, and presented many papers at scientific meetings throughout Italy, first at Pisa in 1839, and later at Milan, Naples, Lucca, and Venice. He spoke, among other subjects, about the color of blood and its iron content, the spongy material in bones, and the edibility of wool, feathers, skin, and hair by analyzing their protein content. In Venice, his paper was concerned with the "pernicious" character of the waters in Lombardy and the Veneto, accusing the Austrian government of imposing by force such harmful drinking water on the populace [15].

Toward the end of the 1840s, Taddei embroiled himself in the question of the population explosion and the suggested measures to curb it, including elimination of hospitals and charity hospices, as well as looking the other way in cases of murder and infanticide. He violently opposed these suggestions on the basis of his own view of scientific equilibrium: the population would cease to expand if access to food diminished, i.e., population growth was directly proportional to available food. His thesis was prescient: only 70 years later, Fritz Haber (1868–1934) perfected a process to "fix" atmospheric nitrogen, thus eventually making fertilizers universally available. The human population increased exponentially thereafter.

Other articles written by Taddei focused on the study of the so-called "stone of hell" or "lunar caustic," silver nitrate ($AgNO_3$) in modern terminology. This compound was used in medicine and veterinary medicine to cauterize infected wounds. It came in several forms fused with other salts. The so-called form "mitigated" form contained a quarter to a third of potassium nitrate (KNO_3), while the so-called "hard" contained 2–5 % lead chloride ($PbCl_2$) or silver chloride (AgCl).

In addition to his scientific activities, which were prodigious, Taddei was also heavily involved with the political ups and downs of his day. He was twice a member of the Tuscan Assembly and, as its President, he fell into disgrace when the Restoration of the Grand Duchy occurred in 1848. He was suspended from his teaching position, and was only vindicated when the successful Tuscan Revolution took place 11 years later, meanwhile devoting himself to his own research and to his family. With the fall of the House of Lorraine in 1859, he took up his teaching once again.

A few days before his 67th birthday, Taddei was appointed director of refining and consulting chemist of the Florence Royal Mint. Improved instruments for casting molten metals was perhaps the last scientific activity to which he applied his efforts prior to his death just a year later, 28 May 1860.

3.4 Luigi Guerri (1823–1892)

Luigi Guerri was born in Florence on 21 June 1823 when the House of Lorraine reigned, by the "grace of God and the will of the nation." The boundaries of that world were the Apennine Mountains to the north and east, the Tyrrhenian Sea to the west, while southward, the unhealthy Maremma swamp barred the way to anyone who wanted to set foot in "Sweet Tuscany." The academic world, however, was made up of a select few, and there was fierce competition for the few places that existed.

Luigi's father was a pharmacist, and following in his footsteps, he enrolled at the Pharmacy School attached to the Hospital of Santa Maria Nuova, and in 1847 he obtained the "spezialino" (pharmacist) diploma.

In 1850, in order to fill the chair of pharmaceutical chemistry, from which Gioacchino Taddei had been banned for his political leanings (for the first time!), public competition was held. The winner, Giovanni Campani (1820–1891), from Siena, invited the 27-year old Luigi Guerri to be his assistant. In this way, Guerri's academic career commenced, although his first publications dated back to 1846, while he was still a student [16].

Giovanni Campani was soon recalled to Siena and was succeeded by Damiano Casanti, son-in-law of Gioacchino Taddei. In 1857 there was another turnover: Enrico Buonamici, a former assistant of Taddei's and incidentally, a cousin of Guerri's, was called to become professor of medicinal chemistry. He taught for three years, during which time Guerri became director of the Royal Pharmaceutical Laboratory of the Hospital of Santa Maria Nuova, where he was to remain for the rest of his life. Guerri developed original interdisciplinary research in pharmaceutical chemistry and medical studies, and gained renown for his pioneering studies on disinfectants. He was also a member of the Municipal Commission of Hygiene, dealing with water quality of Florence. Luigi Guerri was one of the most important researchers and teachers of Pharmaceutical Chemistry of the 19th century.

Before the establishment of the kingdom of Italy, the pharmaceutical profession was regulated by a sea of laws, decrees and ordinances that varied widely from state to state. In Tuscany, the pharmacist was considered a shopkeeper in every respect with the sole obligation of some kind of qualification, called the "matricola" or diploma. In 1859, the Baron Bettino Ricasoli (1809–1880), Tuscan Minister of the Interior, established the Institute of Higher Practical Studies and Specialization, and thanks to this foresight, the two disciplines of chemistry and pharmacy became fully organized by the time that Guerri died at the end of the 19th century.

Luigi Guerri, although also charged with the position of Superintendent of Pharmacies, was nevertheless able to produce a vast quantity of research which, for clarity, can be subdivided into three fields: medicinal chemistry, general chemistry, and analytical chemistry.

In general chemistry his studies embraced the synthesis and study of numerous compounds of phosphorus and iodine (Guerri studied some properties and compounds of red phosphorus and new methods for the synthesis of metaphosphoric and pyrophosphoric acids; he also discovered other synthetic routes for production of potassium iodide and sodium iodide), a new process to produce chromic acid and nitrous acid synthesis.

Luigi Guerri worked assiduously on disinfectants and, as a good Tuscan, engaged in heated debates about his idea of using sulfurous acid instead of hypochlorous acid to combat cholera epidemics that plagued Florence in 1849 and 1855. In 1865, Guerri, in collaboration with Giovanni Battista Fasoli, published a demonstration showing the effectiveness of carbolic acid (phenol) in blocking fermentation processes. To clarify the importance of Guerri's work, we must take a step back: Louis Pasteur (1822–1895) had shown that microorganisms transmitted through the air caused fermentation (also called putrefaction) in wine, milk, water, etc.; Joseph Lister (1827–1912), studying Pasteur's work, hypothesized that open wounds could be subject to "fermentation" and over time they became gangrenous.

On a parallel track, in the early sixties carbolic acid was synthesized and was used as a deodorant in the sewers in some British cities. Then, in 1867, Lister decided to use it on wounds and for disinfecting surgical instruments in operating rooms: a gift of chemistry combined with a little cunning opened for surgery the brightest of horizons.

In 1888 a worried Tuscan landowner approached Guerri with a problem: well that had been drilled at the end of his garden, more than 20 feet deep, contained murky water that grew white and produced a white precipitate. Guerri analyzed the water sample and the sediment. He found that the deposit was nothing more than calcium carbonate and magnesium carbonate mixed with iron oxides. So Guerri, ever practical, suggested to the owner a brilliant idea: why correct the taste of the water, since it has therapeutic properties? So, after verifying the absence of infiltration from neighboring sources, they began to exploit the aquifer [17].

Luigi Guerri had a son, Stefano (1862–1920), who followed in his father's footsteps as a scientist even though he was fond of music and poetry. He completed his first degree in Chemistry at the University of Pisa and later obtained another degree in pharmacy. In 1890, he moved to Florence to work with Hugo Schiff (1834–1915) as a chemist. His rapid return to Florence can be attributed to his widowed father's poor health: he had been struck by apoplexy and required considerable care. In the course of 1891, suddenly but perhaps inexplicably, Stefano Guerri decided to abandon the harsh side of university life and Schiff, passed the examination to work in the Office of Public Health in Florence, and remained there until his death.

At the beginning of December Luigi Guerri had a mild stroke that caused the deformation of the right side of his face. He was conscious and did not suffer much. The next morning the situation deteriorated further and his family rushed to his bedside. On 13 December, the end was near. That day Luigi Guerri was lucid and recognized his family, but toward evening his physical condition worsened. Guerri died the next day, 14 December 1892, at age 69.

In recognition of his great renown, his funeral was celebrated solemnly, and the University was closed for two days. According to some witnesses, the impressiveness of the ceremony and the extraordinary participation of the people prompted them to associate this event with a funeral worthy of a prince or of a head of state [18].

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Chapter 4
Chemists in the Period of the Institute for Higher Practical Studies and Specialization (1859–1924)

Another cornerstone of higher education in Florence emerged in 1859 when the Provisional Government of Tuscany, led by Baron Bettino Ricasoli, established the Institute of Practical Higher Studies and Specialization on 22 December naming Marquis Gino Capponi (1792–1876) as Superintendent. The mission of the Institute was twofold: professional training and specialization. The aim of this institution was to make Florence the capital of Italian culture in anticipation of national independence; so the Institute had to have Chairs of disciplines that would be important to the new nation, held by the most competent and professional educators. Supporters of the Institute were intent upon its achieving constant dialogue between the "Sciences of the Spirit" and the "Sciences of Nature." To accomplish this, four schools were established: Philology and Philosophy, Forensic Science, Natural Sciences, and Medicine and Surgery, aimed at educating young people beyond the limits of university studies and encouraging them in true creativity. This project was somewhat unrealistic and too ambitious, given its modest financial support.

Tuscan universities and in particular the aforementioned Institute were among the protagonists of the Italian scientific and cultural renaissance. The Institute's importance peaked in the years from 1860 to 1910. If the last four decades of the 19th century witnessed cultural dominance of Florence, it was because it emerged within the hegemonic role of its university. The fact that it became the temporary capital of the kingdom of Italy emphasizes the position reached by Florence and by the ability of its politicians to think big. Neither Pisa nor Siena, and not even Bologna, were leaning in this direction although the latter had all it would take to set itself a similar goal.

As in the golden age of the 12th and 13th centuries, Florence had become a prestigious financial and intellectual center and it was thought, in the same way in the 19th century, that the Institute of Practical Studies and Specialization would become a beacon of culture for the newborn kingdom of Italy, seeking to expand its "intellectual domination" far beyond the borders of Tuscany.

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As it turned out, history was not kind to the Institute—it was finally suppressed upon the foundation of the University of Florence.

4.1 Hugo Schiff (1834–1915)

Although Florence had established many scientific chairs in the past, the first Chair of Chemistry, true and proper, came into being only in the 19th century, concomitant actually with the rise of chemistry as a recognized scientific discipline. In 1865, the Minister of Education and renowned physicist, Carlo Matteucci (1811–1868), chose for this high office a German, Joseph Hugo Schiff. Schiff was born in 1834 in Frankfurt to a Jewish family of Spanish origin. Two years after his arrival in Florence he discovered the so-called "Schiff bases," imines formed by the condensation of an amine and an aldehyde (Fig. 4.1).

The Schiff bases constitute one of the families of compounds most widely used not only as reaction intermediates but also in coordination chemistry. Their applications are numerous.

For example, the first synthetic penicillin was prepared through the use of Schiff bases and the determination of transaminases, in order to highlight the presence of liver damage, is based on the synthesis of a Schiff base. They are an essential part of any contemporary course in organic chemistry [1].

In the same period, Schiff also concocted the so called "Schiff's reagent" as a test to identify aldehydes; this reagent is used today to determine the sequence of DNA fragments. It is a mixture of a fuchsine dye (which contains some aromatic amines) with sulfurous acid or bisulfite; sulfonation by the latter disrupts the dye's conjugated chain and renders it colorless. In the presence of an aldehyde, a complex series of reactions with various products takes place: initially the fuchsine's aromatic amines react with the aldehyde to produce aldimines, which further react with bisulfite to produce resonance-stabilized products, restoring the red fuchsine color.

Hugo Schiff (Fig. 4.2) was a restless and tormented genius with a passionate and irascible temperament. If on the one hand he was an excellent research chemist, on the other he was despised by his colleagues and feared by his students [2]. There are numerous stories that have been told about his eccentricities and even about some of his nasty tricks [3].

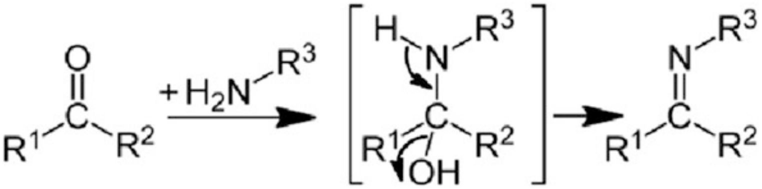


Fig. 4.1 An example of the formation of a Schiff base

Fig. 4.2 Hugo Schiff in his prime. *Courtesy* Department of Chemistry "Hugo Schiff," University of Florence

His first chemistry laboratory was located at the Observatory. In adjoining rooms at his workshop in Via Romana, on 20 September 1870, while bells were ringing in celebration of the capture of Rome, Hugo Schiff and other illustrious Italian chemists, including Stanislao Cannizzaro (1826–1910) and Francesco Selmi (1817–1881), underwrote the birth of the first periodical dedicated to chemical research in Italy, the *Gazzetta Chimica Italiana* (*Italian Chemical Journal*). Schiff was the recording secretary and therefore drew up the list of participants, "but since he is"—as Pietro Saccardi (1889–1981), his student and later rector of the University of Camerino, wrote—"the most malicious German that can be found when the Germans are really bad," he omitted the names of participants present whom he hated, but inserted in their place the names of persons who were absent, but whom he liked [4].

He subdivided his students into "mere students" and "diligent students;" only the latter were considered capable of conducting experiments. In 1877, Schiff won the Chair of Chemistry at Turin. However, because of his uncompromising and vindictive temperament, one evening, as he was leaving the institute, he was approached by some students who, after putting a sack over his head, set about beating him up. From that moment on, he tried hard to get a transfer back to Florence, at which he only succeeded two years later. Once re-established, he requested more space from the administration and thus obtained laboratories in the former stables of the Grand Duke—at the price of having to share the space with the physics department, which led to rows with the physics professor, Antonio Roiti (1843–1921). In fact, one time, Schiff moved massive pieces of metal back and forth along the corridors under the physics laboratory in order to interfere with galvanometric measurements being made in the laboratory upstairs.

Hugo Schiff had always had liberal and revolutionary ideas for which he paid dearly since they led to his 1856 expulsion from Germany. He had contacts with Karl Marx (1818–1883) on the occasion of the organization, in London, of the First International Workers; in Italy he continued to profess revolutionary ideas. In 1894 he was among the founders of the socialist newspaper, "*Avanti!*"

Schiff also brought his revolutionary ideas into his classes: he was one of the first chemistry professors to set up a demonstration table in his lecture room (Fig. 4.3) that connected to a chemical preparation room.

Schiff had no children; he was over fifty years old when he married a young German widow with four daughters to support. Here is a description of Schiff in his later years [4]: "A nice little old man—you know old men are like small dogs—the small ones do the most snarling—with a nice flowing beard, and beady eyes full of malice." Certainly he was not loved by his contemporaries, but for his 70th birthday, in 1904, major European chemists came to Florence to pay him fitting tribute. In homage, they collected a sum of money which Schiff accepted with bad grace, and then doubled from his own pocket, to create a degree award in his name for the best thesis in pure chemistry. The award was given annually until 1952.

Before he died, Schiff drafted a will which provided a small pension for his wife, Ida Fiestmann Merzbacker (1853–1934), and for his stepdaughters and the orphaned daughter of the late Augusto Piccini (1854–1905), a colleague. In his usual maverick spirit, he decided to leave his stepdaughters amounts inversely proportional to the degree of affluence of their husbands: she who had married better would receive less. Faithful to the end to his ideas of social equality and solidarity with the unfortunate, he apportioned his entire remaining assets to establishing a foundation to distribute subsidies to Florentine workers who had become disabled due to accident or illness. This institution, the "Fondazione Ugo Schiff," operated until 1984, facilitating reintegration into the workforce for thousands of people in situations of marginalization or physical disabilities. Obviously, this arrangement did not sit well with his wife, but she kept silent as long as her husband was still alive.

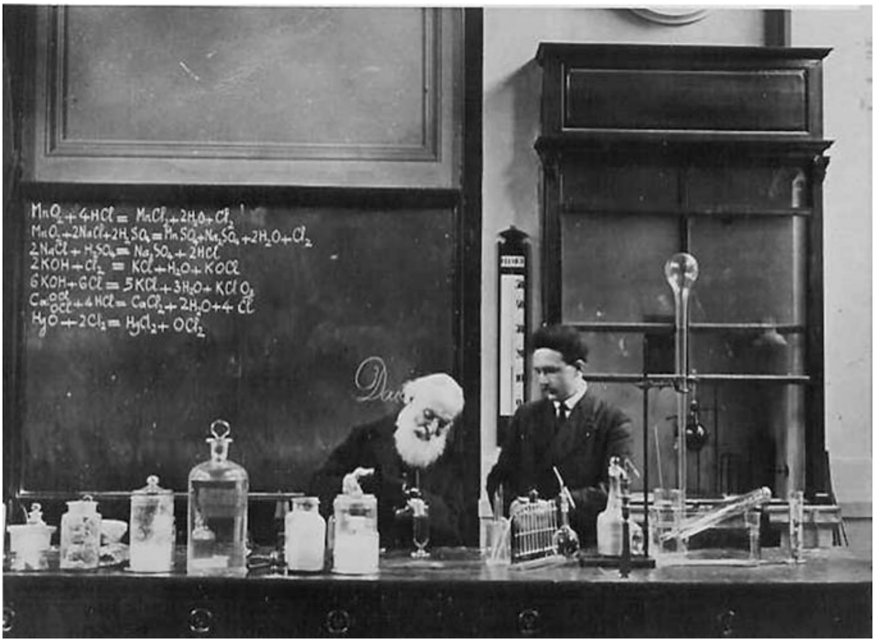


Fig. 4.3 Hugo Schiff (*left*) preparing a chlorine demonstration with his student, Guido Cusmano, ca. 1910–12. Note the fume hood on the *right*; the preparation room is accessed by lifting the movable blackboard. *Courtesy* of Chemical Heritage, University of Florence

After a long and painful struggle with uremia, Hugo Schiff died at age 81 on 8 September 1915.

After his death and with the agreement of the executor, the widow Schiff contested the will, alleging that her husband's health had been in decline for many years and had rendered him a semi-invalid. She sued for compensation for all the time that she had served as his nurse. At the end of a regrettable trial, Ida Fiestmann Merzbacker Schiff succeeded in augmenting her pension by about one-third.

The predictable, as expected, occurred: on leaving the scene, Hugo Schiff did not allow the University to be left orphaned of a famous scientist. He named as his successor Angelo Angeli, a giant in the field of organic chemistry. However, his students joked that compared with Schiff, Angeli was not a man but truly an angel.

4.2 Schiff's Students

To found a "school," to leave a "scientific nursery," to watch it grow and prosper is not an undertaking of small consequence. Florence was home of two great chemists, the German Hugo Schiff and Angelo Angeli (1864–1931) from Tarcento, near the city of Udine. Neither of them knew how to leave a "school," in the term's strict sense, with students and successors who knew how to continue, but most importantly, to innovate and maintain the high-level research of the master. Angeli, shy and insensitive to any human relationship, had many students but no successor. Schiff's turbulent character and tormented genius, in contrast, did not allow him to establish a school; he left only two students able to shine with their own light and not be obscured by their master's oppressive shadow.

Much has been said, even more written, about the famous Hugo Schiff. Less known are the stories of his employees and students. They are not many, considering that Hugo Schiff had a long academic career that began in 1863 and ended the year of his death: more than half a century of development and contact with the Italian and European chemical community yielded, not least due to his difficult character, only a few successors, including Mario Betti (1875–1942), from Lucca, and the Montenegrin, Adriano Ostrogovich (1870–1957).

Other chemists who had Hugo Schiff first as a teacher and then collaborated with him were: Giulio Marzichi (1899–1900), Felice Masino (in 1880), U. Monsacchi (1895–1898), C. Parenti (in 1885), R. Sestini (in 1885), Sevieri Vieri (in 1899) and A. Vanni (1890–1892). None of the latter held academic positions; Schiff evidently did not know how to build a school or, given his working mode, he wanted to be surrounded by an entourage of disciples, not true colleagues. This was, perhaps, his greatest limitation, exceeding even his famous irascible character.

4.2.1 Mario Betti (1875–1942)

Mario Betti was undoubtedly one of Hugo Schiff's outstanding students; the academic world was not slow to recognize this fact: when the post became available, Betti was appointed to the enviable position of successor to Giacomo Ciamician (1857–1922), acknowledged by many as Italy's greatest chemist, at the University of Bologna.

Betti was born in Bagni di Lucca 21 March 1875. He and his twin brother Adolfo (1875–1950), later an accomplished violinist, inherited their father's, Adelson Betti's, family pharmacy.

Mario graduated in 1897 at the age of 22 from the University of Pisa with a concentration in chemistry and pharmacy and began working with the physiologist Moritz Schiff, Hugo Schiff's brother, and Paolo Tassinari. However, he soon left Pisa for Florence where he became Hugo Schiff's assistant from 1898 to 1908 [5]. For a time he also collaborated with Schiff's nephew, Robert. He then worked for two years as a lecturer at the University of Cagliari, Sardinia, and in 1910 he became Professor of Chemistry at Siena. When Schiff died in 1915, Betti effectively assumed the direction of the Chemical Institute at Florence until he was called to fill the prestigious Chair of Chemistry at the University of Genoa, in 1920. On 3 January 1922, the renowned chemist, Giacomo Ciamician, died in Bologna. Seeking to find a worthy replacement, the university administration proclaimed a national competition, in which Mario Betti emerged as the successful candidate: he became Professor of Chemistry at the University of Bologna in the following year and remained there for the rest of his life.

Betti's scientific activity evolved in the field of classical synthetic organic chemistry. In 1900, when he was only 25, he discovered the reaction that bears his name. Mario Betti reported the straightforward synthesis of 1,3-diphenylnaphthoxazine from methanolic ammonia (as the nitrogen source), benzaldehyde and 2-naphthol in methanol. Acidic hydrolysis of the produced ring compound led to 1-aminobenzyl-2-naphthol. This aminonaphthol became known in the literature as the *Betti base*, and the associated protocol as the *Betti reaction* [6–8] which is, in general terms, an amino alkylation among an aldehyde, a primary aromatic amine and phenol with the formation of α-aminobenzylphenol. This is a special case of the more well-known Carl Mannich (1877–1947) reaction.

Betti was also attracted to physical organic chemistry, a field that was then beginning to evolve. He was also active in the field of heterocyclic chemistry, in 1907 devising a method to prepare naphtho-isoxazine [9, 10] derivatives. He was also interested in the relationship between chemical constitution and optical rotation, demonstrating that the degree of rotation is related to the physical-chemical characteristics of the substituents on 'asymmetric carbon atoms and not to their mass [11], as had been claimed in 1890 by the Swiss chemist Philippe A. Guye (1862–1922).

Stereochemistry and, in particular, problems associated with the relationship between chemical constitution and optical rotation of molecules were a central focus of his more mature research. His work by Schiff's side, but especially his formation in a problem-solving environment, led him to devise a method for separation of racemic mixtures of amino acids into their optical isomers via salt formation with an optically-active substance, and then transformation into successive Schiff bases. Betti also tried, ambitiously, to accomplish, as in nature, syntheses that would lead directly to only one optical isomer, experimenting with the addition of chlorine to propylene in the gas phase in order to minimize intermolecular forces and using right and left circularly polarized light [12]. Particularly significant were his contributions related to optical activity within natural substances, leading him to synthesize optically-active compounds with materials exclusively "inorganic," [13] a finding he sent to press shortly before his death [14]. Among his other noteworthy writings are studies of a hydrological nature [15, 16].

In 1929, Betti was appointed Dean of the Faculty of Physical, Mathematical and Natural Sciences in the University of Bologna, and due to his scientific renown, he was named a national member of the *Accademia dei Lincei* in 1932. He also became a member of the Higher Council of National Education, the Committee of the Chemical National Research Council, and the Council of the *Union Internationale de Chimie*. In 1939 he was appointed Senator of the Kingdom of Italy (Fig. 4.4), and in that capacity was active in parliamentary commissions on corporate economy.

Mario Betti, a highly skilled chemist in organic synthesis, possessed great familiarity with the synthesis of chiral molecules, a field that he had cultivated since

Fig. 4.4 Mario Betti (*left*) shown in his senatorial robes at the University of Bologna, ca. 1937. To his *left* 1930 Nobel Laureate for physics, Sir Chandrasekhara Raman (1888–1970), A. Ghigi (1875–1970), Rector of the university in his Fascist uniform, and G.B. Bonino (1899–1985)

1901 when he synthesized the so-called "Betti amine", i.e., β-naphthol-phenylaminomethane, a chiral molecule that he resolved into its enantiomers, using tartaric acid. For almost forty years since that date Betti and his collaborator, Elio Lucchi, (d. 1943) investigated an idea of historic proportions: the first example of deliberate asymmetric catalysis, once regarded as the exclusive domain of microorganisms and enzymes. Betti's original intent was focused on generating a chiral, non-racemic environment around an organometallic compound by coordinating the central metallic ion with an aprotic complexing agent [17].

Although Betti and Lucchi published only two notes on this fascinating topic, their work was known and discussed by many colleagues in the years leading to World War II. Professor Ryoji Noyori (b. 1938), when he received both the chemistry Nobel Prize in 2001 and the University of Bologna's *Laurea ad Honorem* in 2003 for his studies of "asymmetric catalysis," pointed out in his keynote addresses on both occasions [18] that the first example of asymmetric catalysis had appeared in the literature with a paper written by Mario Betti over 60 years earlier [15].

Less than two years after the publication of his first note on the topic, at the height of World War II, Mario Betti died, at 67, in Bologna of an incurable disease. Not even a month before his death on 19 April 1942, he and Lucchi presented a memorandum on the subject entitled "Research on absolute asymmetric synthesis" [19]. Lucchi died (at the front) the next year, thus ending their pioneering collaborative efforts within a largely unexplored field.

