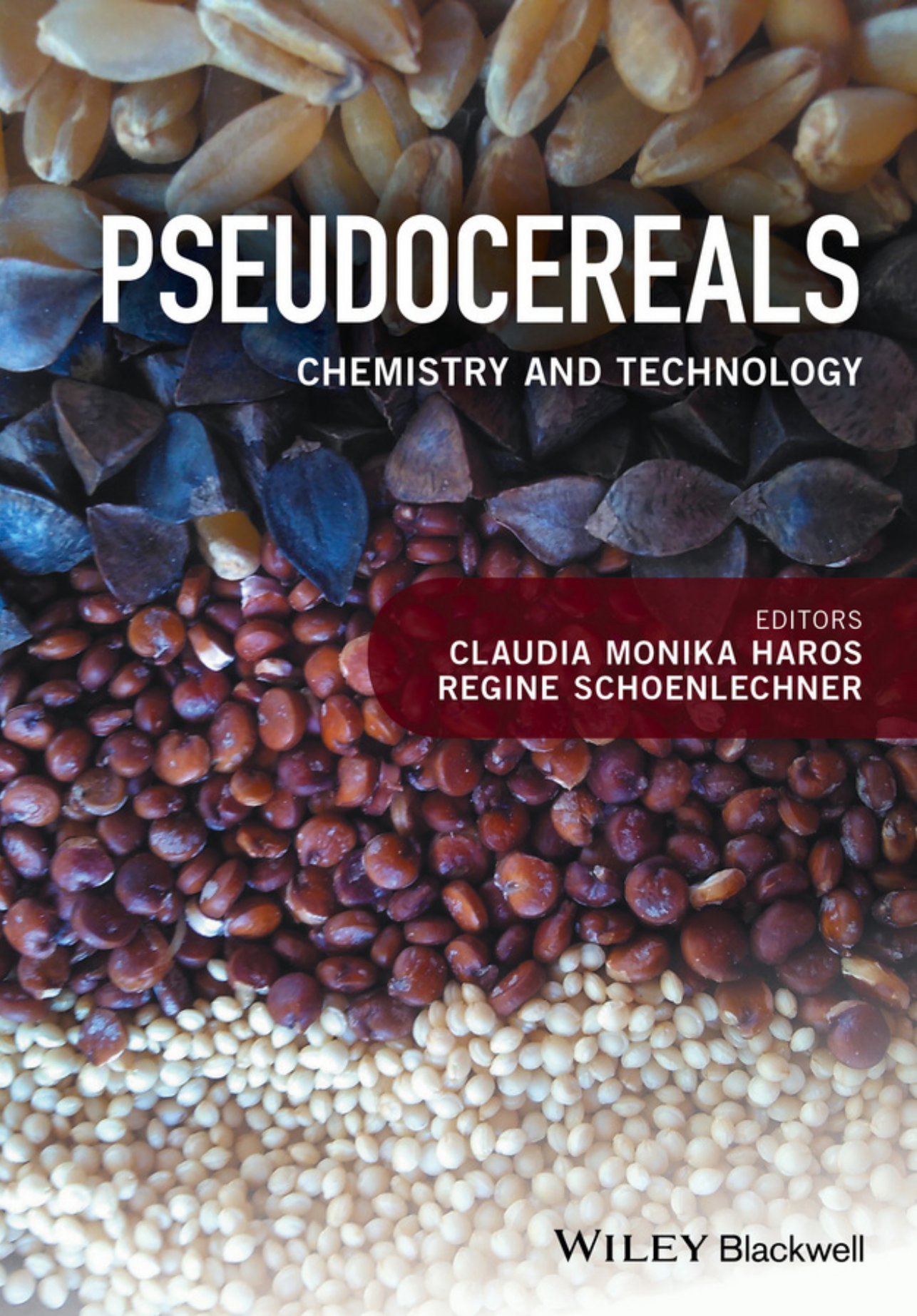
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Pseudocereals

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Chemistry and Technology

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Preface

Pseudocereals are a group of nongrasses, the seeds of which can be ground into flour and then used like cereals. The main pseudocereals are amaranth (*Amaranthus* spp.), quinoa (*Chenopodium quinoa*) and buckwheat (*Fagopyrum esculentum* and *Fagopyrum tartaricum*).