Mario Betti would have been gratified to know that his novel research is enjoying a 21st-Century renaissance as it supports new and exciting applications. Reference [2] acknowledges his seminal work, and Cardellicchio and co-workers report [20]:

> The multicomponent reaction between 2-naphthol, aryl aldehydes and ammonia or amines yields aminobenzylnaphthols in a process known as the Betti reaction, which was first uncovered at the beginning of the 20th century. The aminobenzylnaphthols could be easily resolved into their enantiomers. After a long silence, the results of our research a decade ago on this useful reaction and on the chiral materials produced has stimulated further work in a number of other laboratories. As a result, novel applications of the Betti reaction to produce new chiral aminobenzylnaphthols were reported together with the evaluation of these chiral bases in asymmetric synthesis.

4.2.2 Adriano Ostrogovich (1870–1957)

Another famous student of Ugo Schiff was Adriano Ostrogovich, whose first name is often erroneously reported as Adrian. Despite what might lead one to believe from his surname, he was an Italian citizen, born in Lecce on 16 August 1870 to parents of Montenegrin origin.

Ostrogovich completed his higher studies in natural sciences, chemistry and physics in Florence, and with Hugo Schiff as his mentor, between 1886 and 1890, he obtained his bachelor's degree in chemistry when he was only 20 years old as he, himself, reported with deserved, yet undisguised, pride. He completed his doctorate, also directed by Schiff, three years later.

In 1898, Professor Constantin I. Istrati (1850–1918) offered him an associate professorship in organic chemistry at the University of Bucharest, which prompted Ostrogovich to transfer to Romania. Occasionally moving from one university to another, he remained there for the rest of his long life, becoming a naturalized Romanian citizen in 1912.

However, the chemist from Lecce maintained close, friendly contracts with Italy and with the Florence school. In fact, thanks to his influence, Hugo Schiff was elected an honorary member of the Romanian Society of Sciences in 1904 and, on the occasion of Schiff's 75th birthday, the Academy conferred on him a scroll of recognition for outstanding achievements in science.

Ostrogovich obtained a leave from teaching during 1915–1918 to participate in World War I in Italy, returning to Romania in 1919. Meanwhile, Professor Istrati died during the previous year, and so Ostrogovich was promoted to occupy the vacant chair as a full Professor of Organic Chemistry. Almost immediately thereafter, in August 1919, he was given the task of re-organizing the Institute of Chemistry of the Faculty of Science, University of Cluj, Transylvania, only recently liberated by Romanian troops from centuries-old Hungarian domination. In this city Ostrogovich remained until his retirement almost twenty years later in 1938.

As a former Schiff student, Ostrogovich is credited with introducing “German rigor” into the Romanian chemistry curricula.

His first research interests after leaving Schiff’s laboratory were influenced by his new mentor, Istrati: the structures of cerin and friedelin [21], substances isolated from cork by Michel Eugène Chevreul (1786–1889) in 1807 [22].

Subsequent to this initial foray into the structures of triterpenes, which would have been impossible to resolve in the absence of more modern methods, [23] Ostrogovich’s interests in chemistry developed largely in the field of heterocyclic compounds, and particularly of triazine [24, 25]; for this he enlisted the help of his son, Giorgio Ugo Augusto Ostrogovich [26–28]. In addition, Adriano Ostrogovch became interested in food chemistry, such as determining fat content of beeswax [29] and filed original patents [30] for extracting plant pigments intended to be used as colorants in printing and in philately [31]. He also investigated in detail the structure, reactivity, and functional relationships of compounds derived from reactions of aldehydes and ketones with hydrazine and phenylhydrazine to form hydrazones and phenylhydrazones [32]. Triazines represented a research focus particularly dear to Ostrogovich, an area of inquiry within which he pursued with originality and consistency for nearly half a century, bringing new knowledge related to their synthesis [33], and clarifying, for each derivative, its reactivity [34–36]. Even practical aspects of handling substances in the laboratory did not go unnoticed: Ostrogovich developed an apparatus for dehydration of substances under vacuum, and created a new type of flask fitted with a reflux condenser with a neck adapted for collection of the products of distillation at reduced pressure [37].

However, Ostrogovich’s great passion was not chemistry, but entomology and especially butterflies. When he was still a boy, at the Liceo “Dante” in Florence, his professor of natural sciences and famous lepidopterist, Pietro Stefanelli (1835–1919), instilled in him a love for these creatures. Stefanelli taught Ostrogovich how to catch, store, and organize butterflies into a collection. This instruction was not lost, and his love for butterflies became evident to all when, in drawing up his will, he donated to the Museum of Natural History “Grigore Antipa,” his complete collection of Romanian *Lepidoptera*, consisting of 26,000 specimens, which is listed in the Smithsonian Institution’s Collections Catalog [38].

Ostrogovich remained closely in touch with his native country participating, whenever it was possible, in scientific or cultural events in Italy, as well as arranging for more extended visits of several months. In addition, he published nearly his entire body of scientific work in Italian. His contacts became less frequent with the passing years and then ceased altogether from the late forties onward when, after its defeat in World War II, Romania gravitated into the Soviet Union’s sphere of influence.

On 3 January 1957, on the threshold of age 87, after a long and painful illness borne with lucidity and courage, Adriano Ostrogovich passed away in the arms of his son.

4.2.3 *The Schiff Dynasty*

Hugo Schiff, a hundred years after his death, is now receiving a deserved historiographical revival: from where did this larger-than-life figure come? Much less has been reported of his elder brother, Moritz, who was a scientific giant as well, but also the subject of malicious anecdotes exceeding even those of Hugo. The other members of the family who stand out—Mario, Robert, Roger and George—are respectively sons and grandsons of Moritz—of which little or nothing has been handed down to the present day [40–42].

The first Schiff family member of record is Jacob Kohen Zedek, whose name appears on the headstone of his son Uri Phoebus. In 1481 Uri Phoebus Schiff died at the venerable age of 80, so we can assume that his date of birth should be placed around 1400. His father, Jacob, had served for a time as a leader of the Jewish community in Frankfurt; it is thought that he was born around 1370, a date that is the oldest trace of a Jewish family in Germany. The surname Schiff first appears in "Judengasse" [42] in 1613; in medieval high-German "schiff" means "ampule," which by extension can be used as a distinguishing mark of a pharmacist or physician. In fact one of the family members, Meïr Kohen Zedek Schiff (d. 1626), cited as president of a local Jewish congregation, practiced as a pharmacist. From a modern viewpoint, he can rightfully be counted as the first of the Schiffs who had interests very close to chemistry.

The most well-known members of the Schiff family are certainly Moritz (1823–1896) and Hugo, respectively, the second and eighth children of Joseph Moses Schiff (1784–1852) and Henriette Trier (1798–1888). Both became famous for their discoveries in the fields of physiology and chemistry, to say nothing of their passion for politics. And for both of them, their extremely liberal bent was the reason that drove them to leave their mother country.

Moritz Schiff married twice and had many children. Among these Mario (1868–1915) and Robert (1854–1940) deserve mention. The first was professor of French literature in Florence and the second followed in his uncle's footsteps as a chemist at the Athenaeum in Modena and later at Pisa.

Moritz was born at Frankfurt on Main 28 January 1823. He studied at Heidelberg and eventually received his doctorate in biology at Göttingen in 1844. He emigrated to Switzerland because of his liberal views, and was named professor of comparative anatomy at the University of Bern. He remained in this position as a Swiss citizen from 1854 to 1863, at which time he was called to Florence to become professor of physiology at the Institute of Higher Practical Studies. He remained there until 1876, when, following a scandal of Europe-wide proportions over the question of vivisection, he was forced to leave his post. After a period of moving from place to place, Moritz Schiff landed in Geneva, a tolerant city, where the local university offered him the Chair of Physiology, which he continued to occupy until his death at age 73 on 6 October 1896.

Moritz' son, Robert, was a chemist who lived in his more famous uncle's shadow. Born at Frankfurt on Main on 25 July 1854, he was educated both in

Frankfurt and later at Florence. After completing his doctorate at Zurich in 1876, and thanks to the good graces of his uncle, he became assistant to Professor Stanislao Cannizzaro (1826–1910) in Rome. In 1878, he received his "habilitation" qualification [43] and was named professor of chemistry at the University of Modena. In 1892 he was called to a similar Chair at the University of Pisa where he ended his career in the 1920s.

But Robert's fame is due not so much to his chemical studies as to the fortunes of his wife. In fact, in 1880 he married the very wealthy Luccan noblewoman Matilde Giorgini (1860–1940), the niece of Alessandro Manzoni (1785–1873). After their marriage, the couple moved to Modena, where Robert was teaching chemistry. They had three sons who all legally changed their last name to Giorgini-Schiff, since Giorgini was the name of titled nobility. After Robert moved to Pisa, Matilde and Robert lived at their villa in Montignoso, which was lavishly restructured—it was only finished in 1925, as one can read on a marble plaque placed on a wall outside the greenhouse.

Robert's chemical interests were directed exclusively toward organic synthesis and the study of the physico-chemical properties of the compounds he obtained [44–46]. His first publication appeared in 1875 when he was not yet 21 and close to receiving his degree [47]. Numerous other publications followed, especially in the decade 1876–1885, after which he left scientific research and moved on to the care of the immense patrimony of his wife's family. It is evident that even before the age of 60, Robert had abandoned chemistry, if not teaching, or at least research [48], as witnessed by the fact that his last publications are dated before 1911.

Robert's contributions to organic chemistry were modest. We can say that so much was accomplished by the uncle, so little was done by the nephew. Robert, often compared with his dynamic and brilliant uncle, acquired the unenviable, but perhaps excessive and irreverent, reputation of being an "idler;" his most derisive nickname was coined by a colleague at Florence whose name has not come down to us, but only his witticism: "Schiff was the uncle, 'schifoso' [49] the nephew," with the clear allusion to the grandeur of the one and the worthlessness of the other.

During the World War II period, the villa Giorgini-Schiff, so beloved by Matilde and Robert, was abandoned. In fact, Robert Schiff and his eldest son, Ruggero Giorgini-Schiff, both died in January, 1940. Then Matilde died in June of that same year, while the last of the family, Giorgio Giorgini-Schiff, was forced to flee to France due to Fascist persecution [50, 51].

Hugo Schiff most definitely lived up to his adopted institution's expectations in more ways than one. He was the founding chair of a department that earned an illustrious reputation not only in Italy, but abroad. His autocratic "reign" was *sui generis*: no one could possibly follow comfortably in his footsteps. He not only built a formidable chemical reputation, but also one as a unique character, an iconic figure, with a lasting legacy. Those who followed him as members of the Institute for Higher Practical Studies and Specialization would find a different kind of fulfillment, making their mark in various ways, some with great difficulty, as will be seen in the ensuing profiles.

4.3 Augusto Piccini (1854–1905)

The memory of Augusto Piccini has been lost in time, but the same cannot be said of his work. The youngest of three boys, Augusto was born on 8 May 1854 in San Miniato al Tedesco in the Grand Duchy of Tuscany. He was the only family member who studied science, although he had a relative who was a pharmacist. He took his degree in chemistry at Padua in1876 and 9 years later became professor of general chemistry at the University of Catania. The inconvenience of this peripheral university, both geographically and intellectually, led him in 1888 to accept the Chair of Metallurgical Chemistry at the Rome College of Engineering. Five years later he was called to Florence by acclamation to occupy the Chair of Pharmaceutical Chemistry and Toxicology at the Institute of Practical Higher Studies and Specialization.

Piccini's scientific work began in 1874 as a student (Fig. 4.5) when he published a note about his invention of a new hydrometer. Applying Archimedes' principle, he used his new device to conduct a series of determinations with solids and liquids. Already in this early note, written with youthful energy, one can discern the hallmarks of his later work: clarity and erudition. After graduation he worked with Michele Piccini Fileti (1851–1914) conducting research in organic chemistry, explaining the mechanism of molecular transposition observed by Adolph Wurtz

Fig. 4.5 Augusto Piccini at the age of 17. Kind gift of his niece to one of the authors

(1817–1884) in aromatic amines. This was his only “trespass” into the field of organic chemistry [52].

Piccini excelled at experimentation as evidenced by his investigations in analytical chemistry: he devised a practical method to detect small amounts of nitrate in the presence of large amounts of nitrite. This method interested chemists because it was useful for monitoring the different stages of nitrification of organic matter completed by bacteria. Other analytical investigations followed and they led Piccini increasingly into areas of inorganic and mineral chemistry: analysis of Rome’s drinking water, as well as the inosilicate augite ($(Ca,Na)(Mg,Fe,Al)(Si,Al)_2O_6$) and other minerals found in the vicinity around Rome.

Piccini’s research followed four tracks, outlined below.

4.3.1 The Peroxides and the Limiting Oxygenated Forms

Piccini became fascinated with Friedrich August Kekulé’s (1834–1907) theory of the valence of the carbon atom and how it might help in understanding its spatial orientation in organic compounds, although it seemed not so well adapted to inorganic compounds. A few years after Kekule’s ideas were published, Dimitri Ivanovich Mendeleev’s (1834–1907) periodic law appeared in 1869. This systematic arrangement of then-known elements according to their atomic weights and recognition of the periodic character of their properties seemed to him a fruitful hypothesis, capable of providing new analogies among the elements and laden with the possibility of discoveries of yet-unknown elements. The discoveries of gallium in 1875, followed by scandium in 1879 and later in 1886 of germanium, all elements predicted by Mendeleev’s classification, greatly impressed the young Augusto Piccini.

The first criticism he made of Mendeleev’s table was that the limiting oxygenated form was chosen arbitrarily; it did not always take the higher oxides into consideration. Barium, strontium, and calcium exhibited, besides the oxide MO which marks the limiting form of the group, also the peroxide, MO_2. Piccini raised a question regarding the existence of these compounds. He said that according to some, barium peroxide and manganese peroxide were irregular oxides of a tetra-atomic element, so the limiting form of the elements of the barium group should be MO_2, a form which would upset the entire system. Mendeleev in 1881 replied that the limiting form of the groups had to be fixed with the higher oxide, but of the type where hydrogen peroxide was able to yield salts of the same form. Barium dioxide reacted with acids and does not form salts with the general formula BaX_4, but only with the formula BaX_2, so it is only the oxide MO that should be used to fix the position of the element in the periodic system. Apparently, the idea that peroxides of the hydrogen peroxide type could not yield derivatives of the same form when they reacted with water predominated Mendeleev’s thinking [53]. Piccini wanted to bring some clarity to this subject and addressed the problem on an experimental basis.

The experimental contribution which served to destroy the belief that the peroxides like hydrogen peroxide could not give derivatives of the same type was offered by Piccini. He showed that according to the work of Charles Louis Barreswill (1817–1870), hydrogen peroxide reacted with titanium oxide to generate a peroxide of titanium, and, from this, a series of fluoroxypertitanates by substitution of fluorine for one-third of the oxygens of the peroxide; furthermore, in this series of compounds the oxygen still has the form of hydrogen peroxide. With Giovanni Giorgis (1858–1945) he extended his research to molybdenum, tungsten, niobium, vanadium and tantalum and thus laid the experimental basis for refuting the fallacious belief in "Mendeleev's" peroxides. Before Piccini's generalization, only two examples were known in the literature: Fairley, who had obtained the peruranates and Marcellin Berthelot (1827–1907), who had identified barium persulfate. Following in Piccini's footsteps, similar publications by Friedrich Wilhelm Muthmann (1861–1913), Petr Melikov (1850–1927) and Leo Pisarževskij (b. 1871) described the preparation of pertitanates, perniobates, permolybdates, and perborates, among others. This work served to confirm and extend Piccini's results [54–57].

Piccini looked critically at the formation of hydrogen peroxide and peroxide derivatives; his ideas were also supported by strong arguments from Moritz Traube (1826–1894). According to both, the hydrogen molecule would add itself to a molecule of oxygen to form a compound "not entirely molecular." Piccini proposed his hypothesis that served to explain all the reactions of peroxides, assuming that in these compounds it is not the element X, which is found in a higher oxidation state, but the oxygen that is in a lower oxidation state, i.e., not OX_2 analogous to the O in water and in the corresponding oxides, but in the form OX (or O_2X_2). This assumption accounts easily for oxidation reactions and oxygen's tendency to return to its ordinary OX_2 state.

4.3.2 The Alums

Piccini was obsessed with studying the limiting form of the elements as placed in the periodic table. With this in mind, he took up a new field of research, the synthesis of double sulfates (or alums), a work that enormously stimulated his creativity and enthusiasm [58]. In rapid succession, he prepared the alums of vanadium [59], titanium [60, 61], rhodium [62], manganese [63], iridium, and, finally, of thallium [64] with ammonium and then with the following alkaline metals: cesium, rubidium, and potassium. Piccini ably used his method of synthesizing the rhodium sulfates virtually to quantitatively separate rhodium from iridium in solution. Through successive fractional crystallizations, Piccini obtained the alums of rhodium and cesium free of iridium, and through electrolysis of the alums he was able to obtain pure rhodium.

Synthesis of the double sulfates of thallium with ammonium, potassium and rubidium had an entirely different outcome. These alums [65] were of little interest to the scientific community for over two decades until, in the 1920s, Luigi Rolla (1882–1960) and his assistant Lorenzo Fernandes (1902–1977) started on the trail of the elusive rare earth element with atomic number 61. Fernandes and Rolla, failing with the normal techniques of fractional crystallization to isolate various rare earth elements present in their samples of monazite, and realizing that the sulfates of thallium were well suited for their separation, revived Piccini's old work on these compounds. They eventually announced the isolation of what they thought was the last of the lanthanides, *florentium* [66], but unfortunately, prematurely [67].

4.3.3 Reluctance to Make Space for the Noble Gases in the Periodic System

Thanks to his experimental work, Piccini was able to set the conditions for the concept of the limiting form, a concept little appreciated in Italy but much more so abroad. Along with a few collaborators, he completed all experimental work on vanadium, molybdenum, and titanium. He prepared a number of alums, overcoming major technical difficulties, and in the end, he heaped up new examples of the partial analogies that a single element can have with others, analogies expected by Mendeleev's periodic system and which Piccini little by little verified by experiment. It was this concept of *analogy* that guided his research of nearly half a century. Piccini was an apostle, if not the most effective, certainly the most convinced, of the periodic system. The article he compiled for the new encyclopedia of chemistry, "Numerical Correlations between Atomic Weights and Classification of the Elements," [68] remains a monumental work, a theoretical edifice now outdated by Moseley's atomic number, but which contains valuable insights in the detailed reconstructed history of the periodic law: the triads of Johann Wolfgang Döbereiner (1780–1849), the ranking of Franz Xaver Pettenkofer (1783–1850) and Jean Baptiste André Dumas (1800–1884), to the regularity among the equivalents of Peter Kremers (1827–?), Max von Pettenkofer (1818–1901), John Hall Gladstone (1827–1902), Josiah Parsons Cooke (1827–1894), William Odling (1829–1921), Ernst Lenssen (1837–1870?), and Adolph Strecker (1822–1871).

Piccini demonstrated how out of these attempts emerged the idea of "groupings in natural families" and how the numerical ratios of equivalents gave rise to Louis Joseph Prout's (1754–1826) idea of the unity of matter. Piccini concluded his long exposition by describing the work of A.E. Beguyer de Chancourtois (1820–1886), John Alexander Reina Newlands (1837–1898) and Julius Lothar Meyer (1830–1895). In his writings Piccini was not averse to a certain extent of partisanship aimed at destroying priority claims of the latter three because no germ of the periodic law is found in any of their writings. On every page Piccini wrote, the figure of Mendeleev, large and perhaps overly mythologized, emerged.

When argon and other noble gases were discovered in the atmosphere, a violent storm was unleashed against the periodic system: it was declared by many to be devoid of any practical utility. Piccini, with passionate and almost prophetic words, called his colleagues' attention to the limits of inorganic chemistry (to date ignorant of the atomic number) [69]:

> If the future will show that the new components of the atmosphere are elements that give compounds, [the periodic system] most likely will point to the place they should occupy in the system; or we will confirm them as non-chemical substances and then have to resort to quite different principles of classification where chemical properties are not taken into account, based entirely on physical characteristics and values of the atomic weights.

However once Group 0 was "created" to accommodate these elements, Piccini deplored this decision, calling it "opportunistic," although he never said so publicly. We believe that for all his lifetime Piccini did not believe that the noble gases were true chemical elements like hydrogen, nitrogen, and oxygen [69]. From his dominant position in the drafting of the encyclopedia of chemistry, he deliberately omitted all alternative tables proposed by various authors to make the periodic system, in their view, more "in touch" than Mendeleev's arrangement. He saw no point in changing anything unless it brought more clarity to the situation [70]. However, he did make one exception because the proposal fit well with his own prejudices: Bohuslav Brauner (1855–1935) compiled a table that placed the rare earth elements in Group IV since their limiting form never exceeded MX_4; moreover, Brauner made no mention of the noble gases.

4.3.4 Controversy with Alfred Werner

In 1905, Piccini initiated a last defense of Mendeleev, this time focused on the new periodic table proposed by Alfred Werner [71] (1866–1919) [72]:

> It is easy to say that you have provided a simpler scheme of the elements by looking only at their principal characteristics; but, whether the most principal characteristic is the combining form then, like it or not, here we are back at Mendeleev; or not, then we will continue to grope among subjective opinions, scholarly prejudices, and mathematical exercises, as chemists have done for half a century with little to show for it.

This note, sent for publication only a month before he died, was Piccini's last effort to sustain the Mendeleevian character of the periodic system, a subject that he found ever fascinating and which he contemplated for a quarter of a century, making himself, with his experience, an absolute master.

The extension of the hypothesis of Amedeo Avogadro (1776–1856) to dilute solutions proposed by Jacobus Henricus van't Hoff (1852–1911), opened a new direction for experimental research within inorganic chemistry. Piccini understood the importance of new theories, while, at the same time, he continued to pursue his favorite topic: systematics. The problem that he found most interesting was to understand the isomerism of the green and violet salts of chromium [73] in the form of the sesquioxides, a problem that Werner had addressed with his coordination theory [74].

Piccini, who since 1890, had begun to direct his young colleague Guido Fabris (1862–1939) in the study of violet chromium fluoride, led him to also study the cryoscopic behavior of aqueous solutions of the two chlorides of chromium; from these and other experiments he determined that Werner's hypothesis did not perfectly fit with his results. Piccini, as a prudent person, tried to explain the observed facts and followed with interest the physical chemistry of transition metals, waiting for some phenomenon to arise that might solve the problem—waiting, as we know today, in vain, due to his untimely death. Successfully cultivating the field of inorganic chemistry did not prevent him from staying current in the field of organic chemistry, in which he was interested and highly competent. Many friends consulted him for advice about their research; they always received a kind welcome and useful suggestions. His small close circle of friends met often in his laboratory for lively and cheerful discussions which helped them forget the trials and pettiness sometimes encountered in academic life.

Although Piccini found learning new languages easy, he used his talents exclusively in the study of chemistry: he traveled little and that travel was within Italy. After his father's death in 1886, followed almost a decade later by that of his mother, in 1895, he married a widow, Maria Banchi (1866–1933), and welcomed into his home children from her first marriage. He bought a house in Florence where he and his wife led a relatively secluded life. In 1899, their daughter Elisabetta was born.

Piccini, by reason of both scientific and personal interests, often visited Raffaello Nasini (1854–1931), famous for his studies of helium's chemical and physical properties, as well as Chancellor of the University of Padua. Nasini had married Carolina Ciamician (1861–?), the younger sister of his friend and colleague Giacomo (1857–1922).

When Carolina began to show signs of mental imbalance, she was committed to a mental hospital and Nasini, encouraged by Piccini, fell in love with Piccini's sister-in-law, Evelina Banchi (ca. 1868–1960), with whom he had an illegitimate son, who also became a chemist. A few years later Augusto helplessly witnessed the loss of his beloved brother Giovanni (ca. 1851–1903). After that his own health deteriorated rapidly; he fell into a state of deep depression that perhaps contributed to the decline in his otherwise strong constitution and hastened his premature end. A minor surgical procedure gave rise to an infection that proved fatal; on 15 April 1905 Augusto Piccini, not yet 51 years old, died of septicemia. He was survived by his wife Maria and his beloved daughter, Elisabetta, only six years old. The news of Piccini's death spread rapidly; friends, colleagues, and admirers arrived from all over to pay homage to this outstanding chemist, a man deemed praiseworthy, honest, and upright.

Madame Piccini, sorely tried by the untimely loss of her husband and, concomitantly, of material sustenance, tried for months to hide her husband's tragic death from their daughter Elisabetta. Signora Piccini was forced to send her away to boarding school. As Elisabetta grew up, she wanted desperately to follow in her father's footsteps and, having completed high school, she enrolled in the degree course in chemistry. She was a student of Luigi Rolla, graduating under his guidance in 1923. Elisabetta Piccini conducted research with Luigi Mazza (1898–1978), studying changes in conductivity of mixtures of sulfuric and nitric acids in varying concentrations [75]. These studies allowed Elisabetta to identify two “conductivity minima” due to formation of aggregation products that, unfortunately, she failed to isolate. Her entire work in chemistry and, indeed, almost everything she accomplished, was intended to honor the memory of her father, whom she revered. She remained at the university for a certain period as a volunteer assistant to Rolla who persuaded her to fill the unpaid position while waiting for his colleague Maria Marconi (1900–85) to marry and to relinquish her funded position to Elisabetta. However, Maria Marconi never married and was careful not to leave her job as Rolla’s assistant; and so, reluctantly, Rolla informed the young Elisabetta that it was impossible for her to stay at the university. Elisabetta found some work in chemistry for a time, and then turned to teaching. She later married an ex-World War I pilot and banker, Mario Puccetti (1892-ca. 1975).

4.4 Guido Pellizzari (1858–1938)

Guido Pellizzari was the second son of Giorgio Pellizzari (1814–94), a noted physician [76], and his wife Adelaide Marzichi Lenzi (d. 1910); Guido was born in Florence on 30 October 1858. His older brother, Celso Pellizzari (1851–1925), after obtaining his doctorate in Florence in 1876, moved to Germany to specialize in dermatology [77]. Guido attended private lessons until 1871 when he chose to attend the Technical School (Istituto Provinciale) in Florence and where in 1878 he became licensed in mathematics and physics. In the same year after taking his “Licenza” in Natural Sciences, Pellizzari began to study chemistry at the Institute of Higher Practical Studies and Specialization. At the end of his fourth year, in July 1882, he earned his B.Sc. in chemistry with the highest possible grades. The Chemistry Department was headed by Hugo Schiff, who assigned research projects to final-year students, and he instructed Pellizzari in advanced organic synthesis. He remained at the university as Schiff’s assistant, devoting himself to research on synthesis of the derivatives of succinic, sebacic, and phthalic acids (Fig. 4.6).

In 1887, he obtained a second degree in Pharmacy and, after a short period of two years as Hugo Schiff’s assistant, on 1 November 1889 Pellizzari was appointed professor of Chemistry at the Royal University of Catania. His stay in Sicily was

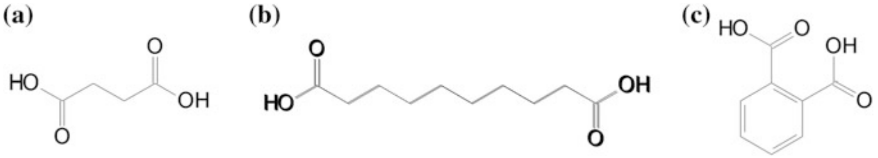


Fig. 4.6 Research of G. Pellizzari on di-carboxylic acids. **a** Succinic. **b** Sebacic. **c** Phthalic

extremely short; in 1891 he was transferred to a more suitable post as Professor of General Chemistry at the Royal University of Genoa [78].

Although he lived most of the year in Genoa as a university professor, Pellizzari, who was unmarried, customarily spent his vacations in Florence in his relatives' home and in that laboratory, located in Via Gino Capponi, where years before he had graduated in chemistry. Despite the fact that he was middle aged, he fraternized with the younger chemists, and was quick to realize the exceptional ability of Mario Betti (1875–1942); Pellizzari invited him to become a member of his team.

Pellizzari (Fig. 4.7) compensated for his not very pleasing physical appearance, vaguely reminiscent of that of the vaudeville actor Ben Turpin (1869–1940), with friendly kindness, always affable and jovial. Thanks to his open and frank manner, he was sincerely loved. He participated in discussions as if he had never been away

Fig. 4.7 Guido Pellizzari at age 56. Department of Chemistry "Ugo Schiff," University of Florence

from Florence, sometimes comforting students frightened by Hugo Schiff's stiffness. It was not unusual even for the old master to seek Pellizzari's advice.

For over 20 years he was devoted to both organic synthesis (for example, the synthesis of *N*-amino-1,3,4-triazole) and also to solving some technical problems related to developing photographic plates. With respect to the latter, he studied and improved the use of organic bisulfites in photographic development.

In 1916, bowing to pressure from his family, Pellizzari returned to Florence and accepted the chair of Pharmacy at the Royal Institute of Higher Practical Studies and Specialization which, in 1924, would become the University of Florence. He retired in 1933 at age 75 and was soon appointed Emeritus Professor [79]. At his retirement party, he used the occasion to arrange for a bust of Hugo Schiff, along with a plaque that recorded his successors, to be placed outside the lecture hall that Schiff made so famous. For unknown reasons, not to mention the outbreak of WWI, that tribute to Schiff was completed eighteen years after his death.

The major events in Pellizzari's life seem to have been curiously displaced beyond the age when these events are normally realized. Just as his mentor Hugo Schiff, Pellizzari became married when he was relatively old; they both married rich widows. Officially retired at age 75, they were scientifically active until they died in their eighties. Both Schiff and Pellizzari found it impossible to have any relationship with women. Both men lived for "their" science and perhaps they insisted on treating their soon-to-be spouses as mere housekeepers. Pellizzari's approach toward women was not as rigid as one can imagine, but at least it was unusual: despite the fact that his wife was a well-known socialite, he confided to a friend that he wished "she would be able to administer his laboratory and get to know the uses and names of all his equipment to such a degree that he could without hesitation make her distill hydrochloric acid." What we do not know is whether she knew her husband's secret desire and whether she would be pleased or not regarding her projected role in the laboratory.

In Florence, Pellizzari started working with Schiff on describing a series of compounds derived from amido-benzoic acid, work which later led to the discovery of the chemical reaction that bears his name [80]. These initial studies represented the germ of important subsequent discoveries. In particular, heterocyclic chemistry attracted his attention when he was still a student. In 1883, Viktor Meyer (1848–97) discovered thiophene [81]; this date would become a milestone in the advancement of chemistry of "heterocyclic compounds"—or, simply, "heterocycles." The chemistry of heterocycles was a topic of great interest; this branch of chemistry was to become a springboard for new and fascinating discoveries. Chemical research on heterocycles was pioneered by researchers such as Emil Fisher (1852–1919) on the purine nucleus [82], and in Italy by Icilio Guareschi (1847–1918), who discovered many pyridine derivatives [83]. Having these chemists as forerunners, Pellizzari conducted the addition of phenylhydrazine with the cyanamide dimer and obtained a derivative of a heterocyclic nucleus. According to 19th century nomenclature and in order to emphasize similarities with triazole [84, 85] he called the new molecule "guanazole," and later brilliantly confirmed its structure [86]. Later, basing his thinking on an analogy between guanidine and urea, Pellizzari described, by means of hydrazine and urea, the synthesis of a molecular core similar to “guanazole” which he named “urazole” [87]. These studies suggested a new synthesis of “free triazole” by the reaction of formamide with formylhydrazine [88]; this reaction, simple, clear, and elegant, was later named after him [89–91]. This new synthetic strategy allowed Pellizzari to develop fully the chemistry of triazole derivatives [92–97].

Pellizzari and co-workers enhanced the research on substituted guanidines [98], which was of particular interest, either for biochemical purposes, or for technical relevance: in fact, some guanidine derivatives, such as the nitro-guanidines were used as explosives, while acyl-guanidine derivatives were widely employed as accelerators in rubber vulcanization. A few years later Pellizzari was able to describe correctly the structure of nitro-guanidine. Combining hydrazine with cyanamide, he obtained the amino guanidine [99]. He later successfully undertook synthesis of triamino guanidine, consisting of a very peculiar six-nitrogen cluster of atoms grouped around a single carbon atom [100].

Although some of these guanidine compounds played very important roles as intermediates during the formation of cyclic compounds, it is worth mentioning the fundamental nature of this reaction, later generalized as the Pellizzari reaction. Pellizzari himself described how he obtained remarkable results in organic synthesis using cyanogen bromide (CNBr) [101, 102] which he had widely employed in his syntheses. Thanks to his work, nowadays it is possible to generate a peptide map using this molecule. To avoid complete hydrolysis of the peptide, the only chemical method not yet supplanted by enzymatic methods involves the use of CNBr, which selectively cuts the polypeptide at the level of methionine. It was during this work that Pellizzari’s health was placed in danger by inhaling cyanogen bromide vapors, whose physiological effects were hitherto little known. He would probably have died in his laboratory if a student had not quickly administered oxygen, however, the acute irritation caused permanent damage to his lungs.

After his mother’s death in 1910, his only family ties were represented by his siblings Celso, a bachelor 7 years his senior, and Maria, 5 years younger, who had married the sculptor Mario Salvini (1863–1940) in her early twenties. After Celso’s death, on Christmas day 1925, the big house got suddenly empty. Guido filled his days devoting himself to music and art. He never missed the most interesting artistic or musical events in Florence. However, solitude did not please him, and so he decided, the following year, to marry Elena Casanuova-Jerserink, a childless widow of Earl Quentin. Mario Betti (1875–1942) described his friend’s and colleague’s future wife as a “loving and distinguished Madame.” At the time of their marriage she was 57 while her husband would soon be 68. She contributed greatly to her husband’s own outgoing style, balancing it with her natural cordiality.

The couple lived in the great ancestral palace in Via della Colonna in Florence for just a dozen years. In 1938 Pellizzari, still in good health, traveled to the International Congress of Chemistry, held in Rome, and he attended the sessions and meetings with energy and youthful spirit. On 1 June, on the eve of the session of the Royal Academy of Italy (the former “Accademia dei Lincei”) he wrote to Nicola Parravano (who, also, was destined to die suddenly), that he would be unable to participate in the usual meeting, being slightly indisposed. In addition, he begged his colleague not to include him in the Commission for the Cannizzaro prize, because, he jokingly added, on the threshold of 80 it would not be prudent to take on long-term commitments.

The following day Pellizzari's health worsened and pneumonia manifested itself in its full severity, leaving him little chance for recovery. Although his condition had worsened causing him to be hospitalized, no one could have guessed that his death would be so sudden. On Friday 3 June 1938 Pellizzari passed away peacefully.

The family all died in a few years: his beloved sister Maria died on 23 July 1946 at age 83, and his widow passed away in January 1952 at almost age 85 years of age. The only branch of the Pellizzari family that survived were Maria's sons, Celso Salvini (1889–1947), an actor, and Guido Salvini (1893–1965), a film director; neither of them had any children.

Guido Pellizzari with his simple, elegant ways and deep kindness, was different from any other chemist that had taught in Florence up to the time his arrival there. In his retirement he received occasional visits from former students, but only one account has come down to us. One day, as a very old man, he received into his home a young man who, because of his age, could not have been one of his former students. The guest reported more or less what happened [103]:

> I was alone with him in the old parlor of his house in Via della Colonna. The conversation was slow. To do something, I opened the buckle of my bag and pulled out a yellowed brochure. It was the abstract of one of his first publications. I leafed through it and pointed out his dedication to my father next to the date of 1 November 1913. Pellizzari murmured: 'The synthesis of urazole and guanazole.' Other names followed, unintelligible but evocative, like those of distant cities or exotic mountains dotting a fantastic map. He did not know that, unlike my father, I did not study chemistry. 'They were really old times,' he added, then stopped and stared at me; I think that only then did he become aware of my bewilderment. He paused. He immersed himself in thought, but not before giving me a big smile.

4.5 Angelo Angeli (1864–1931)

On the occasion of the tenth National Meeting of the Italian Chemical Society a plaque was unveiled at the birthplace of Angelo Angeli at Tarcento [104]. The text was written by Professor Livio Cambi (1885–1968) shortly before he died. It reads [105]:

> Ad Angelo Angeli, figlio del forte popolo del Friuli geniale rivelatore di concezioni precorritrici della chimica moderna studiosi e tecnici italiani partecipanti al X Congresso Nazionale di Chimica alla sua terra convenuti memori dell'opera imperitura con devozione sulla casa natale questa lapide posero 22 giugno 1968.

4.5.1 Beginnings of a Career

Angelo Angeli was born in Tarcento (a town near Udine) on 20 August 1864. It is said that, encouraged by the frequent visits of a maternal uncle, Giovanni Carnelutti (1850–1901), Angelo expressed a great interest in chemistry from an early age. After he attended the Technical Institute of Udine, he later moved to the *Technische Hochschule* (Polytechnic) of Vienna, but he soon transferred to the University of Padua where he met Stanislao Cannizzaro (1826–1910) and Giacomo Ciamician (1857–1922). The latter recognized that Angeli possessed a keen, acute intelligence. In 1889, when Professor Ciamician moved to Bologna, al-though Angeli was still a student, he asked him to become his private assistant. The young Angeli graduated in 1891; two years later his colleagues suggested that he qualify as a university faculty member. Even though in 1895 he finished first in the academic competition for the analytical chemistry chair, bureaucratic impediments obliged him to withdraw his application for that position.

Angeli's career received a significant boost through his friendship with future Nobel laureate Adolf von Baeyer (1835–1917), who encouraged him to accept the Chair of Pharmaceutical Chemistry at Palermo. However, Angeli's introverted nature was such that he not only experienced great difficulties in his relationships with students and colleagues, but his scientific reputation suffered as well, and in particular, abroad. In those years Angeli's behavior regressed and he became more introverted. He found it difficult to speak in public and from that time on, he never participated in conferences or international meetings. Also he loathed speaking on or hearing a voice on the telephone.

Despite these problems he was certainly recognized by some very famous people. Not only Baeyer, but also the 1915 Nobel laureate in chemistry, Richard Willstätter (1872–1942), held him in high esteem. Adolf von Baeyer twice nominated him for the Nobel Prize, in 1911 and 1913. Willstätter wrote on one occasion: "Professor Angeli's work is better than the work of all the other Italian chemists put together on account of his originality, and for its great value, he deserves the highest consideration." Unfortunately, despite the fact that Angeli was nominated many more times, he never received the prize [106].

In 1905, after Augusto Piccini's death, Angeli was called to Florence to occupy the vacant chemistry chair at the Institute of Higher Practical Studies and Specialization, later the Royal University of Florence. The physicist Antonio Roiti (1843–1921), Dean of the Faculty of Sciences, communicated the news to Hugo Schiff (1834–1915) with this telegram: "Angeli accepts. He will write very soon; reply encouraging him because he is extremely shy."

Ten years after his return to Florence, Angeli was invited to fill the Chair of Chemistry vacated by the recent death of Hugo Schiff in 1915. He then assumed the Chair of Organic Chemistry, which was specifically created for him, and remained at Florence for the rest of his life, refusing offers of prestigious chairs at Rome in

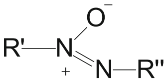
1909 and at Bologna in 1922 (following the death of his old professor Ciamician). He continued to lend his expertise to the Armed Forces in exchange for being relieved of all lecturing and public speaking and, in this role, he commuted among Rome, La Spezia, Taranto, and Florence—almost Italy's length and breadth. To the bottom of his heart, Angeli was always a peripatetic free spirit, but he always felt more at home in Florence than he did in any other place.

He habitually refused to accept any honors or privileges with the exception of the Cross of War, conferred on him for his civilian services as a chemist during World War I. Angeli's scientific productivity was marked by a high level of innovative ideas. In his 40 years of research, he produced 220 publications, among which were five that have been cited by chemists worldwide for many years:

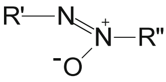
1906 On some oxygenated compounds of nitrogen
1911 Actions of nitrous and nitric acids on indole and pyrrole
1916 On the constitution of azo-compounds
1924 On behavioral analogies among some derivatives of benzene and corresponding aliphatic series derivatives
1930 Researches and considerations about the structures of diazo-compounds.

Angeli was one of the most prolific chemists of his time; his research focused on nitrogen chemistry, particularly the oxygen-containing acids of the diazo-compounds, and in the field of natural products. Prescient were his studies of "constitution and smell," where he related olfactory activity to oxidation capacity, highlighting the chemistry and physiology of smell. His research in aromatic compounds was original and fundamental. To his work on benzene derivatives, he added research on heterocycles such as pyrrole, furan and indole.

Thanks to the discovery of two isomeric derivatives that were markedly different in their chemical behavior, such as the two azoxy isomers depicted by Structures 1a and 1b, where R′ and R″ are two different aromatic or aliphatic groups,



(Structure1a)



(Structure1b)

Angeli experimentally demonstrated the asymmetric structure of azoxy compounds and their isomers [107], thereby rewriting the concept of "oscillation" conceived by August Kekulé (1829–96) with his famous visual metaphor of the "snake biting its own tail" [108]. The principle of his idea is that the $N^+–O^-$ dipole of the azoxy function "protects" the group adjacent to it from electrophilic attack, allowing one to assign a structure based upon the differential reactivity of the two isomers [109].

By these experiments, Angeli laid the qualitative foundations of the concept of oscillation and also that of "structural resonance" which later found a more solid quantum mechanical basis due to the work of a young Linus Pauling (1901–94). He also contributed to discrediting the venerated assumptions of the German chemist, Arthur Rudolf Hantzch (1857–1935) on the relationship of simple stereoisomerism among normal diazo- and isodiazo-compounds. Again in this case, Angeli carefully studied the relationship between the structure and reactivity of compounds, particularly the behavioral analogies of the *para*- and *ortho*-derivatives of benzene [110].

Far from taking offense, in 1931, Hantzsch who had long engaged in battle with Angeli, finding himself in the position of underdog, had the good grace to recognize an uncommonly great talent in his adversary. A few days before Angeli's sudden death, Hantzsch announced his nomination to the Committee of Honor of the German Chemical Society in these words: "I esteem his rich scientific work very highly and I respect him as one of the greatest chemists of his country." Twelve years earlier the Academy of Uppsala had appointed him to replace William Crookes (1832–1919); this gesture was interpreted erroneously as a step closer to Angeli's expected Nobel Prize.

Contrary to what has been conveyed by historians, Angeli and his former teacher Ciamician possessed markedly different characters and temperaments, but nonetheless Ciamician never had a more faithful disciple and staunch supporter. Angeli even argued on his behalf with the doyen of Italian chemists, Stanislao Cannizzaro (1826–1910). He also had a few contretemps with Ferdinand Tiemann (1848–99), co-discoverer of the Reimer-Tiemann reaction and with Theodor Curtius (1857–1928), discoverer of the Curtius rearrangement, diazoacetic acid, and hydrazine. All of their discussions were conducted with great respect and mutual regard.

In all of his dealings, Angeli knew how to forge strong friendships and to earn the esteem of distinguished chemists, above all of the Nobel laureate Adolf von Bayer, who followed his work with almost paternal affection during his difficult years in Palermo, even paying him numerous visits. In Palermo, he was also visited by the German chemist Carl Harries (1866–1923), and he became the friend of Alfred Walter Stewart (1880–1947) in Belfast who often corresponded with him, as did the Nobel laureate Sir William Ramsay (1852–1916), who followed with interest Angeli's publications in the original Italian.

However, Angeli was very reserved, always absorbed in his scientific musings. During World War I he was conscripted and made head of the Explosives Commission. After the disastrous rout of the Italian army largely due to the Germans' use of chemical warfare in the Battle of Caporetto in 1917, he was named President of the Commission for the study of protective measures against poisonous gases. After the war, General Armando Diaz (1861–1928), Chief of Staff of the Italian Army, stopped by Angeli's explosives laboratory in Rome to make his acquaintance. Even after the war, Angeli did not immediately abandon problems related to national defense. In 1926, the Fascist Dictator Benito Mussolini (1883–1945) sent him a telegram [105]: “I am extremely pleased to inform you that the Admiralty Commission in plenary session on 17 October in view of your outstanding civilian and scientific qualities has unanimously appointed you High Scientific and Technical Advisor to the Royal Navy.” [111]. Two years later, Angeli received the gold medal for his unique services rendered to the Italian Navy.

4.5.2 Angeli’s Rule

Today Angeli’s name is relatively unknown not only to chemists but also among historians of science. The reason for this undeserved oblivion is due both to the vastness of his scientific output and the great variety of fields of investigation. He made many contributions to the chemistry of natural products; he continued the research on the anthelminthic santonin already started by his first mentor Carnelutti and later by Cannizzaro. While he was conducting another series of investigations, largely theoretical, on similarities among the behavior of benzene derivatives in ortho- and para- positions, he noticed an unexpected correspondence with aliphatic analogues. This resulted in the announcement of the so-called “Angeli’s Rule” according to which two substituents X and Y, separated by unsaturated chains (conjugated double bonds) or placed in ortho- or para- positions on a benzene ring, generally behave as if they were directly bonded to one another. For example, the product on the right in Eq. 4.1 is expected to behave similarly to the reactant on the left.

$$\mathrm{X - Y \rightarrow X - CH = CH - Y} \tag{4.1}$$

On this basis, in cases where the electronic effect is important for a molecule’s behavior, the interposition of a vinyl group or an aromatic group between the two groups responsible for this effect, can yield compounds that maintain the desired activity, provided of course that this does not interfere with other features essential for interaction, such as the molecule’s shape and volume. An example from biological activity would be the vinyl homologue of acetylcholine that, in contrast to the natural substrate acetylcholine, is not a substrate of the enzyme acetylcholinesterase and therefore does not undergo hydrolysis.

Moreover pyrrole, thiophene and furan are very similar to each other and in formation of their compounds they follow Angeli’s Rule. It was therefore reasonable to assume that, during the process of biological synthesis of protein derivatives, these compounds could cause similar chemical and physiological reactions and special conditions under which a pyrrole group could be replaced by a similar group such as a thiophene or furan. With these brilliant insights Angeli became highly respected in the academic world. When news of his discovery was published in Germany, his idea was called “Die Theorie der Vernachlässigung des

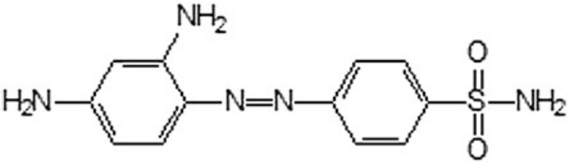


Fig. 4.8 The sulfamide Prontosil® Bayer IG Farben, an example of Angeli's Rule

Benzolkerns" (the theory that neglects the benzene ring). All of this research was collected in a massive monograph in 1924 called "On the similarities between the behavior of some derivatives of benzene and the corresponding derivatives of the aliphatic series" [112] that represents one of the most important chapters among modern organic chemistry theories [113].

"Angeli's Rule" was employed by numerous chemists working in the field of anesthetics (as in the derivatives of para-amino benzoic acid, novocaine and tutocaine) and sulfonamides (as in the case of uliron). For some time chemists had already observed how physiological actions took up para positions in the derivatives that contained the groups $–N{=}N_2$ and $–SO_2NH$, confirming what Angeli expected. Angeli extended his rule to the same radicals that were on two separate benzene rings in the para position to the azo bridge respectively. An example of a molecule following this extended rule is one of the first antibacterial drugs, one that changed the face of medicine, prontosil (IUPAC name: 4-[(2,4-diaminophenyl) azo]-benzenesulfon-amide), (Fig. 4.8).

The chemical reactivity, in general, induced by unsaturated carbon chains, compared to the relative inert characteristic of saturated chains, was denominated by Angeli as "chemical conductivity" long before Erich Hückel (1896–1980) formulated his rule for aromatic compounds.

Angeli's school of organic chemistry produced few but affectionate students. Among them were Guido Cusmano (1882–1956), Livio Cambi (1885–1968), Pietro Saccardi (1891–1981) and Anna Raul Poggi (1899–1961), whose many publications are scattered in the chemical literature of early to mid-20th century Italy. However, others passed away before their time, not even surviving their mentor. Some were victims of their own manipulations or of tragic accidents: Enrico Rimini (1874–1917), Luigi Marino (1873–1922), Luigi Alessandri (1885–1929) and the last, the youngest and perhaps destined to have become the greatest, Dino Bigiavi (1898–1929).

4.5.3 *An Ascetic Life (and Death)*

Angeli was a master in the full sense of that word, and if he did not devote considerable time and energy to teaching, he always had a group of students around him who lavished him with affection and esteem. While aware and proud of his expertise, a morbid form of shyness made Angeli avoid all public scientific gatherings: he never spoke in public, and sometimes even in smaller meetings, he seemed estranged. This personal difficulty did not help to spread his fame; his work became recognized only through the scope and innovative character of his research publications.

By temperament he lived within what could be characterized as monastic simplicity, although his means were rather comfortable. He was afraid that comforts and conveniences might cause him to be stricken by a laziness that would negatively affect his mission.

Many famous scientists from abroad, and especially from Germany, among whom were the already mentioned Richard Wilstätter and Adolf von Baeyer, arrived regularly to visit him in his “humble hut” in via Laura [114] where he had set up a very efficient laboratory. Having finished their visit to his laboratory, Angeli would accompany his guests to a nearby bar to drink good chianti and to offer a triple toast by Angeli, who raised his glass intoned: “to good science, to collaboration, to friendship.” The rest of Angeli’s social life remained shrouded in mystery. It is known through the typescript of one of his assistants during WWI, Pietro Saccardi [3], that he lived a very solitary life. Saccardi, treated almost like a son by Angeli, was often invited to dine with him at a restaurant, and on these occasions it could happen that Angeli would try to confide in his assistant some memory or unveil some aspect of his own personal life outside the walls of the laboratory. “You know,” Angeli would quietly begin to express his thoughts, “I never married, I was totally dedicated to science…” And at other times, his confession might be more heart-rending: “I had a mother and I thought she would never die, now I’m alone; unfortunately, I never had any children, all my relatives live very far away.” Saccardi also had the privilege of getting to know first-hand what an extraordinary character, humanly and scientifically, Angeli was. Those others, few though they were, who really knew him, have expressed such positive impressions that it seems impossible to attribute them all to one person. Saccardi wrote that each interaction with Angeli was “an adventure of the mind with its endless discussions and depth.”

From the time of his 1905 arrival in Florence, Angeli had made his home in a Piazza Santa Maria Novella guest house. One time he commented sarcastically: “I’m a hotel room number and since I am very regular in my habits, one day I came back to my room unexpectedly and what did I find? What did I see? A couple in my bed: they rented out my room by the hour!” Poor Angeli—so scientifically capable, so socially deficient [113].

In his last years, signs of his approaching death appeared more frequently; his colleagues couldn’t but listen with fear to his continual references to it. In 1929, a sudden illness, perhaps a heart problem, almost killed him but, unexpectedly, he recovered.

Angeli worked with his usual untiring pace right to his end. On 31 May 1931, he experienced some difficulty breathing, but without worrying about it, he went to bed (in that same hotel bed that he never changed after that disagreeable incident, absolving the young people because of their age and the innkeeper for whatever altruistic reason). The next morning, Monday 1 June, he did not arrive as usual at the chemistry department. This fact was immediately noticed and aroused fear among both faculty and students who went to Angeli’s house promptly and found him dead in bed. The pulmonary edema from which he had suffered from time to time brought his life to an end in just a few hours during the night. He evidently had some awareness of his end, but he died without calling for help, alone, in austere solitude within which he had lived. Next to his bed his colleagues found a little piece of paper bearing Angeli’s last will, written three years earlier in 1928.