Compared to the true cereals, pseudocereals are still underutilized and cultivation is low but, in recent years, worldwide demand for them has increased immensely, resulting in an increase in their production but also an increase in their price. For many years pseudocereals have been widely recognized for their nutritional value by food scientists and food producers. They contain high-quality proteins, abundant amounts of starch with unique characteristics, large quantities of micronutrients like minerals, vitamins and bioactive compounds and they are gluten free, which makes them suitable for people suffering from various gluten intolerances. For these reasons, interest in pseudocereals has increased immensely since the turn of the century and research efforts have been intensified.

This book summarizes the large amount of recent research on pseudocereals and provides comprehensive and up-to-date knowledge within all the relevant fields of food science. It provides information on the origin of pseudocereals, their botanical characteristics, production and utilization, structure and chemical composition, paying special attention to carbohydrates, fibres, bioactive compounds, proteins and lipids of kernels. It includes dry and wet milling, various food products and applications, as well as gluten-free products. The nutritional and health implications of pseudocereals are also addressed.

We hope that this book will contribute to an increased use of pseudocereals in human nutrition by consumers worldwide.

Claudia Monika Haros
Regine Schoenlechner

1

Origin, Production and Utilization of Pseudocereals

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1.1 Quinoa – *Chenopodium quinoa* Willd (Amaranthaceae)

1.1.1 Introduction

The Andean region, an area inhabited originally by the Inca and Tiwanaku civilizations, is considered the centre of origin of *Chenopodium quinoa* Willd. Native to South America, it is an annual crop with several varieties and it was an important ingredient in the diet of many pre-Hispanic people. Traditional production areas are located in Peru – in Cajamarca, Callejón de Huaylas, Mantaro Valley, Andahuaylas, Cusco and Puno (high plateau); Bolivia – in the high plateau of La Paz, Oruro and Potosi and in the inter-Andean valleys of Cochabamba, Chuquisaca, Potosi and Tarija; and Argentina – in Jujuy, Salta and in the Calchaquí Valleys in Tucumán. It is also produced in Colombia, Ecuador and in the Chilean High Plateau (Barriga *et al*., 1994).

Given its agronomic versatility, quinoa could be produced in regions where the population has no access to other protein sources. The plant adapts well to different agro-ecological soils and climate zones and is a water-efficient crop; it survives under low soil-moisture conditions. The nutritional properties of this crop, the plant's possible uses and the fact that it provides an alternative solution to nutrition problems render quinoa production promising. Nowadays, quinoa is grown not only in the traditional production areas mentioned above but in the United States, Canada, Italy, France, England, Sweden, Denmark, the Netherlands and in Africa.

1.1.2 Origin and History

Archaeological findings show that quinoa was a species commonly used by the ancient Andean cultures. Fruiting branches and loose grain have been found in different regions of Peru and in the Arica coastal area (Chile). Seeds have been found in native burial sites in Chile – in Tarapacá, Calama and in the Calchaquí-Diaguite region. In the New Continent, the Spanish found *colcas* (warehouses) where the natives stored their food and large amounts of quinoa. Quinoa, as well as *kañiwa* (*Chenopodium pallidicaule* Aellen) and other edible plants such as *kiwicha Amaranthus caudatus Linn*, were largely consumed by the Andean inhabitants.

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Heisser and Nelson (1974) pointed out that the archaeological findings in Peru and Argentina date back to the beginning of the Christian era. Accordingly, quinoa is one of the oldest crops in the Andean region, having been grown for approximately 7000 years (Jacobsen, 2013). The Tiahuanaku and Inca cultures played a major role in its domestication and preservation.