He was laid out in the library surrounded by the many books to which he had devoted considerable time for so many years. In accord with the will of his younger brother Vincenzo (1879–1942), Angelo Angeli was buried in the silence of the monumental cemetery “Porte Sante” next to another brother, Virgilio (1872–1918), who had also died in Florence. Neither Virgilio nor Angelo had ever married and neither had any children. Their brother Vincenzo was the only one to continue the family line. His daughters Verdelaura (1915–2013) and Natalina (1920–2007), jealously treasured their recollections of their illustrious uncle who loved to spend summer vacations in the family villa, in Tarcento near Udine.

4.5.4 The Angeli-Rimini Reaction

Angelo Angeli’s name, along with that of Enrico Rimini (1874–1917), is often associated with the chemical reaction that bears their names. In 1896 Angeli, and independently Rimini, discovered the reaction between an aldehyde and a sulfonamide to form a hydroxamic acid; they published their discoveries in the same year [115, 116]. The reaction was mainly used as a chemical test in the dairy industry for detecting the presence of aldehydes as a consequence of food storage. The Angeli-Rimini reaction has been recently applied in solid-phase synthesis [117].

The reaction was conducted as follows. A drop of sample containing an aldehyde is dissolved in methanol or ethanol after which an aqueous solution of sulfonamide and sodium hydroxide is added (Fig. 4.9). The solution is gradually acidified in the presence of the dye “Congo Red.”

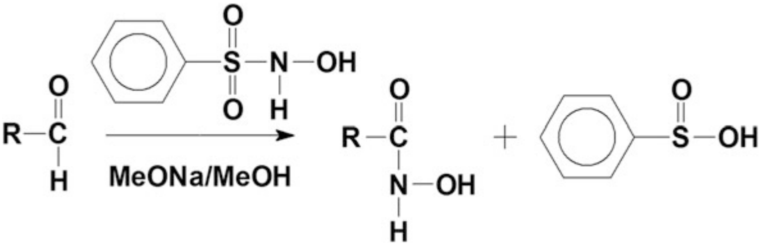


Fig. 4.9 Step 1 of the Angeli-Rimini Reaction: Formation of the acid amide intermediate

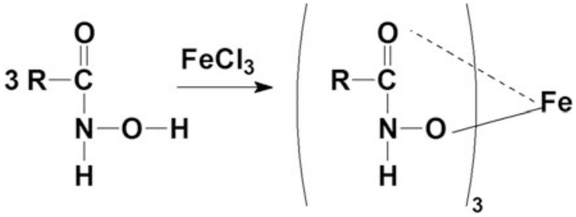


Fig. 4.10 Formation of the deep red complex that confirms the presence of an aldehyde

Addition of a drop of iron(III) chloride in the presence of the acid amide intermediate formed from the aldehyde, results in a chelate complex involving three intermediate residues and a Fe(III) ion, as shown in Fig. 4.10, accompanied by formation of an intense red color due to the chelate complex.

4.5.5 *Angeli's Salt*

The chemical feat that perhaps best illustrates Angeli's intuitive talent was the discovery more than a century ago of the sodium salt of nitroxylaminic acid, also called Angeli's Salt ($Na_2N_2O_3$). $Na_2[ON{=}NO_2]$ is regarded as a classic nitroxyl ($N{=}O^-$) donor, but under certain conditions evolution of NO is also observed [118]. Angelo Angeli found that "*salts of nitroxylaminic* [119, 120] *acid are readily resolved into the corresponding nitrites and the unsaturated nitroxyl residue.*" [121]; Angeli suggested their use as possible in vitro and in vivo sources of HNO, but physiological properties of this molecule didn't attract very much attention until the end of the 20th century.

Angeli's salt can be conveniently synthesized by treating hydroxylamine hydrochloride with excess sodium hydroxide, yielding hydroxylamine, which is

Fig. 4.11 Final step in the synthesis of Angeli's Salt

$$NH_2OH + BuONO_2 \xrightarrow[MeOH]{2\ NaOH} Na_2N_2O_3$$

Angeli's Salt

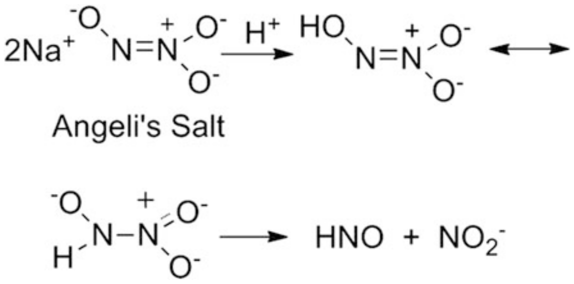


Fig. 4.12 Production of nitroxyl (HNO) by decomposition of Angeli's Salt

further treated with butyl nitrate to produce the salt as a white solid, as shown in Fig. 4.11.

When Angeli's salt decomposes in acid medium, it yields the reactive intermediate nitroxyl, HNO, according to the reaction depicted in Fig. 4.12 [122].

It is generally recognized that Angeli's salt, given its ready solubility in water, its commercial availability, and its kinetic properties, is the compound of choice in studying the chemistry and biology of the nitroxyl donor, which readily generates the nitrosyl radical, –NO. Both molecules have aroused renewed interest in the field of physiology, particularly as agents for treating heart failure, a suggestion timidly proposed by Angeli over a century ago [123].

Today the mechanism of action of this remarkable drug has been properly established and interpreted. The nitrosyl induces vaso-relaxation via an arterial route dependent on a complex biochemical cycle. What becomes apparent is the organism's ability to discriminate the biochemical functions of the vasodilator nitrosyl from those of nitrogen monoxide or nitrosothiols. Angeli's Salt induces vasodilation by the conversion of nitrosyl, at the intracellular level, into nitrogen monoxide and leads to subsequent biological activation.

4.5.6 The "Pyrrole Blacks"

There are many discoveries to which Angeli's name is linked: synthetic organic chemistry brought to the highest possible level with knowledge of the time, the study of chemical constitution and smell, the physiological activity of some molecules (among them the salt that bears Angeli's name) and finally the pyrrole blacks: Angeli studied the close relationship between pyrrole blacks (oxidized and polycondensate compounds with a basic pyrrolic structure) and natural melanin, the dark pigment found in skin, hair, some cancers, squid ink, etc. According to Angeli, in fact, the possibility existed that the amino acid tyrosine is transformed to pyrrole and then to various melanins due to the action of tyrosinase oxidant; with this hypothesis, Angeli clarified not only the nature of the melanins, but also the biochemical process of their origin. This prediction was later confirmed in 1927 thanks to the research by Henry Stanley Raper (1882–1951) and a series of brilliant studies by Pietro Rondoni (1882–1956) [124].

Angeli, shown here in a group photo in Fig. 4.13, would have deserved at least two Nobel prizes for his work, but instead, many remember him as the putative Nobel laureate of 1924, a year when it remained inexplicably not awarded. There is more than one Italian who feels that "Stockholm" only views Italy as the land of poets and artists, and not a nation that contributed Nobel-worthy scientific work to posterity. Certainly, between 1901 and 1934, Italy could have received three awards in chemistry based on the work of Cannizzaro, Ciamician, and Angeli. Or, perhaps, the Italians are sufficiently naïve to think of the Nobels being awarded on merit alone and not swayed by the powerful German chemistry lobbies on one hand and

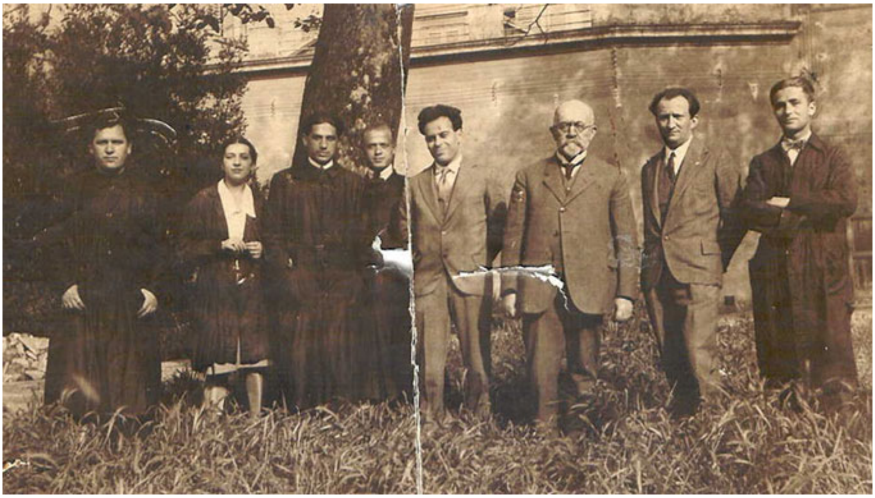


Fig. 4.13 Angelo Angeli, third from right, surrounded by his collaborators and assistants in the courtyard of the Institute of Chemistry, 1928. Department of Chemistry "Hugo Schiff," University of Florence

the French on the other. At least in the early decades of the 20th century, it seemed that only crumbs had been left to the countries on the periphery of "big science."

In 1906, as it was said at the time, distinguished Judges felt constrained to award the prize of the Royal Academy of the Lincei to both Angeli and to another scholar. Rereading the documents today, one marvels at their strange reasoning: the assignees recognized Angeli's work as "fantasy" while they commended the other awardee for his "systematic" research. In 1911, other distinguished chemists of the Academy, in conferring the award to Cannizzaro and not knowing how to express Angeli's genius, found a way out by classifying it according to the highly questionable criterion of Wilhelm Ostwald (1853–1932): he was a big "chemical romantic"! Indeed Angeli stands out as the greatest theoretical and experimental chemist Italy ever had, but for decades his name fell into a kind of undeserved oblivion.

Only in very recent times has Angeli's great genius been brought into the limelight, but even that has been piecemeal, with citations of his work showing up here and there. Such is the case with organic conducting polymers.

Most people think, however erroneously, that the story of conducting polymers began in the 1970s thanks to joint work of Hideki Shirakawa (b. 1936), Alan G. MacDiarmid (1927–2007), and Alan J. Heeger (b. 1936) on polyacetylene. In 2000, these three scientists were awarded the Nobel Prize for their contribution to the field of conjugated organic polymers. The language of the Nobel Committee further consolidated this erroneous view by improperly claiming that their work had led to the "discovery" of conducting polymers, when in fact theirs was a brilliant "perfecting of a discovery already made." Only recently, in studying original work that led to the synthesis of these materials, has Professor Seth C. Rasmussen (b. 1966) provided an account of this latest chapter in the history of science. Although on one hand such pioneering research was deserving, on the other, given the era in which the research was conducted, it could not possibly have been awarded a Nobel Prize. Still, the story deserves to be told with careful objectivity.

The conjugated organic polymers have attracted a growing interest in both academic and technological circles due to the fact that they bring together electronic and optical properties of traditional inorganic semiconductor materials. The most popular are plastic materials due to their flexibility and low production cost. Some organic polymers have shown an increased capacity, quasi-metallic in certain cases, for electrical conductivity, in their oxidized states (similar to doped p-type semiconductors) or in their reduced states (n-type). The study of these materials has enormously helped our understanding of the field of organic electronics, resulting in development of organic photovoltaic cells and of so-called OLED, or organic-photodiodes, the next generation of the more well-known photodiodes or LEDs [125]. The first real success in production of an organic polymer with significant conductivity is due to the work of Donald E. Weiss (1924–2008), who with his Australian associates in 1963 carefully studied polypyrrole.

However, already in 1915, Angelo Angeli, treating pyrrole with a mixture of hydrogen peroxide and acetic acid, observed formation of the so-called “pyrrole blacks.” He proceeded as follows: one gram of pyrrole was dissolved in a minimum amount of acetic acid, after which were added about 3 g of 50 % hydrogen peroxide. The solution turned green-brown within a short time and, in the space of two days, black. After spontaneous precipitation, Angeli recovered a black powder that he purified by washing it with water and sodium sulfate. The product proved to be insoluble in any solvent and in acids, but not in bases. Subsequently Angeli realized that these “pyrrole blacks” could be obtained by simple use of the most common oxidizing agents: nitric acid, potassium-dichromate, lead dioxide, chromic acid, oxygen and light, oxygen and ethylmagnesium iodide, potassium permanganate and some species of quinones. Comparing the results obtained using different oxidizing agents led Angeli to conclude: “These observations are especially interesting because they demonstrate that the formation of pyrrole blacks very probably is preceded by the polymerization process of the pyrrole molecule, which is accomplished more or less rapidly depending on the reagents that are used [126].”

The “pyrrole blacks” greatly interested Angeli because they were reminiscent of the natural pigment that carries the name of melanin; also by elemental analysis he observed that the ratio N:C:H of “pyrrole blacks” was almost identical to the values obtained for melanin. The characterization of the structure of the “pyrrole blacks” at the end of the 1910s was a daunting task, limited by the polymer’s complexity and insolubility; it was also difficult to oxidize. However Angeli succeeded in his work: looking among the decomposition products of pyrrole and indole derivatives, he could formulate the hypothesis, which proved valid, according to which the pyrrole ring was at the center of the structure of the “pyrrole blacks” (i.e., the polymer which then took the name polypyrrole). Angelo Angeli also proposed that the structure of the “pyrrole blacks” contained units of pyrrole linked by carbon-carbon double bonds. It should be noted that his proposed structure is very similar to that accepted today [127, 128].

Angeli was a reserved person; there is little information left of him or his thoughts. We may never know why his curiosity was driven in this or that direction. But Angeli was also a genius, and certainly revered as such by his students and esteemed by his colleagues but nobody knew nor understood the depth of his thoughts, nor the broad scope of his work. He abandoned his study of pyrrole blacks in 1920; we do not know why. Probably with the limited means of chemical investigation of the time he had deduced everything possible and so devoted himself to other endeavors. In 1930 he returned to the subject, and left open the possibility of starting an extensive research project on the polymerization of many heterocyclic compounds, but he never lived to accomplish it: within the year he passed away. But his research in this field was not lost: unexpectedly Riccardo Ciusa (1877–1965), another student of Giacomo Ciamician, became interested in generating analogues of graphite; starting with furan, thiophene and pyrrole, he took up Angeli's baton.

Angelo Angeli's work constituted a wonderful story, perhaps the most brilliant in the history of the University of Florence. But much more work has to be accomplished in order for him to become fully recognized in both the profundity of his thought and the grandeur of his experiments.

4.6 Angeli's Students

4.6.1 Guido Cusmano (1882–1956)

Guido Cusmano was born in a small town on the island of Elba, 7 June 1882. Due to his father's professional commitments, in 1901 the family moved to Sardinia where Guido began his university studies in Cagliari. He completed his chemistry studies in 1905; three years later he also earned a degree in the life sciences. From a young age, Cusmano stood out due to his scientific acumen, manual dexterity, and experimental precision, qualities that led Giuseppe Oddo (1865–1954), professor of general chemistry, to employ Cusmano as a collaborator. Over the years, Cusmano was fascinated by organic chemistry and natural-products chemistry. His early research was on the constitution of santonin, an anthelminthic derived from flower heads of *Artemisia maritima*. Cusmano then began studying limonene and pinene, leading him to a lifelong passion for terpenes and camphor. In 1910, Professor Ugo Betti (1875–1942) proposed Cusmano as an assistant professor of general chemistry in the Florence chemistry department, at that time still directed by Hugo Schiff (1834–1915). The position was not easy for two obvious reasons: it entailed great responsibility, aggravated by his chairman's difficult nature. However it was also in Florence that Cusmano found a colleague who would eventually become, in Cusmano's own words, "a master loved and revered," [129] Angelo Angeli (1864–

1931). It was also in Florence that Cusmano encountered both exciting new ideas emerging in the field of organic chemistry internationally as well as new physico-chemical techniques that were supporting and reinforcing that discipline.

With Schiff's death in 1915 and Angeli's move to Rome in 1916 to work for the Ministry of the Navy [130], Cusmano found himself catapulted from a simple assistant to the person responsible for the entire Institute: from running the laboratory to teaching courses in organic chemistry. Once World War I ended, the normal competitions for professorial positions resumed and, in 1921, Guido Cusmano was selected as chair of medicinal chemistry at the University of Sassari. After a brief stay, he transferred first to Parma, then to Pisa and, finally, in 1926, to Genoa. Here he remained, despite numerous importunate invitations he received urging him to return to Florence: he was tied by bonds of affection for the new Institute of General Chemistry at San Martino d'Albaro that he had founded (in another part of Genoa).

As a teacher Cusmano stood out for his originality and passion. He carefully prepared his lectures, diversified the subject matter, continually updated the curriculum to keep it current with latest developments, and adapted everything to meet changing student needs.

For his entire life Cusmano held immense affection and extraordinary admiration for Angelo Angeli; even a few months before his own death, Cusmano recalled for his students how the "master," breaking his usual cantankerous silence, would allow him to participate in his (Angeli's) ingenious insights or brilliant discoveries, which later would materialize in works written in a clear, concise style.

Cusmano's earliest interest was focused on chlorophyll, to which he dedicated some years of his scientific activity to elucidate their structures [131]. Later, he transferred his interests to an extensive study of the reduction of aromatic nitro compounds with platinum and hydrogen [132]. Cusmano's accumulated knowledge of aromatic nitro compounds led him to "play" with opening and closing heterocyclic rings, e.g. ring-into-ring conversions, or ring transformations of heterocycles, comprising an interesting focus for mechanistic studies and synthetic design.

In his seventh decade, Cusmano was struck by a form of cancer that would take his life in a very short time. Despite being aware of his desperate state of health, Cusmano could not remain apart from his laboratory, which he continued to visit even on the threshold of death. Guido Cusmano, at age 73, died on 28 February 1956 and rests, according to his wish, in a small cemetery and sunny place on Monte Sant'Ilario (Elba) [133].

4.6.2 Raoul Poggi (1899–1961)

Anna Raoul Poggi—son of Cavalier Piergiovanni and his wife Angiolina Zerboni—was perhaps the youngest student of Angelo Angeli to attain a university chemistry chairmanship. He was born 16 July 1899 in Vicchio nel Mugello (a village several kilometers north of Florence). There is an oral tradition, passed on from generation to generation among chemical circles, but never confirmed, that Poggi's father had always wanted a daughter, and to bear witness to his unfulfilled desire, he placed the name "Anna" ("A.") as a prefix to "Raoul."

Called to the front lines during World War I, Raoul Poggi participated in latter stages of bloody battles that characterized that war. Wounded and mutilated during the battle of the Piave, Poggi was decorated with the Military Cross in the field [134]. Discharged from the army as a war hero, he limped heavily for the rest of his life. This disability did not prevent Poggi from graduating in chemistry in 1923; in the following year, he also completed his studies in pharmacy. Later, with the rank of captain, he served in the Italian government's Military Chemistry Center. And so, despite Poggi's terrible wartime experiences, he pursued a brilliant academic career, beginning as a volunteer assistant to Angeli. Although, by the age of 30 he was already a professionally qualified lecturer in organic chemistry, Angeli's death caused a setback to Poggi's promising career: in fact, he had to wait 19 years before becoming a full professor at the University of Cagliari in 1950. And, in early 1951, he was elected dean of the Faculty of Pharmacy.

What happened during Poggi's 19 years of waiting? From 1931 to 1950, Poggi filled the post of assistant to the chair of organic chemistry at the University of Florence. Thanks to his lively, unconventional, and fertile intellect, his research interests ranged over the entire spectra of organic, analytical, pharmaceutical, and applied chemistry, resulting in numerous publications in all of these fields [135–137].

Poggi's early studies dealt with oxy-azo compounds, followed by the determination of phosphorus and arsenic in natural organic substances. A study financed by the Ministry of War kept him occupied for a long time and led him to correlate the presence of double bonds between carbon atoms in oil-based lubricants used in gunpowder [138]. In 1932, together with Giovanni Speroni (1910–84), only recently graduated, Poggi discovered the first organic derivatives of selenium [139].

A few years before Angelo Angeli's death Poggi published an original study on the stereo-reaction kinetics of the condensation of aldehydes with cyclic ketones, earning the "master's" warm approval. Together with Angeli, in 1928, he completed a comprehensive study on the chlorination of many saturated and unsaturated chemical species, deriving empirical laws among the different classes of derivatives [140].

After Angeli's death, Poggi became increasingly interested in the field of pharmaceuticals, which resulted in some wonderful practical discoveries: the solubilization of antibiotics and vitamins; proper dosage of sex hormones that had been identified in Germany in the late 1930s; separation and structural analysis of several physiologically active natural products such as belladonna, *Rauwolfia serpentine*, and *Lawsonia inermis*, by means of paper and column chromatography [141].

At a relatively advanced age, he married one of his students, Dr. Sara Sacchi (b. 1911), who became one of his most valued collaborators.

Death, as we know, is the fate of every individual, but in the case of Raoul Poggi, that statement seemed like an oxymoron: his health was stable, his body solid, and even youthful-looking. Yet, while still in his early sixties, he was struck by one of those evils that no one ever wants to talk about. Suffering from great pain and an enervating weakness over a period of more than three months, he died at Careggi Hospital in Florence on 24 August 1961, leaving behind his loving wife and two young sons [142].

4.7 Nicola Parravano (1883–1938)

Nicola Parravano was born on 21 July 1883 in Fontana di Liri, a commune located about 65 miles southeast of Rome,. His parents were Giuseppe Parravano and Alessandrina Nardone. The Parravanos were one of the most prominent families in Italy; the family atmosphere fueled Nicola's innate passion for chemistry. His paternal grandfather and father, both served as mayors of his birthplace for over forty years, were also both pharmacists. His brother, Luigi, continued the family tradition by studying pharmacy and also by becoming mayor of their hometown from 1926 to 1939.

Nicola attended elementary school in Fontana di Liri, and followed a classical education in secondary school at Arpino and, later, matriculated at the University of Rome.

At 21, he graduated in chemistry with honors and, after a short period as an assistant in the summer semester of 1909, he obtained a scholarship, to work in Walther Nernst's (1864–1941) physical chemistry laboratory in Berlin. On Parravano's return to Italy, he pursued more deeply his research on the manufacture of steel, cement, and explosives. In 1911, for two years, he was deputy director of the chemical laboratory (in Rome) for explosive substances. He returned to the "fold" of the University of Rome in 1913 and developed an interest in metallurgy under the guidance of Emanuele Paternò (1847–1935). Over time, he became a dominant presence within the chemical community. Thus, at only thirty years of age, Nicola Parravano became the chair of Chemistry and Technology at the Royal University of Padua (1913) and, in 1915, that of Physical Chemistry (the first established in Italy) at the Florence Institute of Higher Practical Studies and Specialization. In 1917, the Royal Academy of the Lincei awarded Parravano the Royal Prize in Chemistry.

Nicola Parravano, despite a relatively short career in science, was author of over 150 scientific monographs, of which less than half a dozen were associated with the period of his stay in Florence. In Florence, chemical research had been stalled for over 10 years, ever since Augusto Piccini died in 1905. Ugo Schiff, nearly 80 years old, was ubiquitous in the laboratory but mentally and physically unable to contribute vigorously to new discoveries. To compound matters, the Great War that was consuming the financial and intellectual resources of most of Europe, impelled many members of science departments in Florence to volunteer for the front lines. Consequently, on his arrival in Florence, Parravano found an Institute that was essentially a semi-desert. Even if it were not for the logistic problems that he found, Parravano's restless character meant that Florence would become only a brief stopover on his career trajectory. And so it was that Nicola Parravano, finding an Institute that was stripped and practically dismantled, decided to devote himself comparatively more to the Supreme Army Commission of Explosives Inspection and Control than to modernization of the laboratory. The budget was highly inadequate and research languished during the four years that the young Parravano was at the controls. His successor to the chair of Florence, Luigi Rolla, found an institute where changes were imposed only by time and neglect. It was in worse condition than it ever had been in the time of Ugo Schiff.

However, parallel to the situation at the chemistry institute, Parravano, a shrewd politician, was slowly building his own financial and moral structure [143]. He became flagbearer of the idea of science as a "social force." He devoted his full support to the fascist regime and from the resultant power base, he received substantial funding. During Mussolini's dictatorship, he was held up as a prototype of the "fascist scientist," attentive to technical problems and applications, rather than to basic research [144].

In 1919, Parravano was appointed Professor of General and Inorganic Chemistry at the University of Rome and, in 1923, he took over management of the Institute of Chemistry. From that moment on, his rise to power and fame was unstoppable. In 1925, he topped off all of his other career achievements with that of Director of Pharmacy, and two years later he also added the title of Dean of the Faculty of Science at the same university. In 1926, he became a member of the Higher Council of Education and in 1927 also that of Health. To this he added the chairmanship of the Committee of Civil Mobilization, membership on the Commission for the Chemical Industry, as well as a consultant for the Ministry of Corporations. Parravano founded in Milan the Ernesto Breda Scientific-Technical Institute for research in science and technology of metals. He was among the first to be elected to the Academy of Italy in 1929, and simultaneously became Vice President of the Italian Society for the Advancement of Science, obtained a position on the National Research Council, acceded to one of the forty seats in the Academy of Sciences, held a place of honor at the Supreme Commission for the Testing of Explosives, to say nothing of his taking over the presidency of the High Consultative Commission on Flammable Substances. He was also a Board member of numerous Italian and foreign chemical companies (Swiss, French, Polish, Spanish, and Romanian). His obsessive search for visibility concealed an underlying desire to reach the highest position, his ultimate goal whether on the national or international level, was to go from the small Italian Presidency of Chemistry, to that of greater visibility: the International Union of Chemistry, and from the Presidency of the Consultative Commission on Explosives to the high-sounding Presidency of the National Fascist Federation of Industrial Chemists [145].

In addition, Parravano received many awards in the form of medals and found that he enjoyed sporting the baroque livery of Academic of Italy. He added to his roster of accolades the "LeBlanc" Medal of the French Chemical Society, the Commander of the SS. Maurice and Lazarus Award, Commander of the Legion of

Fig. 4.14 Madrid 1933. International Union of Chemistry Conference. Parravano is seated in the first row, fourth from the right

Honor, and a Grand Officer of the Crown of Italy. And he was lucky enough to avoid the carnage that was consuming so many fighters on the front lines of the war.

He was a supporter of the idea that industry, in order to develop and adapt to the needs of a nation undergoing major social transformations, should be based on scientific and technical principles. In this, Parravano discerned the need for collaboration between science and industry. He planned, organized and directed the Institute of Scientific Research in Steel that Ernesto Breda (1852–1918), founder of the eponymous industrial company, had created in those years in Sesto San Giovanni. He was later among the major and most qualified organizers of the National Institute of Chemistry, and later the National Research Council. He worked closely with Guglielmo Marconi (1874–1937) who always showed him great respect and consideration. He was several times a member of the Higher Council of Education and the Board of Health. Parravano's frenetic activity as a scholar, and at moving adeptly in the salons of industrial northern Italy, he knew how to become appreciated in Italy, abroad (Fig. 4.14), and especially, by the fascist regime. But despite his numerous awards and positions of great prestige, the award that Parravano coveted most because it was the most prestigious, finally arrived, shortly before his death in 1938: his appointment as a member and then Director of the Academy of Italy.

In 1938, after assuming the presidency of the Italian Association of Chemistry, Parravano organized the X International Congress of Chemistry. This congress served as an effective propaganda weapon of the Fascist regime, which had funded it, as well as his personal triumph. In the imposing panorama of the new home of the University of Rome, 2500 Congress attendees (among whom were 1600 foreign visitors) grappled with the overall theme, "Chemistry in the Service of Man." In his inaugural address delivered before the King of Italy and Emperor of Ethiopia, Vittorio Emanuele III (1869–1947), Parravano pronounced with high-sounding rhetoric: “All scientists are looking to us” and concluded by raising a hymn to chemistry: “Ours is a Divine Science.” At the height of his career’s parabola as scientist and politician, on 9 August 1938, he suffered a heart attack that removed him from the land of the living at the age of just 55.

In the posthumous commemoration of 1939, Parravano’s colleague, Pontifical Academic Francesco Giordani (1896–1961), addressing the Holy Father present at the meeting, trod a fine line between exaggerated hyperbole and the simple obsequies owed to the deceased. These excessive manifestations of condolences, always present in similar circumstances but absurdly exaggerated during the fascist regime, made the ceremony a grotesque farce. Not lacking in all of this ceremony was the posthumous “last laugh” that the “Baron” managed to accomplish even while high-sounding testimonies about human mercy rained down on his remains: news was given out, no one knows by whom, of the existence of a large sum of State money directed to the municipal coffers of Parravano’s birthplace, no one knows how, and, just incidentally, administered by his brother, Luigi.

4.8 Luigi Rolla (1882–1960)

Luigi Rolla has been entered in the history of chemistry for the so-called “*florentium* fiasco,” his announcement of discovery of the last missing rare earth element, and his later retraction. He worked at the University of Florence during fourteen crucial years of the 20th century (1921–1935), fraught with terrible tragedies on a global level, but also, and above all for thousands of scientists, a period that witnessed a number of developments and revolutions in physics and chemistry that have changed the course of Western civilization. In the first instance, Rolla, during that period, was the charismatic leader of a generation of chemists at the University of Florence, whose leadership had the potential of preparing the basis and accelerating the development of new technologies and theories. Instead, the story of *florentium* overshadowed everything he did and marginalized any other type of scientific productivity that he may have accomplished. Although Rolla was a chemist, he mastered the most advanced mathematical tools, being among the first in Italy to diffuse new knowledge of atomic theory and quantum mechanics. His work on vapor pressure at very low temperatures and the determination of ionization potentials of the elements provided experimental support for the third law of thermodynamics and the law of mass action respectively.

4.8.1 Early Life and Career

Luigi Vittorio Maria Rolla was born in Genoa on 21 May 1882, the next-to-last son of Giuditta Boggiano (1848–1902), from La Spezia, and Giovanni Rolla (1839–

1917), an accountant. Both his grandfather Eugenio (1807–90) and his great-grandfather Giovanni Battista had been foreclosure agents for the city of Genoa. He completed all of his early schooling and university studies in Genoa, earning his university degree in 1905. He was a student of Guido Pellizzari (1858–1938), under whose mentorship he wrote his thesis in organic chemistry, and Antonio Garbasso (1871–1933), a physicist, with whom he reproduced in the laboratory the physical phenomenon of the "mirage." In December 1908, he won a post-doctoral position in Berlin and worked in the laboratory of the physical chemist Walther Nernst (1864–1941). He attended the lectures of two Nobel laureates in chemistry, Jacobus Henricus van't Hoff (1852–1911) and Emil Fischer (1852–1919). While in Berlin, he also became acquainted with another Nobelist, Svante Arrhenius (1859–1927). Among Nernst's students, he became close friends with Hans Von Warteberg (1880–1960), Arnold Eucken (1884–1950), Walter Hans Schottky (1886–1976) and Nicola Parravano (1883–1938).

Back in Genoa in the summer of 1909 he continued to work at the university until 1915, when he was called to the front as an artillery officer. During that time he worked in the photo-telemetry service initiated by Antonio Garbasso (1871–1933). Back in Genoa in 1919, along with Luigi Belladen he devoted himself to a thorough study of thallium selenides. The close of what Rolla himself described as the first period of his life, ended in 1921.

4.8.2 The Second Period in Luigi Rolla's Life

After a brief period as a professor of chemistry at the Royal University of Sassari, from 1 January to 15 October 1921, Rolla was called to fill the Chair of the Department of General and Inorganic Chemistry and to direct the Institute of Higher Practical Studies and Specialization of Florence [145]. Due to the large influx of students in chemistry and medicinal chemistry, a pavilion was built on the premises of the physics library since the physics department had recently moved to Arcetri [146]. The chemistry laboratory, which had been expanded in 1879 by Hugo Schiff, had become inadequate. So Rolla, on his own initiative and at his own expense, launched the work of reconditioning nineteen rooms. Five years after Rolla's arrival, the Institute he directed could be claimed to be the best-equipped in Italy: a machine shop, two classrooms and four other rooms on the ground floor, seventeen rooms on the first floor and three rooms in the attic, all rearranged and equipped with power outlets delivering direct and alternating current, tables, cabinets and state-of-the-art scientific equipment. To attain this level of excellence Luigi Rolla resorted to obtaining special government grants as well as private donations, to say nothing of his own "personal sacrifices." Senator Felice Bensa (1878–1963) donated 595,000 lire, Rolla's brother, Fernando, 50,000 lire, Rolla himself, 150,000 lire; the Mining Society of Montevecchio and other philanthropists contributed a total of 70,000 lire, while the Ministry of Education committed 160,000 lire over 10 years.

Ever since his arrival in Florence, Rolla conducted research on the group of rare earths with the specific intention of isolating the element possessing atomic number 61. He studied new methods of fractional crystallization, the method of choice for separating rare earth elements. He worked first with small, then with immense quantities of material so that in the 1930s the Institute possessed, as its Director declared with great pride, "the richest and purest collection of cerium oxides in the world [147]."

Rolla divided his research group by assigning to each a different area of original investigation. With Giovanni Canneri (1897–1964), Rolla investigated the vast unexplored field of preparation of rare earth metals and their alloys. To Giorgio Piccardi, Professor of Physical Chemistry, fell the area of spectroscopic investigation. As Rolla reported [148]:

> the electrical properties of flames into which salt samples were aspirated led to the measurement of ionization potentials which cannot be determined spectroscopically, and to the study of the spectra generated with low excitation energies that are also of interest for chemical analysis.

A glance at the impressive list of publications (about 200 within 1924–34) prompted one to realize the high standards as well as the rapid pace at which the Institute's scientific activity unfolded, and not only in the field of the rare earths.

With Luigi Mazza (1898–1978) Rolla published two papers on "Photoelectric Cells" and "Systems Telegraphy and Telephony Infrared Radiation," although a portion of this work was partly protected by military secrets and patents [149]. In fact, in the four-year period from 1926–29 the Inspectorate of Engineers sought Rolla's expert advice, who in his youth had already conducted optical investigations on the nature of a mirage. The statements of General Guasco were nothing short of enthusiastic; certificates of recognition from the Royal Army took concrete form with the ample renewal of financial support. These systems, known as "Photoelectric Cells Rome," could overcome the most adverse weather conditions; their production was contracted to private industry, but the patents were transferred to military authorities. The "sponsor" of "Photoelectric Cells Rome" was Senator Emilio Bodrero (1874–1949), who became aware of their existence at the industrial show Optics at Padua in 1927. Since that time, Rolla and Mazza had intensified their relations with military authorities, periodically sending them precise and regular reports of their findings in the infrared field. In addition to works already cited, from 1929 onward, Rolla and his collaborators reported excellent results in night photography with infrared rays. These reports were secretly received by the Inspector General of Engineers and by a limited group of specialists.

It is only by indirect means that we have learned of the contents of some of these reports. In a 26 August 1929 letter addressed to Rolla, the Minister of National Education, His Excellency Giuseppe Belluzzo (1876–1952), expressed his pleasure and deep gratitude to Rolla. In addition, Belluzzo briefly listed the numerous investigations of interest to the military [150]:

- Creation of the photoelectric resistance cell "Roma" for detection of infrared radiation, but of a type superior to and cheaper than the American version

- Definition of an equipment system for dark infrared radiation telegraphy
- Construction of complex portable transmitters and receivers for long-distance secret telegraphy, even in the case of fog.

In addition to these projects, Rolla collaborated with the General Directorate of Naval Weapons and Armaments in studying the following:

- A system for the detection of the marine horizon by naval units even under hazy conditions (improvements to the problem posed by shooting at marine targets from a horizontal platform)
- An automatic gyrocompass successfully tested at the "Galileo" workshops in Florence
- A photoelectric device for the determination of the horizontal velocity of artillery shells
- An apparatus for the nocturnal detection of naval units
- An automatic gyroscope, successfully tested at the Italian Manufactured of Optical Systems "Galileo" in Florence
- A photoelectric device for the determination of the horizontal speed of artillery shells
- An apparatus for the detection of nocturnal naval units.

This summary list implies, albeit roughly, that Rolla possessed a very broad knowledge of physics and technology and that his research interests were aimed mostly at Italy's war effort. Not surprisingly, though, his national prestige continued to grow and his "academic race" was pursued at a dizzying pace (prizes, awards, chairmanship of agencies, and appointment as national delegate for international congresses) despite the earlier fiasco of *florentium*. Certainly Rolla, a dedicated nationalist and sincere fascist, learned to maintain a respectful distance from Nicola Parravano, recognizing that the hierarchy, not well sketched out at the national level, saw him as the greatest representative of fascist Italian chemistry. In the same period Pietro Saccardi (1889–1981), Angelo Angeli's interlocutor when he was a student, took a wrong step at the beginning of his academic career by not recognizing Parravano's authority, and thus hindered him in any way that Parravano could. As a result, Saccardi was "relegated" to the peripheral University of Camerino, where he briefly served as Rector.

The fourth point regarding Rolla's research on behalf of the General Directorate of Naval Weapons and Armaments alludes to his possible involvement in the study of radar. There are no vestiges of information supporting this conjecture except for the fact that the engineer, mathematician, Admiral, and Vice-President of the Academy of Italy Giancarlo Vallauri (1882–1957) [who worked with Guglielmo Marconi (1874–1937)], in congratulating Rolla and Mazza for their innovative research, also charged them with convening a series of conferences at the Higher Institute of Communications of the Royal Navy.

4.8.3 *Innovative Science*

Two interventions of extraordinary importance in helping us to understand Rolla's thoughts are discourses he presented in 1922 and in 1936, an interval encompassing his entire career in Florence.

Not a year had passed since his arrival in Florence when Rolla, on 5 November 1922, was invited by the Faculty of Science to present the opening address of the academic year. According to long-standing custom, the address was held in the auditorium of the Institute of Higher Practical Studies and Specialization. In his talk, Rolla seemed to speak as a rational positivist, espousing a position that regarded science as a metaphysic of absolute certainties, almost the foundation of a scientific religion. Actually, Rolla did not convey this openly, not because he did not feel in a certain way that he was a late-positivist, but because throughout his career he expended little ink on the matter, leaving only a few vague lines regarding his philosophical conception of science.

Rolla was fundamentally an experimenter. Chemistry, and, in particular, physical chemistry and thermodynamics were, for him, not limited to a series of equations, but their significance went well beyond the mere understanding of abstract principles.

Rolla's intuition was different: while his peers, many of them great physicists, were developing completely new theories about nature, Rolla was capable of exploring existing ideas from a completely new perspective, and usually with better results. The only way he could truly understand physical concepts was to approach them in his own way; the end result sometimes appeared radically different from the conventional viewpoint.

In Berlin, where Rolla completed his postdoctoral work, he assisted at the last stages of the "conflict" between the atomists and the energists, and he likewise found a way to get in touch with *Lebensphilosophie* [151], which was replacing the late positivistic philosophy of Bertrand Russell (1872–1970) and Ernst Mach (1838–1916) and that, according to historians of science like Paul Forman (b. 1937), enabled the birth of quantum physics [152]. At the beginning of the 1920s, a fully mature Rolla seemed aware that the major tenet of what he called "chemical theory" could not possibly be the conservation of matter and energy; he foretold for the universe, seen as an isolated system, in the absence of other forces "[…] a reduction in its equilibrium temperature, so that there would be no possibility of transformation or of movement of life, i.e., the end of the world." It is certain that the phrase with which Rolla closed his discourse was unique among his own writings [153]: "The idea of God will always be found useful by men tired of the search for truth. However you want to imagine it, the scientist as the ignorant one, the great as well as the humble, you cannot help but think that Someone set everything in motion by dictating these laws."

For Luigi Rolla, chemistry in the 1920s, was nothing more than a set of thermodynamic and radioactive processes, or at least it was what was previously cited in his discourse, taken together with the recent work of Einstein's theory of general relativity and that of his mentor Walther Nernst, who uttered the prophetic words about the energy contained in atomic nuclei: "We live on an island of guncotton and fortunately we have not yet discovered how to light the fuse [154]." From the ether theory, imagined differently in various historical periods, Rolla expounded his idea about the formation of chemical elements [155]:

> […] you can go one step further and suggest that the atoms that are formed directly from the initial energy [156] are the heavier elements with atomic numbers greater than uranium. Therefore, these highly radioactive elements would disintegrate rapidly and release a great deal of energy.

Radioactivity, for Rolla, was fundamentally important in imagining the formation mechanism of the fixed stars. It was precisely radioactivity and his glimpse of the potential of nuclear energy that enabled him to conceive of a mechanism according to which an "ultimate synthesis" could bring about an "immortal universe," an idea that is no longer regarded as acceptable.

What made Rolla special as a scientist was a willingness to explore a problem from every viewpoint (chemical and physical), deal with it in every aspect, and resolve it. This facility was a product of his deep intellect and his tireless ability to concentrate. Rolla, although he had tried to find a missing element (atomic number 61) for most of his academic career, did not believe in chemical atoms, but, rather, in physical atoms. He isolated (or at least tried to do so), manipulated, cooled, condensed, and ionized atoms and molecules throughout his career but he never synthesized a new molecule or any intermediate compound. Rolla felt that he was more of a physicist than a chemist. Regarding chemistry, Rolla foresaw hard times, if not its death. After its 19th century triumphs, chemistry was heading toward a decline that seemed exactly to coincide with the revival of physics, as atomic physics, which Rolla looked upon with awe and suspicion, regretting that he had not embraced its study, however timidly, in his youth.

Barely a year after his return to Genoa, in a speech on February 19, 1936 at the opening session of the Ligurian Section of the Italian Association of Chemistry, Luigi Rolla spoke of new horizons for chemistry [157] and of all the points he cited, not one belonged to organic, synthetic, industrial, analytical, or biological chemistry! The topics addressed were, in fact: bombardment of atoms with neutrons; transmutation of the elements; radio-elements; artificial radioactivity; behavior of the rare earths (Rolla had discovered the natural radioactivity of samarium and neodymium [158]); Enrico Fermi's (1901–54) recent experiments; deuterium; heavy water; heavy hydrogen compounds; and, finally, heavy-oxygen isotopic reactions. Rolla's horizon always remained unchanged: to establish the causes and laws of the differentiation of matter. Chemistry was relegated to a marginal role and chemists were downgraded to the mere manipulators of these "differences" in matter; in fact, his words are eloquent: "Chemists expect that the technology [of the physicists] has progressed so much, that these experiments can also be performed in their laboratories” [151]. Chemistry in particular, from Rolla’s point of view, would never be anything more than a vassal science of physics which would soon lose its autonomy. These were almost prophetic ideas, so much so that, even today, we talk about all this, but without arriving at a shared outlook by all interested parties.

4.8.4 The Fiasco of Florentium

When, in 1919, Luigi Rolla was called to occupy the Chair of General Chemistry, he brought with him a solid reputation as a scientist earned through his work at the renowned Walther Nernst’s school in Berlin. Rolla was to become the scientist who dominated Italian chemistry during the period between the two world wars (Fig. 4.15).

In the attempt to direct new light on the Periodic Table, Rolla began to measure the energy needed to remove an electron from an atom of each element, from

Fig. 4.15 Official portrait of Luigi Rolla. Department of Chemistry “Hugo Schiff,” University of Florence

hydrogen, the smallest, to uranium, the largest atom then known. In so doing, he had to study all of the known elements very carefully. Although he had no trouble purchasing common elements like iron and copper commercially, for others he had to isolate them from mineral species in the laboratory. And in particular he had to engage in fractionation of that group of elements that bore the fascinating name "rare earths." These elements, far from being actually "rare" as their name would imply, could be found in many different minerals, but possessed the inconvenient property of being so similar to one another that separating them was extremely difficult.

At the beginning of the 20th century, the entire scientific community knew that only one rare earth element, specifically number 61, had not yet been discovered. In 1922, Rolla thought he had discerned its presence in some minerals, but the amounts treated were so small that he wanted to wait to repeat his experiments with more material. His assumptions were twofold: element 61 was a member of the rare earth group, and its occurrence was so rare that large quantities of starting materials would be needed to isolate the infinitesimally small quantity present in the usual rare earth mineral samples. The economic resources of the University were limited with respect to these large quantities, but unexpectedly a Genoese industrialist, Felice Bensa (Fig. 4.16), donated the exorbitant sum of one million lire to the Chemical Institute and, with this injection of funds, the search regained its momentum. From Brazil, two metric tons of monazite sands arrived in Florence; the

Fig. 4.16 Senator Felice Bensa, Genovese industrialist and friend of Luigi Rolla. He personally donated large sums of money to modernize the Chemistry Institutes at Florence and was a great supporter of the research on the isolation of *florentium*. Property of the authors

technical personnel of the university undertook the task of constructing porcelain chemical equipment such as evaporating dishes and filtering apparatus of immense proportions.

For two years, chemists labored in silence in the large laboratories of the Institute in via Gino Capponi, at one time belonging to the Ministry of War, and presently refurbished to meet demands of this new research focus. Finally, in the spring of 1924, Rolla and his young assistant, Lorenzo Fernandes (1902–77), announced that they had photographed the "fingerprints" (i.e., the characteristic spectrum) of element 61. The hunt could be said to have ended, but rather than celebrate, Rolla became assailed by doubts. He was aware that many scientists had been ensnared in the fatal error of having announced a discovery that later was proven to be false. So then, what should he do? He was standing at a crossroads: to announce a discovery prematurely or to lose priority of the discovery? Fernandes, marked by the impulsiveness typical of youth, exerted pressure on his director to publish the findings. Rolla hesitated, but certainly he shared Fernandes's enthusiasm: if he announced the discovery of a new element, he would be the first and only Italian to have done so.

The prospect of success caused him to set aside his last reservation and in June 1924 Rolla handed a sealed envelope to the Accademia dei Lincei containing the results of his analysis. The envelope's contents was to remain secret until he or other chemists produced further evidence supporting the existence of element 61: in this way, he could defend the priority of his discovery without exposing himself to making a false claim. The researchers returned to their efforts of trying extract this elusive element from tons of raw material when, like a bolt from the blue, a group of American chemists announced the discovery of element 61. The team from the University of Illinois had worked on the same material as Rolla and arrived at the same results. B. Smith Hopkins (1873–1952) named "his" new element *illinium* in honor of the state and university where it was discovered. The dismay in Florence was great. After an initial period of bewilderment, Rolla raced to Rome and requested that the Academy lift the seals on the envelope that he had deposited there two years earlier.

The Accademia dei Lincei convened the most famous scientists and intellectuals in Italy, and from the platforms of those conferences discoveries were announced, controversies were stirred up, and prophecies were made. Rolla, during the formal session that October, set forth with great skill the role that it was up to Italy to play in the world. Reviewing the great scientific events of past years, Rolla came to talk about his own work. At the end of his discourse, with the clear intention of giving it maximum importance, he excited the audience with the announcement of the sensational discovery of a new element. The message was launched to the world in a context of spectacle: "the element sought in vain for so long, the rarest of the rare earth elements would have to repeat, by saying its name, the name of that most Italian of Italian cities, where Dante expressed the spirit of our race. For this element, atomic number 61, we propose the name of *florentium* and the symbol Fr [159]."

In Italy the news was surrounded by a dizzying spate of nationalistic propaganda. And the conferral of laurels was not long in coming to Rolla and his team: he was elected as a member of the Accademia dei Lincei and Fernandes was appointed professor. On the opposite sides of the Atlantic, meanwhile, a fierce controversy began to rage to determine the name of the element: should it be called *florentium* or *illinium*? However, the years passed without anyone being able to physically isolate this element, and consequently, the naming issue was unresolved. This problem insinuated its way into the minds of Rolla and Fernandes in the form of a difficult question: Could this indeed be a false discovery? But the applause of the Lincei academicians regarding Rolla's sensational announcement drowned out the whispers of a possible future disillusionment. Over the years, however, the relationship of respect and collaboration between the two discoverers fell apart and Lorenzo Fernandes left the university under a cloud.

In 1942, after 18 years of intense effort, the Florentine chemists still had not succeeded in extracting even a fraction of a milligram of *florentium*, and so, another of Rolla's co-workers, Giorgio Piccardi, convinced his director to retract the news of its discovery, which he did by nestling it in a long document outlining the history of rare earth research at Florence in a minor Vatican journal [160].

Three years later, element 61 was, indeed, discovered but only among uranium's fission products [161]. It was found to have no stable isotopes and those discovered had very short half-lives, so Rolla and Fernandes were searching in vain for the ghost of an element that had disintegrated away many millennia earlier [162]. The three discoverers, Jacob A. Marinsky (1918–2005), Lawrence Glendenin (1918–2008), and Charles Coryell (1912–71) eventually named the element promethium, after Prometheus who dared to gift mortals with fire, at the suggestion of Mrs. Coryell [163]. Promethium's discovery in the earth's crust had to wait until 1968 before it was found in uranium-bearing deposits of the natural nuclear reactor at Oklo, Gabon, thanks to tremendous efforts of an American team of scientists headed by Paul Kuroda [164].

In contrast to Rolla, B. Smith Hopkins remained supportive of his claimed discovery until the end of his days. With his second wife, May Lee Whitsitt, he traveled the length and breadth of the U.S. and spent a considerable fortune in a vain attempt to save "his" *illinium* from oblivion [165].

On 8 November 1960, Luigi Rolla passed away at Genova where he had moved some time before. Giorgio Piccardi, his co-worker and successor at the University of Florence, when questioned by his students about their ghostly element, would stop his lecture and look fixedly and in silence at the assembled class. Then he would break out into a wide but inscrutable smile and with convincing and persuasive words would say [166]: "My dear students, the great Poincaré defined science as the graveyard of hypotheses; if in it our own is also buried, I will be honored." Then, with a courtliness devoid of all affectation, he would resume his lecture from the point where he had been interrupted.

4.8.5 The Creative Drive Gives Out

On 27 April 1932 in the Genoa family home, Ferdinand Rolla, a merchant who had privately contributed large sums to equip laboratories that were directed by his brother Luigi, passed away at almost age 59. It was a great blow to Luigi; upon his return to Genoa in 1935, he tried to rebuild the family unit with his still-living siblings: Eugenio, Carlo, and his loving sister Teresa.

Rolla's 1936 return to Genoa coincided with a period of great enthusiasm for teaching at the expense of gradual withdrawal from research. During the years of World War II, research, even on rare earths, stopped altogether and Rolla started to undertake historical work such as the history of Italian forerunners in the field of thermodynamics. Subsequently he published the obituary of Walther Nernst and substantial literature designed to make known innovative texts in atomic physics to an audience of chemists. In this regard we need only to mention Rolla's reviews of: "Fundamentals of Atomic Mechanics" by Enrico Persico (1900–69), "The Atomic Nucleus" by Franco Rasetti (1901–2001), "Alchemy in Our Time" by Ginestra Amaldi (1911–94) and Laura Fermi (1907–77) [167, 168]

In the summer of 1941, a long period of waiting began for Rolla as he was shuffled among those offices, ministries, universities, and authoritative colleagues that were supposed to facilitate his election, in a few months, as an active member of the Academy of XL. On 20 October, elector-members were convened; then on 24 November voting took place: Rolla was the first to become elected. But then the engines of bureaucracy began to grind: on 16 December, the Minister Giuseppe Bottai (1895–1959) submitted to King Vittorio Emanuele III (1869–1947) the voting results; on 23 December, the Ministry of National Education accepted the royal directives and only on 30 December were the results communicated to interested parties. Even more complex and paradoxical was the affair relating to the swearing in of the newly-elected. There was a frantic exchange of letters, notes, and telegrams among the Ministry, the Academy and the person concerned: would Rolla have to swear an oath to the regime? Eventually the Ministry proposed an exemption based on the fact that Rolla had already sworn his allegiance as an Aggregate Member of the Royal Academy of Italy. In August of the same year, Rolla sent a letter to a friend expressing his resentment at what he termed "academic games" by alluding to a late 19th century French comedy: "*Le Monde où l'on s'ennuie*" [169].

Early in 1943, George De Hevesy (1885–1966) was nominated for the Nobel Prize by Luigi Rolla, the only nomination received by the Nobel Foundation that year. When, in 1945 the Nobel Commission awarded the prize retroactively (due to World War II), it was based on the only nomination that De Hevesy had received in 1943, that is, Rolla's.

Life in Genoa grew more difficult for Rolla: beginning in January 1944, the city experienced increased bombing raids by the Allied Forces, so much so that by late spring, they occurred almost daily. It was during this tragic period that on 15 April Rolla's brother, Carlo, a surgeon, passed away, almost 66 years old. Finally, in

1947, Rolla was elected a full member of the resurrected [170]. Accademia dei Lincei. Although he had achieved very prestigious honors, he never felt fully gratified and in fact on 23 May 1950 he wrote regretfully to his friend and colleague Domenico Marotta (1886–1974), President of the Academy of XL [171]: "Dear friend […] it is not worth-while making the effort to show myself off. […] Being sparing of words means indifference and I must confess to being indifferent because I am old and world-weary."

On 1 January 1948, Rolla's older brother (by 10 years), a lawyer, passed away. In the same year, a communication from the IUPAC Inorganic Chemistry Nomenclature Committee served to open an old wound [172]. W. Conard Fernelius (1905–86), Chair of the Committee, and Charles Coryell of the Massachusetts Institute of Technology consulted Rolla regarding the tricky issue of naming element 61. This query was not an obligatory act of courtesy but a clumsy attempt to neutralize the interference of another "discoverer," B. Smith Hopkins. A year before, the actual discoverers, Marinsky, Glendenin, and Coryell on one hand, and the physicists Marion L. Pool (1900–82) and Lawrence Larkin Quill (1901–89) on the other, had submitted a series of proposals on how to name it.

In years past, back in Florence, Rolla had recognized his error in claiming discovery of element 61, which he had named *florentium*, but his rival, Hopkins did not do likewise for "his" *illinium*, forcing the nomenclature commission to defer its official naming for another year. Rolla remained quite bitter about this awkward attempt to involve him at the international level, and on 22 April 1949 on the occasion of a meeting of the Italian Chemical Society he stated clearly to those present that he had decided to abstain from any kind of interference or involvement. His speech was received with a burst of applause, but it did not succeed in hiding his profound dismay and pain for having to relive the frustrating incident of 20 years before.

Luigi Rolla was a man of profound intellect and full of ideas, but he was also poisoned by his belief that he was being persecuted due to jealousy regarding his genius: he was constantly bringing up his failures, never managing to separate himself from them. And also even when his numerous students periodically demonstrated their great affection for him, in halls of universities within half of Italy, he was spoken of as a person of "woeful talent." The major part of his work (on element 61) was laughed at as a bungled mess and he was condemned to the fierce silence that befits a nonentity.

Almost 100 years after the fleeting triumph of *florentium*, there are still historians of science interpreting the dreams and secrets of this baffling scientist. No one has ever considered Rolla as great, yet when we talk of element 61, his name is mentioned more than its actual discoverers. On another level, his close contacts, both culturally and politically, with fascism, led to a rapid eclipsing of his figure both as a person and as a scientist. At the end of World War II, the Italian chemical industry experienced a period of intellectual stagnation due to its isolation and, before that, to war's ravages; this depression was balanced, where possible, with valuable input of new ideas and therefore precluded Rolla, who by then was considered "over the hill." After the *florentium* debacle, the vast horizon of chemistry-related activity suddenly, for Rolla, became an unreachable, empty dream.

Some years later, at Genoa, a jubilee celebration was organized to recognize Rolla's 75th birthday. Two hundred of his former students and followers participated. This event was poignant because it followed in the spirit of the organizers of that long-ago occasion (1922) when Rolla invited his students and assistants for a friendly convivial meeting on a hillside above Florence. To celebrate the jubilee, a gold medal was struck bearing on one face the effigy of Saint John the Baptist, patron saint of both the cities of Genoa and Florence, and on the other face, the inscription enclosed within a laurel wreath that read: "To Luigi Rolla master of science, of life, on his 75th birthday. From his students. 21 May 1957" [173]. While this initiative touched "the person" very deeply, for "the scientist," it did not dispel ghosts of the past for long.

Rolla's passing from this world in 1960 was a departure silent and bitter, enclosed within his beloved University of Genoa, surrounded by a bevy of promising young people who would eventually become full professors: Giorgio Piccardi (1895–1972), Giovanni Canneri (1897–1964), Luigi Mazza (1898–1978), Aldo Iandelli (1912–2008), Corrado Rossi, Piergiovanni Garoglio (1900–82) and Alberto Malquori. When Rolla died in Genoa, there was great mourning among his many disciples. However modest was the homage conveyed by the international scientific community. Perhaps it was undeserved recompense for a person whose scientific stature was certainly out of the ordinary.

Luigi Rolla led a retired, lonely life in an old mansion in via Pastrengo, in Genoa's center, now too large for him and his devoted sister Teresa (1884–1975), his lifetime companion. They were the only ones left of a brood of six children, the only Rollas to whom was granted a serene, lengthy old age. When Luigi Rolla was 78 years old, he had a premonition of his death. He begged his nurse to call his sister for a final farewell. As one of his disciples, Professor Luigi Mazza, reported: "Luigi Rolla died on 8 November after a brief but virulent illness […] his desire was for the news of his death to reach his academic colleagues after his burial occurred [174]." As unique and inherently sad circumstance would have it, Luigi Rolla's death on 28 March 1975 marked the extinction of the large Rolla family. None of his father's four brothers married or had children and the same fate happened to his six children, among whom were included the chemist Luigi and his devoted sister Teresa.

Much has been written of Rolla's faithful disciple, Giorgio Piccardi, in some respects a controversial scientist and nonconformist professor ostracized by the official Science community. He was a character in some ways the polar opposite of the master, but the fundamental flavor of his work was optimism. Rolla's exquisite work, a prototype of sound and orthodox research, more or less flowing from technology, was always on the verge of turning into a nightmare, undermined on the one hand by his connivance with the fascist dictatorship, and on the other by the horror of the internationally-derided fiasco of *florentium*. If Piccardi, his successor in Florence maintained, despite the misfortune of his research, an invulnerable innocence, Luigi Rolla was a man who strove, with no chance of success, to regain academic dignity and independence that was sacrificed to the politics of the regime. Another probable reason for Rolla's descent into oblivion is that he was, perhaps, a physicist within a community of chemists who never understood him; but what was, perhaps, unforgivable was that he never neglected an occasion to point out their differences and, once he retired, recollections of him also vanished. Rolla deserved to be remembered as one of those scientists or technologists, who rose above criticism, even that of historians, because their deeds are ever before our eyes, compelling and consistent, but with Rolla, this was not to be.

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Chemistry Meeting convened in his native place and mindful of his imperishable work with earnest resolve placed this plaque at the house of his birth, 22 June 1968." Friuli, located in extreme northeast Italy, is an historic region with its own cultural identity and language. Udine is its principal city

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124. Tuscan oncologist noted for having studied immune mechanisms implicated in the pathogenesis, diagnosis, and therapy of infectious and neoplastic diseases. He was certainly one of the first to assert that pellagra was caused by a diet deficiency. He was President of the National Tumor Institute from 1935-56
125. The reason for awarding the 2014 Nobel prize for physics could be distilled into a simple two-word Latin motto, PLUS LUCIS. These two words summarize and celebrate Isamu Akasaki (b. 1929), Hiroshi Amano (b. 1960) and Shuji Nakamura (b. 1954), the three Japanese scientists who developed blue LEDs, an essential component of most modern lighting systems, portable flashlights, and Christmas tree lights, not to mention the latest generation of television screens. Their work, which was carried on in the 1990s, revolutionized lighting technology. With a blue LED you can have white light sources which are much more efficient and economical than are incandescent and neon lamps
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127. The authors would like to thank Prof. Seth C. Rasmussen for allowing us to examine the manuscript of his in-depth history of the pyrrole blacks while it was still in press
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Chapter 5

Chemists in the Royal University of Florence Era (1924–46)

Following a series of reforms in the Italian educational system in 1923, the Institute of Higher Practical Studies and Specialization was transformed, at the end of 1924, into the Royal University of Florence. The purpose of the reforms was to gradually reduce the number of Italian universities, with the unhappy but foreseeable suppression of private institutions, and to establish a state-supported university in every political region of the country. For Tuscany, the government's choice was Pisa, where the university had been transferred in the time of Lorenzo the Magnificent (1449–92). The inclusion of a secondary university at Florence was the result of an energetic, almost desperate effort by many members of the ruling classes and the local cultural scene. The state budget was still high at 2.4 million lire; the City added 950,000 lire, the Province 475,000, the neighboring towns a total of 70,000, the Savings Bank and the Chamber of Commerce both donated 500,000 and 25,000 respectively as one-time contributions. The total subvention came to 4.5 million lire, including private donations.

In addition to political problems at the national level, which greatly limited the University's growth, the cultural domination of Florence over the other university cities of Tuscany, and in particular of Pisa, was not facilitated by certain subsequent events: the political focus was shifted more toward the south, while big industry centers moved northward. Tuscany saw itself in retreat, as it were, with the prospect of the flight of industrial enterprises and, concurrently, its progressive loss of clout in national politics. If, in addition to all this, we consider the concomitant bankruptcy of the city of Florence, it is understandable how the city and its university showed signs of a strong setback. Although it apparently survived without major trauma, it focused immediate attention upon what was already an emerging situation: a disenchanted resignation to the transfer of the capital to Rome and a profound economic transformation of Italy that relegated Florence and its university to roles always less influential on the national scene.

Particularly evident, of course, were the obligations imposed by the state system, primarily regarding tax deductions. After annexation of the Grand Duchy, many Florentines felt downgraded from their status of "citizens" to that of mere

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"taxpayers." This feeling was accompanied by a marked aversion to the national university system established by the 1922 reform, which was considered not only responsible for the weakening of Italian scientific and technological prowess and the consequent loss of a competitive edge worldwide, but also of the privileged place of the corporate interests of scholars and men of law, pursued at the expense of science activity. It was in this somewhat gloomy academic atmosphere that the scientists discussed below lived and worked.

5.1 Mario Torquato Passerini (1891–1962)

The Passerini synthesis is one of the oldest and most important multicomponent reactions (chronologically preceded by the reaction of Biginelli [1] and followed by the equally well-known Ugi four-component condensation reaction [2], currently widely studied for its originality in terms of application and mechanism). Surprisingly, little information is available regarding its discoverer, the Florentine chemist Mario Passerini. The reasons for the lack of a biography of this scientist can be traced, in part, to Passerini's reserved nature, reserved to the point of erroneously being perceived as "shadowy."

This complexity of things, combined with a research area low in popularity and of no apparent use in biochemical or synthetic chemistry, led to Passerini's slide into oblivion. Taking advantage of the original documentation recovered in the university archives and of material kindly provided by his family, it is finally possible to present a biographical sketch of this outstanding chemist within the context of contemporary chemical research.

5.1.1 Heir of a Chivalric Family with Scientific Traditions

Mario Torquato Passerini was born on 29 August 1891 in the municipality of Casellina and Torri, presently, Scandicci, a huge Florentine suburb. He was the third son of the five children of Count Napoleone Pio Passerini (1862–1951) and his first wife, Vittoria Matilde Ghetti (1865–1908). Napoleone Passerini was the only son of the wealthy Count Pietro da Cortona Passerini, a relative of the famous Cardinal Silvio Passerini (1469–1529), a patron of the Renaissance in Florence.

Mario's father was not only of noble lineage but an agronomist famous and celebrated for selecting for his farms the "Chianina" breed, an Italian line of cattle, formerly used as draft animals, but now raised mainly for meat production. ("Bistecca alla fiorentina", or "beefsteak Florentine style," consists of a T-bone traditionally sourced from Chianina.)

Napoleone Pio spent almost all of his long life on his estate near Florence, where he created the very first Italian Technical Institute of Agriculture (1884). In addition to science, he indulged in his two other great passions: hunting and fishing. Only in 1923, when he was almost 60 years old, Napoleone Pio was appointed professor of Agronomy and Agriculture at the University of Pisa. Rarely has a scholar showed so much versatility, certainly helped by possessing an immense fortune as well as great talent: he created a school, an experimental farm, a chemical laboratory, a seismographic and meteorological observatory, and an impressive public library. Many of these scientific interests were transmitted to his son Mario Torquato.

Napoleone Pio Passerini also passed on to his children Onorina, Lina, Gino, Mario, and Lapo a great love for art, literature, music, and above all, for science. His elder son, Gino Passerini (1889–1961), became a distinguished professor of Hydraulics, son Mario was a professor of Chemistry, while Napoleone Pio's youngest son, Lapo Passerini (1900–66), earned a doctorate at the University of Florence.

Mario Passerini attended secondary school in Scandicci before going on to pursue the study of mathematics and physics at the Institution of Higher Practical Studies and Specialization in Florence. His studies were interrupted by World War I's outbreak, when he was commissioned into the Italian Defense Health Service. After brief service in the Alps, Mario Torquato graduated in Chemistry and Pharmacy, receiving his license in late 1916. In 1919 he received the Cross of Merit; he resigned his commission as lieutenant in 1920. In the late 1920s he married Natalia Sanguinetti (1898–1976), one of the first Italian women to graduate in pharmacy. The couple had one son.

5.1.2 The Passerini Reaction

Almost certainly, the most famous of Passerini's discoveries was the generalization of the simple reaction for characterization of a newly synthesized product, *para*-isocyanide-azobenzene. This experiment came about almost by accident in 1921, when he was not yet in his 30s [3]. The "generalization" of this reaction was not correctly interpreted immediately; it took several years before Passerini correctly recognized its specificity [4].

In 1921, he published his first paper on what would later be called the "Passerini reaction." This three-component reaction, a carboxylic acid, a carbonyl compound (such as a ketone or an aldehyde) and isocyanides, opened the way for direct synthesis of hydroxylated carboxamide.

The Passerini reaction followed the reaction of Pietro Biginelli (1860–1937) who, in 1891, proposed the "revolutionary" idea of a multi-component reaction [5–8].

A few months after announcement of the discovery, Passerini sent a second note to the Italian Chemical Society, concerning this multi-component reaction. To ensure that the above-mentioned reaction could be regarded as a general reaction, he repeated it with different isocyanides and ketones. Surprisingly, the product he obtained always involved the addition of three molecules: an isocyanide (R–NC), a ketone, and an organic acid.

Subsequently Passerini tried to determine the reaction mechanism for this new type of reaction. At first, he proposed a trimolecular process but, shortly afterward, he was inclined to propose a different mechanism, more consistent with traditional rules of organic chemistry. This mechanism would have proceeded through a non-isolable intermediate, generated by addition of the ketone to the acid, which would have, finally, reacted with isocyanides.

It is evident, reading Passerini's articles, how he from the very first suspected and hoped that his reaction could be a general multi-component reaction.

It was only two years later that Passerini had an opportunity to return to this, his work; he published two additional notes, more extensive and containing more details. He added, however, very little novel material: he noted that the subclass of cyclic ketones were well-suited for multi-component reactions. His fourth and final note on the Passerini reaction was published in March 1924 [9]. In this work, Passerini unequivocally demonstrated that "his reaction" was a general reaction involving isocyanides, and aromatic aldehydes or ketones, in the presence of organic acids. Passerini regretted that, still examining the reaction mechanism, based on intermediate formation, he had failed to isolate it, although he referred to unspecified chemical and physical experiments by which he hoped "to ascertain its existence."

Two additional papers completed the work, but played down the discovery: two substances, such as camphor and santonin, despite possessing a ketonic functional group, did not react with isocyanides. In an appendix to his last paper, he demonstrated that halogenated ketones were able to react with isocyanides; the reaction took place either by using simultaneously a mixture of aldehydes and ketones, or a mixture of organic acids [10, 11].

This organic reaction is the first multi-component reaction based on isocyanides; it currently plays a central role in combinatorial chemistry. Recently S. E. Denmark and Y. Fans have developed an enantioselective catalyst for asymmetric Passerini reactions, whose reaction mechanism is not well understood even to this day [12].

Two different reaction pathways have been hypothesized for the Passerini reaction: the first one is supposed to be ionic (Fig. 5.1); the second one, concerted (Fig. 5.2). In polar solvents such as methanol or water, the reaction proceeds by protonation of the carbonyl followed by nucleophilic addition of the isocyanide to produce the nitrilium ion, **3** (below). Addition of a carboxylate gives the intermediate, **4**. Acyl group transfer and amide tautomerization yield the desired ester, **5**.

In non-polar solvents and at high concentration, a concerted mechanism is hypothesized [13]. This mechanism involves a tri-molecular reaction among the isocyanide, the carboxylic acid, and the carbonyl in a sequence of nucleophilic additions. The transition state (below) is depicted as a 5-membered ring with partial covalent or double bonding. The second step of the Passerini reaction is an acyl transfer to the neighboring hydroxyl group, **2**. There is support for this proposed

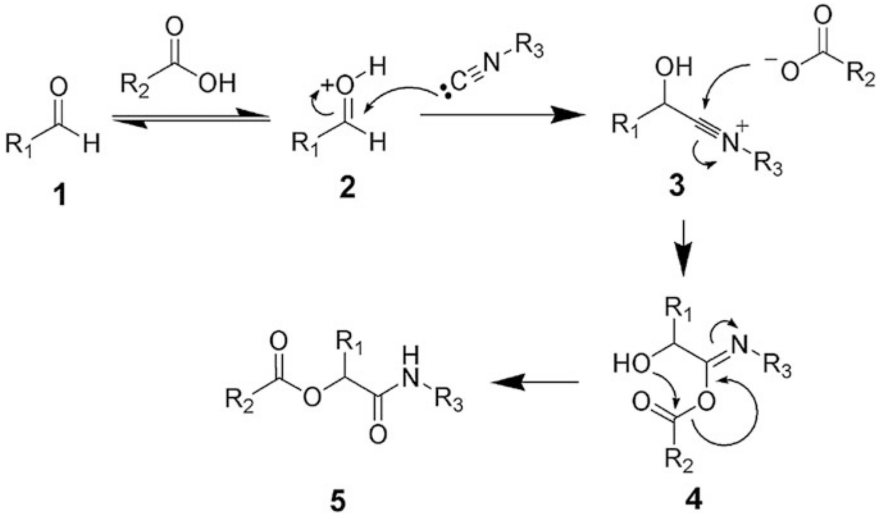

Fig. 5.1 Passerini reaction, ionic mechanism

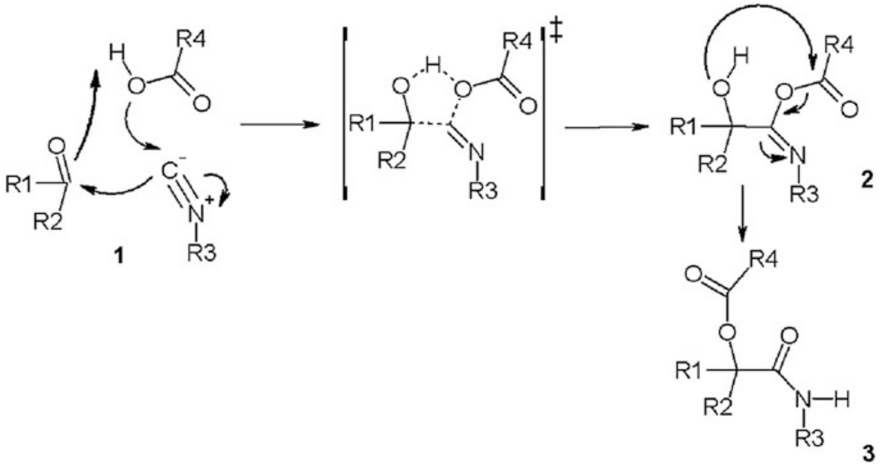

Fig. 5.2 Passerini reaction: concerted mechanism

reaction mechanism: the reaction proceeds in relatively non-polar solvents (in line with the transition state) and its reaction kinetics depend on all three reactants. Nowadays it is thought that the Passerini reaction does not follow an ionic pathway, as was assumed by its discoverer.

The renewed popularity of the Passerini multicomponent reaction is due to its application in the preparation of polymers from renewable materials and peptidomimetics [14–17].

5.1.3 Academic Career

In October 1916, Guido Pellizzari became director of the Pharmaceutical Laboratories at the Institution of Higher Practical Studies and Specialization of Florence; Passerini joined him there several years later. Passerini graduated in 1916, and was enrolled in 1920 as a Doctor of Philosophy student. His scholarship expired in 1924; the Chairman of the Advisory Council of the Institute arranged for him to become Pellizzari's research assistant. In this role, Passerini helped him mentor selected Ph.D. students.

In 1930 Mario Passerini became professor of Medicinal Chemistry at the Royal University of Siena. At a relatively advanced age he had a son, Pietro Passerini (1932–2008), destined to become professor of geology at the University of Florence. In 1936, Mario moved back to Florence, as professor of Pharmaceutical Chemistry (Fig. 5.3 was photographed when he was Director of Pharmacy).

From 1937 onward, Passerini was no longer interested in isocyanides and their related reactions. Meanwhile World War II arrived. The racial laws promulgated in Italy, paralleling those of its German ally, created a massive brain drain through flight. The research atmosphere was not what it was in the 1920s. The University of Florence, in a short period of time, lost nearly its entire teaching faculty. Despite the Nazi occupation of Florence, the University of Florence survived World War II

Fig. 5.3 In the first row, on the right, the Director of the School of Pharmacy, Mario Passerini, receives Arrigo Serpieri (1877–1960), Rector of the University of Florence, ca. 1940. Kind gift of the daughter-in-law of Professor Passerini to one of the authors

without major damage, which meant an inestimable start-up advantage later for the city and the University. However World War II brought a long period of stagnation in Passerini's research: scientific papers decreased both in quantity and quality. Passerini decided to change his research interests. He dealt with the characterization of many natural substances found in the leaves of *Olea Europea*, in the *Lygustrum japonicum*, and in flowers of *Helichrysum italicum* [18–20]. These were the subjects of his last publications.

5.1.4 The Later Years

A very reserved individual, sometimes being incorrectly perceived as "shadowy", Mario Passerini always felt strongly regarding his duties and responsibilities as a citizen and university professor: he held several academic and administrative positions with ease and dedication. After his father's death, on 11 May 1951, the challenging task of continuing management of the Agricultural School passed on to him and his siblings, Onorina, Lina, Gino, and Lapo. For this reason, it was impossible to maintain the family villa, including many original furnishings; it was sold and transformed, in recent times, into a large luxury condominium.

Mario Passerini was a heavy smoker, particularly of cigars (sigari Toscani); this unbridled passion led to early-onset health problems. In this regard, some curious and often hilarious stories circulated about his habit. Since he lived in Florence but taught at the University of Siena, he arranged for his classes to meet very early in the morning. He would take the first train to Siena, occupying an empty compartment, and quickly lit up. If a hapless commuter stumbled into his compartment, by now saturated with cigar smoke, the commuter would quickly exit, leaving the great professor in splendid isolation, triumphant in "his kingdom of solitariness and smoke."

He was forced to retire at age 70, but his passion for research, the desire to be close to former colleagues and young people kept him going regularly to the Institute of Pharmacy. He used to move around using a bicycle that he left each morning in the basement near the University Building entrance.

His methodical precision made Passerini's ordinary day quite predictable: at 7 P.M. he went home by bicycle. One evening, he was unaware that the access hutch to the cellar was open and he inadvertently fell down the stairs. It was a serious accident that compromised Passerini's health. He was hospitalized and, contrary to all predictions, after a long period of hospitalization, he seemed to become fully recovered. Unfortunately, nothing might have presaged what would happen shortly thereafter. On 16 November 1962 at the age of 71, Mario Passerini, affected by asymptomatic atherosclerosis, suffered an acute ischemic attack and died at his Florence home.

5.1.5 Conclusion

Passerini's arrival in Florence had been preceded, as described in a previous chapter, by two other famous chemists. Perhaps these two forerunners possessed greater scientific stature, but lacked something in their characters: the first one, Hugo Schiff, was of a sanguine temperament and unfriendly, with a certain level of nastiness that alternated with flashes of rare humanity. Schiff was violent and aggressive toward his students, prone to sudden outbursts of extreme behavior. Angelo Angeli, the other prestigious predecessor, was a true gentleman, meek, lenient with his pupils, but hampered by pathological shyness and reluctance toward public life. The second generation of Florence chemists was represented by Passerini, who embodied a sober, good-natured Florentine of the upper classes. One could claim that he became a chemist by chance or by upbringing; he was certainly talented, but one could easily imagine that, if his childhood had taken a different turn, he could have become a diplomat, a successful businessman, or even a gentleman farmer.

5.2 Giorgio Piccardi (1895–1972)

The words Isaac Newton used to describe his own work are also well suited to the character of Giorgio Piccardi [21]:

> I do not know what I may appear to the world; but to myself I seem to have been only like a boy, playing on the sea-shore, and diverting myself, in now and then finding a smoother pebble, or a prettier shell than ordinary, whilst the great ocean of truth lay all undiscovered before me.

Giorgio Piccardi was, in some respects, an eclectic chemist, since his career embraced many research fields. An intellectually lively personality, he continually found new research areas in all that surrounded him. His mind was a source of new hypotheses and ideas that carried him forward along with many of his colleagues, but Piccardi himself never stopped the process of construction and demolition, demonstrating a critical acumen without rival. His true nature, which was respectful of life but deeply secular and agnostic, could be said to have been equally directed toward all the wonders of Creation.

5.2.1 Early Life

Piccardi was born in Florence on 13 October 1895. In 1913 he enrolled at the Royal Institute of Higher Practical Studies and Specialization, where he began his chemistry study under the guidance of Hugo Schiff (1834–1915). His studies were interrupted by the outbreak of World War I, and not yet twenty, he was drafted and sent to the front as a member of the Alpine Corps. The long years of absence from home and the tragedies of war deeply marked Piccardi's psyche; despite his wartime heroics, which earned him a silver medal for valor and the rank of captain, he was not tormented by the territorial losses that Italy suffered during the war nor was he infected by the more deadly fanaticism of some returned "warriors." His was a quiet heroism.

Piccardi was taken prisoner in 1917 and interned in Hungary. He was not slow to create an escape plan, digging a tunnel under the barracks and hiding excavated material in the attic of the building. After grueling work and some risk of becoming discovered, he managed to escape. Three days after wandering in the Hungarian countryside, Piccardi was recaptured and brought back to the camp. When passing through the gate, a detachment of Hungarian soldiers saluted the colors of the flag, but Piccardi, as he later confessed, thought that they intended to shoot him. Following this escape attempt, he spent several months in a punishment cell.

He returned to Italy in 1919, after nearly losing his life by contracting pleurisy in an Austrian prisoner-of-war camp where he had been transferred. During the last year of the war and the first year of peace, Piccardi could not communicate with his family. The letters they exchanged were never delivered—on either side; this caused his father to believe that he had lost both of his sons in the war. He received news of Giorgio's older brother, Tommaso, who had died at the front—another Piccardi who was awarded a silver medal, but unfortunately posthumously.

To the tragedy of the loss of a brother was added Piccardi's mother's death in 1918 following the pandemic of "Spanish flu," and then the agonizing death of his sister Laura who died of tuberculosis 8 July 1920—the loss of three family members within a short time. After the misfortunes of war, Piccardi tried to resume a normal life; the first sign of his revival was his graduation at Turin in 1921.

Giorgio Piccardi met his future wife, Nella Forti (1900–64), daughter of a wealthy Jewish merchant family, in the summer of 1921 during a trip to the mountains. At that time Nella was one of only two women members of the CAI [22]. According to a later recollection of one of their daughters, Nella was brash and impulsive, and sometimes reckless, characteristics that attracted the young Giorgio Piccardi who was by nature very different. Like Giorgio, his future wife loved horseback riding, playing tennis, swimming, and painting. Nella Forti was an active person, a lover of the outdoors, an expert rock climber, with great fondness for hiking in the mountains. In Giorgio's company, climbing in the Dolomite Alps was opened to her. With respect to riding, she considered it old-fashioned for a woman of the 20th Century to ride sidesaddle. Since the old tailor specializing in riding clothes refused to sew a pair of pants for her out of extreme shyness in taking a woman's measurements, Nella bought a pair of military pants and puttees, and with this outfit rode around, causing more than a little stir. The young couple was married in 1922, and in 1923 they were blessed by the arrival of their first baby, Oretta. On 4 August 1924, Maria Stella was born and less than two years later, on 6 May 1926, the youngest, Anna, arrived. Giorgio often said that he would liked to have had at least one boy to whom to pass on a great passion for sports, sailing, and mountaineering. After the birth of their third daughter, Giorgio decided to give up and began to give their daughters a boy's typical playthings: Erector sets, pedal cars, and more.

Meanwhile, Nella Piccardi created in her house in Borgo Pinti a veritable cultural circle. In addition to her close family circle it was not uncommon that personages like the painters Renato Guttuso (1912–87), Onofrio Martinelli (1900–66) and Giorgio de Chirico (1888–1978), or the writer Arturo Loria (1902–57), or the physician and partisan Aldo Cucchi (1911–83), as well as her musician uncles such as composer Mario Castelnuovo-Tedesco (1895–1968) and the teacher Ferdinando Liuzzi (1884–1940) appeared on the scene. Another character in Piccardi's extended family was the chemist Luigi Rolla, Giorgio's future director. Having no family, Rolla would frequently "camp out" in the Piccardi home. The Piccardi daughters remembered him as a "kind-of uncle" or, sometimes, as a type of grandfather. Giorgio and Nella did not remain married for long due to their diverse characters and antithetical interests. By 1938, the couple had already formally separated; Giorgio set up house in Genoa, the city in which he had been awarded the first chair of physical chemistry in Italy.

5.2.2 *The Career of an "Unfortunate" Scientist*

Giorgio Piccardi's scientific research extended for a period of about fifty years, and ended the year of his death in 1972. His career can be divided into two major parts. The first part comprises his physical chemistry research which continued until about 1940; the second period can be described as research on the influence of environmental variables on non-traditional systems of chemical, physical and biological evolution, which fall outside of thermodynamic equilibrium. Of this last period, which continued for three decades, much has been written, both good and bad, while very little has been said about his research in physical chemistry. It is for this reason that the present book seeks to redress this lack of homogeneity in the study of the work of Professor Piccardi, recalling his valuable initial work in physical chemistry.

After his brief interlude at Turin [23]. Piccardi returned to Florence and, with Luigi Rolla's guidance, he worked as a volunteer assistant, engaging in his first research projects; among them was the fractionation of rare-earth minerals in search of element 61. To move this immense undertaking forward, Piccardi became one of the first Italian chemical spectroscopists. Although he was only one of Rolla's many students, he was not the most popular nor a primary beneficiary of what such an opportunity could offer. Before Piccardi's arrival, Rolla had designated the young Lorenzo Fernandes, co-discoverer of *florentium*, as his primary assistant, but after the tragic outcome of this false discovery and Fernandes' summary dismissal, Rolla still seemed to ignorePiccardi, favoring instead, Giovanni Canneri (1897–1964).

Piccardi's initial research projects extended over a period of time as he searched for a promising new line of investigation, substantially independent of Rolla's influence. He concentrated his efforts on finding an innovative method to investigate homogeneous gaseous systems that differed from those classically based on conductivity. There were few jobs available in the early 1920s and Piccardi's proved to be a dead end, or at least not full of discoveries as he had expected. So he embarked upon a far-reaching commitment divided into three major lines of investigation: static chemical electrical phenomena, ionization potentials, and electron affinity, plus many spectroscopic investigations.

The results furnished evidence of Piccardi's delicate research capabilities. The upshot was that he and Rolla established some relationships between the general experimental data pertaining to ionization potentials, atomic structure, chemical nature, and the periodic system. The next step was to measure directly the electron affinity of atoms and neutral molecules. Pursuing their investigation of the entire periodic system, it did not take long for these two chemists to note the special character of the rare-earths.

Determining the ionization potentials of some rare-earth elements marked the start of a very original line of work, and Piccardi's first encounter with that family of elements that would persist for almost twenty years. Shortly afterward, he pursued another investigation, one related to chemical problems associated with astrophysics: the chemical composition of heavenly bodies. He studied red stars, comets, planets, and sun spots, observing saturated and unsaturated organic molecules, absolutely exceptional work given their location in outer space. Piccardi, beyond dwelling on methods of spectroscopic investigation, seemed to focus on the importance of his findings as confirming that the laws of chemistry and physics applied throughout the entire universe [24].

Another large group of investigations, about a dozen, included special analytical research and new analytical methods of the rare-earths, based on an organized study of molecular spectra, nearly a complement to his earlier work in chemistry at high temperatures. A simple theoretical insight, not entirely original, which flows from this research is explaining from electronic considerations differences in spectrographic sensitivity of an isolated element versus one mixed with traces of other elements.

In early 1930, after the stormy departure of Lorenzo Fernandes and his consequent removal from research and characterization of *florentium*, this task was passed on to Piccardi. Piccardi wrote reluctantly of this episode; in his articles he never mentioned the name *florentium*, replacing it with the less compromising name "element 61." There is no doubt that the disappearance of Fernandes first opened the way to the chairmanship for Giovanni Canneri (1897–1964) and, later, for Piccardi. In three years of uninterrupted toil, Piccardi completed an unprecedented quantity of experimental work, using the bromate method, borrowed from American colleagues. Also completed in this "useless race after a ghost," were over 56,000 fractional crystallizations of neodymium-samarium-bearing materials. And 50,000 of the 56,000 fractions were accompanied by spectroscopic, roentgenographic, and color-comparison checks [25].

Fig. 5.4 Giorgio Piccardi photographed at work in his laboratory during the year of his retirement, 1966. Kind gift of his daughter, Maria Stella, to one of the authors

This ambitious effort, lasting over the entire time that Rolla was at Florence (up to 1935), did not yield the expected results. Piccardi followed his director to his new Genoa headquarters and there, after about five years, he obtained, at the age of 43, the long-awaited position of Professor of Physical Chemistry (Fig. 5.4).

Earlier in his life, Piccardi dabbled in art as well, and one of the products of his efforts was his self-portrait, an image that has never before been published (Fig. 5.5).

During the years that preceded World War II's outbreak, research on *florentium* dwindled to nothing, mainly because when he became a full professor, Piccardi engaged in his own autonomous research projects, dissociating himself from Rolla, a move that he could not have previously afforded to make.

Thanks to Giorgio Piccardi, the study of interfacial systems both in the curriculum and in research, came to be regarded important in the field of physical chemistry. Indeed, he directed his school towards studying interfaces and surface

Fig. 5.5 Giorgio Piccardi, Self-Portrait. Courtesy of the family of Giorgio Piccardi

phenomena and their applications. His patented invention of the double-wire tensiometer for studying liquid-gas interfaces has been a major research instrument in the biological sciences (for example, in studying breast milk).

5.2.3 Fluctuating Phenomena

In the last twenty-five years of his life, Piccardi focused his research on the study of time as an essential coordinate of the dynamics of natural processes. He investigated so-called *fluctuating phenomena*, or, rather, non-inertial evolved processes as subjects influenced by external forces exposed to exchange of energy and/or matter. Among these agents, he considered terrestrial, solar, and cosmic variables. He studied several chemical reactions in aqueous solution (the hydrolysis of bismuth chloride, which in water yields a semi-dispersed precipitate, BiOCl) and observed the phenomenon of water's *activation* when it is subjected to the action of long-wave electromagnetic fields. Piccardi noted that the time factor is not homogenous in each successive instant. He hypothesized the existence of not-perfectly-reproducible phenomena which merited scientific study. These were phenomena or processes that involve the action of low-frequencies and very small energies, which are usually regarded as insignificant since they produce very small effects. Time, as a succession of equivalent instants, constitutes basic dogma of mechanistic science. However, nature does not follow these canons. To reaffirm his hypothesis, Piccardi wrote [26]:

> Not being able to reproduce the condition in which a test is carried out, there is the problem of recording the instant and period of time in which the experiment is carried out. One hour is not identical to another one precisely because phenomena are fluctuating. The date and hour characterize a physical situation which changes over the course of time. Time in chemistry, biology, and perhaps psychology and sociology, is not only a duration but a coordinate. Some objects are sensitive to these spatial actions and others are insensitive, and among the latter are aqueous systems and colloidal systems in particular.

From Piccardi's observations, the realization emerged that sun spots and associated phenomena have an influence upon chemical reactions [16]. One of the most important factors is the annual cycle linked to variations in the position and velocity of Earth in its helicoidal movement with respect to the galaxy, due to the combination of the elliptical movement of Earth with the rectilinear one of translation of the sun toward the constellation Hercules. In March, when Earth is on the equatorial plane and its velocity is at a maximum, the coagulation of bismuth salt is (on average) low, while it is high in September when the movement of our planet is perpendicular to the equatorial plane and Earth's velocity is at a minimum [27].

5.2.4 After the War

Giorgio Piccardi's father, Ludovico, widowed toward the end of WWI, returned to live alone in his large Villa di Capalle, near Florence. In his late old age, he moved in with his younger son, Giacomo (1901–75), father of Giovanni Piccardi (b. 1929), a well-known analytical chemist at the University of Florence. Ludovico died at almost 82 years of age on 13 September 1944.

The changing conditions following the outbreak of WWII obliged Giorgio Piccardi to return to Tuscany where he pursued his research at a war-torn university with a temporary appointment. After the war, in the academic year 1946–47, he was called to become chair of physical chemistry at the Faculty of Natural Sciences, Mathematics, and Physics at the University, a position that he occupied until 1965.

At the time of his appointment, he experienced the joy of becoming a grandfather: his first grandchild, Olimpia, was born at the close of 1946. She subsequently became a well-known actress and director of the San Remo Festival. The happiness of the large family—comprised of daughters, sons-in-law, and, by this time grandchildren—was dimmed in 1964 with the death of the matriarch, Nella Forti. She died in Rome, after months of struggle and suffering, from a malignant tumor. In the following year, Giorgio, having reached mandatory retirement age, left the direction of the Institute of Physical Chemistry, but that step did not bring an end to his research. He rented two rooms in the Palazzo Capponi in Florence where he conducted his investigations for another seven years.

In the spring of 1972, Piccardi, gravely ill from cancer, departed Florence and moved in with his oldest daughter, Oretta; when his condition worsened, he transferred to the nursing home run by his son-in-law. However, even from his hospital bed he dictated papers to be published, made corrections to galley sheets, and continued producing scientific communications that someone else would read in his place at international meetings. He was an active scientist right to the very end of his days. He died on the night following the winter solstice of 1972, two months after turning 77.

Piccardi, described in the literature as "Master of the Sun," [28] was understanding, friendly, and quiet, but he was also decisive and determined. He was an affectionate, generous father of three daughters, whom he cared for and loved. His role as "maestro" for his students, collaborators, and family was constant, helpful, and unforgettable. His activities were not limited to chemistry, but also to many other pursuits such as sailing, astronomy, and painting. Piccardi, with his two decades of work at Florence, opened up an innovative pathway into science, but after his death the research was carried on predominantly abroad. Only recently, have some working groups in Italy made progress, and, in August 2002, the "Laboratorio Biometeorologico Giorgio Piccardi" was inaugurated in Filignano di Isernia (Molise) [29].

In a certain sense he changed the way scientists think about their discipline: he was a forerunner of interdisciplinary science and pioneered new pathways that many of his colleagues did not follow or simply did not understand. Now, after these many years, it can be said that what Piccardi accomplished was not in vain because his work and ideas have not been lost but continue to live on.

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Chapter 6
Chemists in the Period of the University of Florence (1946–Present)

Having reached the start of the sixth chapter, we provide a useful gloss to underscore the intellectual honesty owed to those readers who are less knowledgable of the subject at hand. We are aware that, in presenting this chapter, encompassing the contemporary scene at the Department of Chemistry of the University of Florence, we may highlight certain facets of the story regarded by some as unimportant, or we may pass over certain episodes where a further story needed to be told. However, we believe it necessary not to wait for the material addressed to settle down, while real lives remain in motion—we hope that we made the correct editorial choices and decisions.

Returning then to the narrative, we can certainly assert that the terrible cost in human lives and material goods due to World War II, caused by heavy Allied bombing and the movement of the front in August 1944, affected the University of Florence far more deeply than did World War I.

On Saturday, 25 September 1943, Florence experienced its first air raid. At the beginning of the war it had been declared an "open city" because it did not contain any war industries nor did it serve as a nerve center for the fascist armies, so it was considered unnecessary to deploy any anti-aircraft defenses. Therefore, Allied bombing took Florence by surprise; in official reports of the defense, it did not seem to be among the main military targets. By the time the attack was over, 225 civilians were dead, and an unknown number were injured. On that occasion the senior lawyer, Cesare Merci (1853–1943), the last of the Superintendents of the Institute of Higher Practical Studies and Specialization, also perished. In subsequent years, the low level of material goods and the lack of clout reflected by the presence of only one tenured chemistry professor, posed an insurmountable obstacle because chemistry in Florence could once again have assumed a role, if not the primary role, at least a central one, within the national scene.

The fall of the Fascist Regime seemed to open up certain new career opportunities for those persons who had long bided their time in the shadow of influential fascists. Commissions for the purge of Italian fascists from the university system arose in the midst of very strenuous resistance by and large by men who were compromised by

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cooperation with a 20-year fascist regime. The commissions acted with integrity despite attempts at certain forms of bribery. For example, some fascist professors promised to support and use their influence on behalf of young communist or liberal assistants in order to make their advancement easier—all they had to do was declare that these “former Fascists”—the bosses during the Fascist era—were forced to do what they did, even to the point of perjury, but in reality, they were not dedicated Fascists at all. They even dealt leniently with dissidents and Jews.

Returning to the local level, subsequent decades, despite growing numbers of new professorships and the flourishing of new learning, Florence suffered a heavy setback in the 1940s: the ruling class grew during the Fascist period, a period in some ways of cultural stagnation, and this growth did not favor the scientific training of those intending to become teachers; unlike their masters who had specialized in foreign universities, many Florentine academics after World War II had been trained strictly in isolation and with very little capacity for interaction and cooperation with high caliber foreign colleagues.

Finally, the rigidity of the university’s internal structure, often a familiar phenomenon elsewhere as well, constituted an element of extreme weakness.

6.1 Giovanni Speroni (1910–1984)

Giovanni Speroni, was born in 1910; he graduated from the University of Florence in 1932 with his thesis mentored by A. Raul Poggi (1899–1961) on synthesis of organic derivatives of selenium, a subject to which Speroni devoted himself over subsequent years. In 1933 he completed a second degree in pharmacy.

Speroni was a young assistant in 1937 when Adolfo Quilico (1902–82) was called to become the Chemistry chair at the University of Florence: the influence of this new master led Speroni to enter the field of isoxazole research, an area in which Quilico led an established research group in Milan since 1929. Reactions of nitric acid with acetylene and other organic compounds lead to products from which were isolated various isoxazole derivatives with the 3-position free. This observation suggested that fulminic acid (HCNO) could be a key intermediate in these reactions. Quilico and Speroni verified, in fact, the formation of isoxazole derivatives in the reaction between acetylene and fulminic acid by this mechanism. Although acetone was present as a solvent, it was also involved in the reaction. This result was encouraging [1]. Similar considerations were also true for benzonitrile oxide (C_6H_5-CNO), an aromatic analog of fulminic acid: the presence of diphenylfuroxan, the dimer of benzonitrile oxide, was identified as a byproduct in the synthesis of isoxazole derivatives from benzohydroxamic acid chloride and sodium enolates. This suggested the possibility that benzonitrile oxide was the reaction intermediate. Indeed, the same reactions with the use of benzonitrile oxide in place of benzohydroxamic acid chloride, yielded the same products. Not only that, Quilico’s group found that compounds with carbon-carbon triple bonds reacted with benzonitrile oxide to produce the expected isoxazole derivatives [2].

These methods were referred to as "fulminic syntheses of isoxazoles." It is important to note the similarity of these reactions with those already known: transformation of diazoalkanes to pyrazoles and azides to triazoles. Recognition of these pathways opened the way for the concept of 1,3-dipolar cycloaddition. Speroni also contributed to knowledge of isoxazole chemistry by clarifying the structure of the Betti acids [3, 4] and conducting extensive studies on the physical properties of isoxazole and its derivatives.

Following World War II, Speroni became Giorgio Piccardi's assistant since Quilico, in the meantime, had moved to the University of Milan. In 1948 he resigned as assistant and assumed a reduced teaching load because he was appointed Director of the Center of Studies on Pesticides of the Montecatini Company, located at Signa (near Florence). Speroni presented a review of pesticide chemistry at the 1956 "Chemistry Days" at the Milan Fair. His research produced, among other substances, a pesticide of the thiophosphoric ester family, patented under the name of Rogor: "the active compound is O,O-dimethyl-S-methylcarbamoylmethyldithiophosphate [*sic*] $[(CH_3O)_2PS\text{-}S\text{-}CH_2\text{-}CO\text{-}NH\text{-}CH_3]$. It is a very useful product in the treatment of fruit trees because its strong pesticidal activity is accompanied by low toxicity [5]."

Giovanni Speroni's scientific interests ranged from synthetic organic chemistry to physical properties of organic compounds, to consideration of important structural information obtainable from these studies. These latter studies were so well-known that Speroni was commissioned to write the chapter on "Physical and Chemical Properties of Isoxazole and its Derivatives" in the review on isoxazole chemistry edited by Adolfo Quilico [6]. This chapter collected various properties of isoxazole and its derivatives: density, surface tension, water solubility at various temperatures. Data from these measurements indicated augmented self-association in compounds with the 3-position free. Extensive research was directed to determining the dipole moments of isoxazoles in benzene and, for comparison, in dioxane. Speroni invented and constructed the device to measure dielectric constants, from which the dipole moments of organic substances were obtained.

The dipole moments of isoxazoles with various functional groups are in agreement with the structure assigned to the "Betti acid" and with the properties of isoxazolcarboxylic acids [7, 8].

In systems capable of tautomerism, such as derivatives of isoxazolin-5-one, the UV spectra of those with methyl derivatives corresponding to each of the tautomers in the same solvent can be compared. It is thus possible to assess approximately the degree of equilibrium of the same tautomers in various solvents. This method was subsequently applied by other research groups as well.

When Speroni became a tenured Professor of Organic Chemistry at the University of Naples (1952), he developed a friendship with Salvatore Califano (b. 1931) that would last a lifetime, as well as their fruitful collaborative research on the IR and Raman spectra of isoxazoles and nitriles [9–12].

Speroni was always interested in cultural heritage: as early as the end of the 1930s, he was busily studying Etruscan archaeological artifacts. With gravimetric as well as spectroscopic and polarographic analyses conducted on a bronze vase from Vulci he was able to document the differing chemical compositions of the vessel and its handle, attributing this to the needs of a different production system for the vase's two parts. Using the same methods, he also analyzed various lead objects from Populonia (8–9th centuries BC) held in the collection of the Archaeological Museum of Florence. He found that the lead was 99 % pure but contained impurities of Cu, Bi, Ag and Sn or Sb in some cases, information that could help identify the mineral's provenance [13]. Speroni also studied a large terracotta pot from the same museum and a number of coins from the treasure of Populonia, including the patina with which the coins were covered.

Giovanni Speroni's passion for archaeological artifacts and works of art caused him to react with alarm when the flood that hit Florence and Venice in 1966 submerged part of the artistic heritage collections in both cities. He put his extensive experience at the disposal of the organizations involved in an unprecedented work of recovery. Upon his suggestion, a commercial acrylic resin, Paraloid B 72, was used as a transparent, reversible adhesive for the protection of painted surfaces. Since then, it has become customary to use this material for protecting paintings, including frescoes. Speroni also suggested that all paintings on wood be gathered within in an environment with controlled humidity to make the drying process gradual [14].

Speroni received many medals and awards. Among them are a certificate and a medal awarded by the Minister of Education on the first anniversary of the flood for Speroni's contribution to the recovery of cultural property during an emergency.

Speroni possessed uncommon organizational skills and was capable of forward-looking initiatives. In fact he advocated regular meetings regarding Organic Chemistry, which later became the Congress of the Division of Organic Chemistry of the Italian Chemical Society. He also organized national conferences on pericyclic reactions. It was through his efforts that the University of Florence established centers on the chemistry of heterocyclic compounds and on the conservation and restoration of works of art. In the 1970s, during a delicate period of transition for the university, Speroni made a notable contribution to its management as pro-rector and as Dean of the Faculty of Mathematical, Physical and Natural Sciences. He never shirked from engaging in manual tasks such as carpentry, gardening, and cooking, with excellent results. But among his passions, music occupied a prominent place, perhaps originating from his childhood, since his mother had been a teacher of piano and voice at the Cherubini Conservatory in Florence. When he was asked what music meant to him, he remarked, after a moment's pause: "Music is the most important thing in my life [14]." In fact, many more things were important to Giovanni Speroni. His son, Puccio, said of him [15]:

> I believe that it was important for him to show, if only to himself, that he would have been successful in any field he chose, and even be better than most. He was a formidable carpenter, knew classical music to his fingertips, knew all about wines and vines, had committed to memory almost all of Russian literature, could do bricklaying and plumbing very well, and… was also a great cook.

He wrote the obituary of his mentor, Adolfo Quilico, who died in December 1982 from a malignancy, and only a little more than a year later, after prolonged suffering, Speroni died at his home in Santa Margherita Ligure 14 March 1984.

6.2 Luigi Sacconi (1911–1992)

Luigi Sacconi was born 28 February 1911 in Santa Croce, a town situated between Florence and Pisa. In 1941 he graduated in Pharmacy from the University of Florence, and soon afterward he obtained a position at the University of Parma. In 1942 he moved to Turin where he obtained a second degree, this time in Chemistry. Finally, in 1943, he moved to Florence with the rank of Assistant Professor. He became Professor of Inorganic Chemistry in 1954 at the University of Palermo, where, due to his moral rigor and rigidity in teaching, he became the subject of threats from the local underworld.

In 1960 Sacconi (Fig. 6.1) returned to his Alma Mater to become a member the Faculty of Mathematical, Physical and Natural Sciences. A tireless worker and organizer, he founded the Institute of General and Inorganic Chemistry of the

Fig. 6.1 Luigi Sacconi (third from *right*) with his research group in Berlin, ca. 1975. Gift of Professor Renata Barnini-Bertini

University of Florence and then the Laboratory CNR (National Research Council) “Institute for the Study of Energy and Stereochemistry of Coordination Compounds,” whose scientific development coincided with development of coordination chemistry to which Sacconi greatly contributed by synthesizing a large class of new compounds with unusual geometries [16, 17] and new electronic properties [18]. He was before his time in his use of physical methods in the study of modern chemistry and pursued this track in particular in magnetochemistry [19], in X-ray diffractometry [20], in calorimetry, in visible and IR spectroscopy [21] and nuclear magnetic resonance [22, 23] techniques.

Sacconi created a large, influential school of inorganic chemistry, known and respected both nationally and internationally. He left teaching for reasons of age in 1981; five years later in 1986, Sacconi was appointed Professor Emeritus. In the previous year, he was among the founders of the National Group of History and Fundamentals of Chemistry (GNSFC) at the Academy of Sciences called the “XL.” He actively participated in the first national congress of this new, prestigious body at Turin where he presented an autobiographical memoir entitled “The Chemistry of an Autodidact, or Memoirs of an Irresponsible Person.” This text was to serve as Sacconi’s scientific last will and testament. Not too long afterwards, he suffered a debilitating illness and died on 1 September 1992, at age 81.

6.3 Enzo Ferroni (1921–2007)

Walther Hermann Nernst, the great German scientist, Nobel laureate in Chemistry, and father of the Third Law of Thermodynamics, had two Florentine disciples: Luigi Rolla and Giorgio Piccardi. The latter became professor of physical chemistry at the University of Florence. Piccardi had studied fluctuating phenomena well before Ilya Prigogine (1917–2003). His best disciple, later successor, was Enzo Ferroni who, upon Piccardi’s retirement, was promoted to the Chair of Physical Chemistry at the University of Florence. Ferroni had also served as director of the Department of Chemistry and Professor of Physical Chemistry at the University of Cagliari, Sardinia.

Ferroni was born in Florence on 25 March 1921; during World War II, he studied at the Royal University of Florence where he graduated in chemistry *magna cum laude*. Shortly after the war’s end, he reorganized the laboratories and volunteered as a teacher and instructor. When he was still a student at the University of Florence, he met with the famous chemist Richard Willstätter, a 1915 Nobel laureate. Willstätter, a Jew, was forced to flee Germany in 1939 and enjoyed a period of relative peace in Italy before settling in Switzerland where, in 1942, he died of a heart attack. This elderly German chemist, living in extreme poverty after the Nazis had seized all his property, left a deep impression on the young Ferroni. Thereafter he repeatedly claimed that he learned a lot more talking to Willstätter than he had in an entire college course.

In the years just following the war, Ferroni met Professor Giorgio Piccardi; their friendship grew from their mutual deep interest in science and art in Florence, and was not slow to bloom. It was also during those years that Ferroni moved to Belgium to engage in postdoctoral research. In Brussels, he met and became well-acquainted with Ilya Prigogine (1917–2003) with whom he soon began to share a deep interest in the study of the thermodynamics [24] of surface phenomena [25, 26].

For much of his professional life, Ferroni was a physical chemist, first a Professor at the University of Cagliari (1961–65) and then in Florence (1965–1991). In 1967 he was elected President of the Faculty of Sciences and in 1976 Rector of the University of Florence. Five years after his retirement he became professor emeritus.

However, on Friday 4 November 1966, Ferroni's scientific interests changed drastically: after a month of rain, the Arno river overflowed its banks, flooding the city of Florence, causing untold damage to life, to private property, and to cultural heritage [27]. This event, now known simply as "The Flood," produced, as a result, a revolution in the field of art restoration. No other single event had done as much: a large part of this "revolution" was led by Ferroni, who devoted his efforts and expertise to restoration of paintings and frescoes. Ferroni tested and developed innovative technologies in the field of cultural heritage conservation.

On 10 November 2006, during the "Conservation Legacy of the Flood" Symposium held in Florence at New York University's Villa La Pietra, to commemorate its 40th anniversary, Ferroni's name echoed repeatedly in the conference rooms, along with numerous references to "his method" based on barium sulfate incorporation for consolidation of murals. On that occasion it was said that without his indomitable work, almost half of the frescoes that can now be admired in Florence's museums, frescoes by Cimabue, Fra Angelico and many others, which, in 1966, were covered by mud, polluted water, and oil, would have been lost forever.

Ferroni's enthusiastic interest in chemistry and the arts served as an inspiration to his students. His influence was all the more powerful because he was not only a good chemist, but also a person of wide culture and broad interests. For his meritorious service, in 1967 he received the Gold Medal of the Secretary of Education of the Italian Republic, followed a year later by similar recognition by the Minister of National Education of France, Alain Peyrefitte (1925–99). He received the gold medal from both the Italian Society of Chemical Physics and the Italian Society of Chemistry of the Environment and Cultural Heritage. He was a member of numerous Italian and foreign academies, including the Société Française Chimique, the Georgofili Academy and the New York Academy of Sciences. He was also president of the Academy of Design, founded by Cosimo I de' Medici, Grand Duke of Tuscany, on 13 January 1563.

Ferroni was not only a colloid chemist, and a leader and pioneer of applied sciences for the preservation of cultural heritage [28], but he was also a person with a unified vision of culture. During the three years that he was Rector he did not give up contact with students; he continued to teach physical chemistry. For Ferroni, the primary function of the university was teaching. “The students are my employers,” he often repeated, being capable of making “tongue in cheek” remarks on almost any occasion.

A lesser known aspect of Ferroni’s scientific activity is his work on stable aqueous suspensions of coal powder and polyelectrolytes dispersed in water, such as Kelzan and Taxad [29]. Ferroni successfully employed such suspensions in the industrial sector.

To cite Ferroni’s scientific work would be similar to telling half of a story: he was a man of letters and a man of science, a scholar and a historian. Among his scientific writings appear many chapters of monographs in multi-volume works such as *Enciclopedia della Chimica* [30] and “History of the University of Florence” [31].

He survived his beloved wife Paola—they married in 1946—by about a year. His wife’s death, in fact, caused in him a sudden, and soon fatal, decline in health. Enzo Ferroni died in a Florence hospital on 9 April 2007 at age 86, after several years of suffering. The couple had no children or close relatives, but the memorial service was attended by a host of colleagues and former students—they arrived from all over. He would certainly have called them “family,” or his other “children.” His passing was mourned in Italy and abroad and those who received from Ferroni their first introduction to physical chemistry can certainly be regarded as a fortunate generation of chemists [32].

6.4 Franco Piacenti (1927–2002)

Franco Piacenti was born in Florence on 1 July 1927. He completed his entire course of study in his hometown in 1951, majoring in Chemistry under the guidance of Luigi Sacconi (1911–92). Immediately after graduation, he moved to Milan Polytechnic Institute where his mentor was the future Nobel laureate Giulio Natta (1903–1979). At that time, Natta was conducting research on the polymerization of polypropylene which, in 1963, earned him his Nobel Prize, which he shared with Karl Ziegler (1898–1973), who prepared the catalysts that Natta used in his research [33].

In 1955 Piacenti moved to the University of Pisa where he held the positions of assistant professor and lecturer. In Pisa he was able to work with another great figure of Italian Industrial Chemistry, Professor Piero Pino (1921–1989), helping to rebuild the obsolete chemical laboratories in the Institutes of the University. In 1968, named to occupy the chair of Industrial Organic Chemistry, he moved to the University of Florence where he remained until his death in 2002.

Piacenti’s scientific activity focused on the study of the activation of small molecules such as carbon monoxide and hydrogen, and in particular his attention was dedicated to hydroformylation of olefins, to carbonylation of saturated and unsaturated substrates, and to the hydrogenation of unsaturated substrates [34].

In the hydroformylation of olefins, he studied the mechanism and the industrial applications of the process in collaboration with Montedison SpA. The results of Piacenti's scientific work appeared in prestigious national and international journals, led to the filing of several patents and the conferral of the gold medal of the Division of Industrial Chemistry of the Italian Chemical Society in June 2002, a month before his death.

The Florence flood of 1966 caused a dramatic turning point in Piacenti's scientific career. All of Florence, and particularly chemists, were concerned about the challenge posed by recovery of numerous works of damaged art. Convinced, in fact, that chemistry could make a significant contribution and remediate much of the damage caused by the flood, Piacenti coordinated, together with Professors Giovanni Speroni (1910–1984) and Enzo Ferroni (1921–2007), a research group in this area seeking to furnish a scientific basis for the conservation of cultural heritage artifacts. As a member of the Advisory Board for Chemistry of the Consiglio Nazionale delle Ricerche (CNR) [35], he promoted research in this area. Initially, Piacenti obtained funding to begin research in that field. Soon thereafter, three centers were established to study the causes of deterioration and methods for conservation of works of art; these were based in Milan, Florence and Rome. Piacenti was director of the Center in Florence from its inception in 1974 until 2002, when the three centers were merged into the Institute for the Preservation and Promotion of Cultural Heritage (ICVBC) which, thanks to Piacenti's activities, became based in Florence.

He was the first chairman of the Working Party "Chemistry for the Conservation of Cultural Heritage," which was created in 1987 by the Federation of European Chemical Societies. He was a member of the Scientific Committee of the Project on Cultural Heritage of the CNR and the USA-Italy Workshop "Conservation of Cultural Heritage." He was also responsible for an international research project in collaboration with North Carolina State University on the use of solvents under supercritical conditions.

The activity carried out by the Center for the Study of the Causes of Deterioration and Methods of Conservation of Works of Art, expertly led by Professor Piacenti, resulted in identification of objective parameters for evaluating the conservation status of a work of art, enabling correct scientific interpretation based on strict protocols [36].

Piacenti intuited the possibility of using fluorinated polymers and similar materials for protection of stone substances. His ideas raised the scientific world's consciousness to the need to identify and synthesize targeted products capable of meeting the requirements of use in the field of conservation of cultural heritage. Piacenti introduced the use of fluorinated organic polymers for the protection of monuments of great historical and artistic interest such as the Cathedral of Prato, the Cathedral of Lucca, and the Loggia dei Lanzi in Florence. Piacenti also handed on to his collaborators a model of scientific rigor, critical objectivity, and a passion for preservation of works of art. He also contributed to the education of future researchers by helping to establish a Ph.D. program in Science for Conservation of Cultural Heritage. Piacenti coordinated the formation of the faculty and provided, together with Professor Curzio Cipriani (1927–2007), a substantial contribution to establishing a three-year degree in Technology for the Conservation of Cultural Heritage at the University of Florence. He also provided the stimulus for developing non-destructive analysis techniques including NMR-imaging, in the field of preserving cultural heritage, to evaluate both the effectiveness of water-repellent treatments and the porosity of stone artifacts.

Suffering for some time from incurable cancer, Franco Piacenti died at age 75 on 2 August 2002 [37].

6.5 Ivano Bertini (1940–2012)

For about half a century Ivano Bertini, or "The Professor" as he was known among students, dominated with his stature—both scientific and physical—the landscape of Florentine chemistry. Born on 6 December 1940, he obtained his degree while he was not yet 24, and a position as a lecturer before the age of 29; six years later he became a full Professor. Over the years he received prestigious, well-deserved awards, including honorary degrees from Sweden, Greece, and Italy. A member of the European Academy, as well as of the Accademia dei Lincei, Bertini presided over countless organizations and scientific institutions, but what is even more to his credit is his favorite organization: CERM, namely the Centre for Magnetic Resonance, University of Florence, which he directed until his death.

Ivano Bertini's *curriculum vitae*, his academic awards, and his prodigious list of publications are indeed impressive, and equally impressive was the enthusiasm for research that he, more than anyone else, knew how to transmit to his students, instilling confidence and encouragement to those who elected to undertake research activities.

Bertini strongly believed in the universality of science and in the profound interchange of ideas among scientists worldwide. These ideas, which today are taken for granted, were certainly not the norm in 1968 when, at 28, he travelled to Princeton University to become a research associate. From that experience, he understood the importance of a mutual exchange of ideas among various scientific communities. Named full Professor in 1975, he encouraged his students to go abroad for a postdoctoral appointment, not only to master the language of science but to commit themselves to weave a web of human and scientific relations, establishing the exchange of ideas, ever wider and more fruitful.

He was able to grasp and presciently develop the combination of sciences which, in the 1990s, were quite far apart from one another: bioinorganic science, which later evolved into structural biology, systems biology, and the emerging area of

Fig. 6.2 Ivano Bertini. Courtesy of Professor Renata Barnini-Bertini

metabolomics [38], with nuclear magnetic resonance, a technique carried to its maximum potential worldwide by his enormous, formidable, heterogeneous research group, consisting of many different scientific disciplines and nationalities [39].

Ivano Bertini (Fig. 6.2) did not believe in academic hierarchies, and often treated a student with more respect than someone of his own rank. In a scientific discussion he could also listen to opinions different from his own. It happened sometimes that, without much courtesy, he utterly rejected those ideas with his usual vehemence. If the other party could show the soundness of their reasoning, overcoming the obstacle of Bertini's prickly character, they knew that his remarks would be helpful, and that he was willing to help anyone.

Sometimes it happened that he was perceived as some sort of giant, or so it might appear to an outsider. His colleagues related to him in an almost servile manner, but for younger members of the department, he was regarded as more like an old man, which greatly changed the dynamics of subordination into actually familial bonds of affection. Over the years, in collaboration with equally fine colleagues, Bertini built one of the most renowned magnetic resonance centers in the world as well as, perhaps, a one-of-a-kind biotechnology laboratory with technical expertise in protein expression and production.

In 1994, Bertini's team made a discovery that represented a milestone in their field: they determined for the first time using NMR the structure of a paramagnetic metalloprotein [40], and subsequently many others. In making discoveries of this structural nature, innovations in the field of laboratory protocols and the theory associated with use of paramagnetic constraints in the resolution of biological structures by nuclear magnetic resonance spectrometry were able to help one another [41–44]. Fields such as bioinformatics and genomics, thanks to the research of Bertini's group, entered the domain of chemists' practices. One of his most recent discoveries for which is foreseen considerable development in the coming decades and to which Bertini wanted to dedicate his future research was the individual metabolic fingerprint, envisioned to become a major scientific highway in years to come.

In the field of structural chemistry, perhaps the most prolific and closest to his background as a chemist, Bertini reported the first structure of a paramagnetic protein in the solid state, to which were joined new studies of protein systems of high molecular weight and finally the discovery of sedimentation as method for studying solid state systems unable to crystallize.

Ivano Bertini has enshrined his discoveries and innovations in about 1300 scientific publications of various kinds, a harvest of successes for himself but also for his team, which has been able to work together, both in Europe and abroad, without allowing interference of intellectual or parochial rivalries. As witnessed by the extensive body of scientific literature, Ivano Bertini and his team were able to determine the structure of 150 proteins.

With the work of Enzo Ferroni, Ivano Bertini, Piero Paoletti (b. 1931), Lucia Banci (b. 1954), Claudio Luchinat (b. 1952), Salvatore Califano (b. 1931), V. Schettino (b. 1936), Dante Gatteschi (b. 1945), Roberta Sessoli (b. 1963), Luigi Dei (b. 1956) and many others, it can be claimed that chemistry, in Florence, has lifted up its head and moved beyond its pale, almost ethereal, postwar image and has set its sights on a horizon far broader and more distant than the surrounding Tuscan hills.

Metabolomics, nonlinear spectroscopy and the study of molecular materials with low dimensionality [45], are three lines of research that occupy three distinct chemical centers at the University of Florence. These three centers represent the department's areas of greatest strength. The latter area, on molecular materials, takes pride of place with the important discovery that metal ions coupled in a molecule can act as single-molecule magnets manifesting hysteresis, a phenomenon once thought due only to cooperative effects. The discovery of these superparamagnetic molecules has been a turning point in the study of molecular magnetism and has earned Roberta Sessoli, a lead member of the team, the coveted chemistry prize of the Accademia dei Lincei. This prestigious award was conferred for the first time in 1973. It was actually a continuation of the Royal Prize for Chemistry, awarded every ten years by the Accademia. For Florence's School of Chemistry it was the fourth award since the founding date of its institution in 1879: the first was to Angelo Angeli in 1905; in 1923, Pellizzari won the prize; in 1993 it was Ivano Bertini's turn, and in 2013, the prize was awarded to Roberta Sessoli, who was also the first woman to receive this prestigious award.

Ivano Bertini, did not much like official ceremonies. His status, however, constrained him, from time to time, to accept honors, awards, and prestigious positions. A few were genuinely welcome: the Presidency of the Italian Chemical Society

(1993–1995), the Accademia dei Lincei prize, previously mentioned, and Bertini's election as a member of the Academy of San Miniato Euteleti. This recognition was doubly welcome since Bertini was born in San Miniato and was to occupy the seat that had been filled many years earlier by another famous Florentine chemist, Giacchino Taddei (Sect. 3.3).

Ivano Bertini died in Florence on 7 July 2012 after a brief, unsuccessful battle with cancer. His increasingly debilitating illness did not prevent him from working—albeit with extreme weakness—until the approach of the end, almost proud to appear in public in a state of extreme exhaustion, as evidenced by his last two public appearances in June 2012 on the occasion of the celebration the ten-year FiorGen [46] and the transfer of the gold florin [47] Bertini received from the hands of the mayor of Florence, Matteo Renzi (b. 1975). His name has become a benchmark for excellence in innovative chemical research. In his memory, the Italian Chemical Society established the "Ivano Bertini Gold Medal," an honor awarded to a researcher under age 40 in recognition of particularly significant, innovative contributions in any field of the chemical sciences.

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38. Metabolomics is the systematic study of the "chemical fingerprints" left by specific cellular processes. The metabolome is the collection of all the metabolites of a biological organism, which are the final product or products of metabolic reactions that occur in a body. While the data of proteomic analyses do not explain fully what might happen in a cell, the metabolic profile may provide a snapshot of the physiology of that cell. This analysis allows one to verify

the biochemical status of cellular metabolism and reveal any alterations underlying chronic diseases or even those not yet recognized, identifying not only disease states in themselves, but also pre-pathological stages connected to risk factors of disease outbreaks.

39. Besides CERM, another center of excellence in Europe and part of the University of Florence is the LENS; it is the point of reference for research with light waves based on fundamental multidisciplinary approachs. The LENS, European Laboratory for Nonlinear Spectroscopy, was founded in 1991 by the physical chemist Salvatore Califano and his many collaborators. This center is a place where physicists, chemists, and biologists work "shoulder to shoulder," sharing tools, experiences, research topics, scientific perspectives and ideas with the common goal of using laser light to investigate matter from different viewpoints and under different conditions.
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46. The not-for-profit Pharmacogenomics Foundation, alias FiorGen, promotes applicative studies that aim to exploit structural knowledge of the human genome to: (a) identify more effective therapeutic targets, new disease indicators, and drug responses; (b) develop innovative drug therapies, designed taking into account the genetic diversity in individual patients. Projects initiated and developed by FiorGen are aimed primarily, but not exclusively, at the major disease categories that are causes of death in the population: cancers, cardiovascular diseases, and degenerative diseases of the nervous system.
47. The civic recognition called "The Fiorino d'Oro of the city of Florence," consists in the reproduction of the ancient gold coin called the "Fiorino," first struck by the Florentine Republic in the 14th century, that the City Council (or the Mayor) confers on distinguished guests or deserving citizens.

Chapter 7
Conclusion

This book is a collection of essays that explore the history of the Department of Chemistry at the University of Florence through its many transformations over the years and through many of its outstanding faculty members. These scientists lived, worked, and many had family roots, in Florence. They “did chemistry” long before chemistry took form as an academic discipline and they left a legacy of forms and customs, to say nothing of a remarkable body of research, that propelled the department to world-class status in the 20th century.

These experts, as teachers, instilled in generations of chemistry students a sense of inner peace despite the chaos that surrounded them during the years of the fall of the Grand Duchy of Florence, the unification of Italy, through two world wars and decades of economic decline. After World War II, a rarefied cadre of elite professors was less and less desirable since a new model of teacher-student relationships was evolving into working teams that allowed the department to “rise from the ashes,” so to speak, to become a force for innovation on the world scene.

However, looking at the world scene, it is hoped that chemistry at Florence will become more universal and less parochial. Perhaps far too many faculty members are inbred, having studied in Florence and then joined the faculty in Florence. It was a good start for the Institute of Higher Practical Studies and Specialization to call a foreigner, Hugo Schiff, to occupy the chair of chemistry. Other Italians, from Friuli, Liguria, Calabria, and Lazio, have occupied that same chair, but later on, the department spiraled into a narrow regionalism. We all know that unless the creative urge continues to be stimulated and cultivated, especially by the influx of new ideas and methodologies, it is soon exhausted within a few years [1]. The time has come to attract others to the department and for Florence itself to provide other universities with its graduates and thus continue to develop the intellectual dynamism that has characterized the last few decades of the department’s activities.

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Chapter 8
Postscript

Regarding the biographical and scientific information about the chemists discussed in this volume, we had recourse to both primary and secondary sources: archival documents, bibliographic sources, unpublished material deposited at the Department of Chemistry, and the latest "hagiographies" orally transmitted by the still-living relatives and staff members who were able to supply us with anecdotal material and other stories drawn from their memories.

Perhaps some will object to the fact that some persons who were part of the history of the department were omitted—a reality that had to be dealt with and a judgment call that had to be made given the editorial limitations of this book genre. We would have liked to include the contributions of Giuseppe Orosi (1816–1875), Pietro Biginelli (1860–1937), Sergio Berlingozzi (1890–1957), Giovanni Canneri (1897–1964), Vincenzo Caglioti (1902–1998), Adolfo Quilico (1902–1982), Danilo Cozzi (1916–2004), and Valerio Parrini (1924–1989), but that would have required an additional volume. For the same reason, we may have omitted some relevant details, but for those who are interested, the archives and manuscripts in the university library are available for your perusal.

One final word: one aim of the present work was to offer to the public a text characterized by simplicity and informality, unencumbered by too many notes and references. Therefore, the many sources that we consulted, largely from the periodical and archival literature, have been listed as endnotes following each chapter. The bibliography that follows, however, presents some suggestions for general reading designed to enlarge upon some of the topics covered in the body of the work. Because of the nature of the topic, some of these references are only available in Italian.

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8.1 A Brief Annotated Bibliography

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This volume focuses on the scientific culture in the period of time following the Napoleonic wars and before the fall of the Tuscan government as an independent state in 1859. In Italian.

Amaldi G; Fermi L (1943) *Alchimia del nostro tempo*. Hoepli: Milan The wives of Edoardo Amaldi and Enrico Fermi tell the story of the development of the new physics from the inside, drawing much of their information directly from what they knew of their husbands' lives in the laboratory. In Italian.

Cochrane E (1976) *Florence in the forgotten centuries, 1527–1800: A history of Florence and the Florentines in the age of the Grand Dukes*. University of Chicago Press: Chicago IL. This is a very scholarly monograph that will probably tell you more than you want to know about the historical background of Florentine chemistry's development up until the period of the Museum of Physics and Natural History as described in Chapter of the present work.

Coppini VP (1993) *Il Granducato di Toscana: dagli anni francesi all'Unità*, Utet: Torino. Interesting view of the economic and social condions in the Grand Duchy of Tuscany in the period of the Napoleonic wars and its subsequent absorption into the French Empire. The French academic system was adopted and still influences the educational landscape of Tuscany today. In Italian.

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Fontani M, Costa M, Orna MV (2015) *The lost elements: the periodic table's shadow side*. Oxford University Press: New York Chapter IV.9 (pp. 289–309) tells the fascinating story of how florentium, "the metal of the Florentines," morphed into illinium, cyclonium, and finally, promethium.

Forman P (1984) *How cultural values prescribed the character and lessons ascribed to quantum mechanics*. In Stehr N; Meja V (eds.) *Society and knowledge*. Transaction Books: Piscataway NJ; pp. 333–347. This book is a controversial interpretation of quantum mechanics' influence on culture. Scientists adjusted to the intellectual environment by dropping Newtonian causality from quantum mechanics, thereby opening up an entirely new and highly successful approach to physics.

Gatteschi D, Benelli C (2015) *Introduction to molecular magnetism: From transition metals to lanthanides*. Wiley: New York. An introductory textbook about the rapidly growing field of molecular magnetism was written by two professors from the University of Florence, former students of Luigi Sacconi and Ivano Bertini.

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medicina, farmacia, fisica, igiene, mineralogia e geologia, agricoltura, alla bromatologia, biologia ecc. Unione tipografico-editrice: Torino, 18 vol. This great scientific work was compiled by Icilio Guareschi with the cooperation of the noted scientists of his day. It is listed as a rare book and available only in Italian.

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O'Neil MJ, ed. (2006) *The Merck index, 14th ed*. Merck Research Laboratories: Whitehouse Station, NJ. The organic name reactions mentioned in this volume can be found in the pages ONR-1 to ONR-111 along with the pertinent primary sources.

Reinhardt C, ed. (2007) *Chemical Sciences in the 20th Century. Bridging Boundaries,* Wiley: New York. Nobel Laureate Roald Hoffmann declares in the preface to this volume: "History tells us how human beings acted, and asks us to think about the motives and consequences of their actions…we are pushed gently toward alternative perspectives, towards tolerance, towards empathy." An excellent case for studying history of any sort!.

Schettino V (2004) *Le scienze sperimentali ed esatte nell'Ateneo Fiorentino*. In Marinelli A, Cardini F, Guerrieri F, Rogari S (eds.) *l'Università degli Studi di Firenze 1924–2004 (2 volumes)*, Leo S. Olschki: Firenze; Vol. 1, pp. 201–250. This two-volume history of the University of Florence written on the occasion of its 80th anniversary includes a chapter on the experimental and exact sciences, as cited in this reference. In Italian.

About the Authors

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