In 1586, Ulloa Mogollón mentioned the use of quinoa by the Collaguas in Bolivia. Quinoa was widely grown in the valleys in the north of Chile. In 1558, Cortés Hogea found quinoa crops in Chiloe Island. In 1583, Pedro Sotelo observed its existence in Argentina, in the Calchaquí Valley and in Córdoba (Tapia, 2013). Quinoa is a species with a wide-distribution multiple-diversification centre of origin. Its greater diversity and genetic variation took place on the shores of Lake Titicaca. According to Lescano (1994), today quinoa is distributed in the entire Andean region, from Colombia to the north of Argentina and Chile. A quinoa group was found in the region of Concepción, which is located at sea level. The geographical distribution of quinoa ranges from latitude 5° N in the South of Colombia to latitude 43° S in the IX Region of Chile, and from altitudes that go from sea level by the Chilean Sea up to 4000 m in the Peruvian and Bolivian High Plateau. The diversity of quinoa has been associated with five ecotypes: high plateau (Peru and Bolivia), inter-Andean valleys (Colombia, Ecuador and Peru), salt flats (Bolivia, Chile, and Argentina), warm valleys (Yungas, Bolivia) and coastal zone, lowlands (Chile). The plant's germplasm is associated with subcentres of diversity, considered as descendants of a central gene pool of the domesticated varieties around the Lake Titicaca basin. Toro (1971) studied quinoa from the Puno and Cuzco High Plateau and established a relation between crop age and its domestication and the usage of expressions of Quechuan (*Kinua*) and Aymara origin (*jupha* and *jiura*). Those terms are evidence of quinoa domestication by the Aymara and Quechuan people.

According to Wilson (1990), *Chenopodium hircinun* is included among the possible quinoa descendants, which evolved and domesticated the quinoa as we know it nowadays. There are four *Chenopodium* species related to quinoa, distributed in the south of the Andes, which are progenitors from which the modern quinoa varieties evolved: *C. carnosolum, C. hircinum, C. incisum, C. petiolare* (Mujica and Canahua, 1989). Originally, the Bolivian Southern High Plateau was identified as the quinoa genetic diversity centre (Gandarillas, 1979). Then, Christensen *et al*. (2007) worked with molecular approaches and simple sequence repeat (SSR) microsatellites, and suggested that the quinoa genetic diversity centre was the central Andean High Plateau from Peru to Bolivia. He indicated that the possible entry point of the Ecuadorian accession was the High Plateau from Peru to Bolivia. The molecular data showed the Ecuadorian and Argentine limited diversity of the Ecuadorian and Argentine quinoa germplasm. This may result from the small number of available samples and the limited germplasm conservation *in situ* in those areas. The information obtained confirmed that the possible entry point of the Ecuadorian accession was the plateau from Peru to Bolivia. Christensen *et al*. (2007) also stated that Argentine varieties had their origin in the northern Chilean plateau and in the southern coastal Chilean zones. This proves that Chilean quinoa is similar to its Bolivian counterpart, found in the southern high plateau. The genetic analysis led to the conclusion that quinoa has existed as two different gene pools:

- Quinoa from the Andean high plateau with the associated weeds complex (quinoa *ajara* or *ashpa*) *Chenopodium quinoa* variety *Milleanum* Aellen, known as *Chenopodium quinoa* variety *melanospermum* Hunziker.
- Coastal quinoa from the centre of Chile and south lowlands.

According to recent information, based on microsatellites and concerning quinoa diversity from the Argentine northeast (Costa Tártara *et al.*, 2012), a greater quinoa diversity is found in the Andean foothills and the east subtropical lowlands that surround Gran Chaco and the Pampa. This emphasizes possible germplasm movement patterns of old and modern quinoa in the region of Bolivia-Argentina-Chile. Molecular evidence suggests that genetic erosion has been affected by four events (Jellen *et al.*, 2011). The first might have been produced when two quinoa diploid descendants hybridized. The second one was when quinoa was domesticated from its tetraploid wild relatives through several cycles of seeds and crop exchange in new zones and climates. The third event might have occurred during the Spanish conquest, when quinoa was established as food for the indigenous communities (Cusack, 1984). The fourth event might have been caused by human migration from rural areas high in the Andes to urban centres. The countryside was therefore abandoned and the quinoa germplasm was lost (Fuentes *et al.*, 2012).

1.1.3 Botanical Characteristics / Species / Varieties

1.1.3.1 Species / Varieties

The *Chenopodium* section contains four subsections: Cellulata, Leiosperma, Undata and Grossefoveata:

- The Cellulata, alveolate pericarp pattern, 2n = 4x = 36, which includes *Chenopodium quinoa* Willd and *Chenopodium, berlandieri* ssp. *nutalliae*, and its domesticated and wild relatives *Chenopodium quinoa* ssp. *melanospermum* and *Chenopodium hircinum*, respectively.
- Leiosperma, smooth grains: *Chenopodium pallidicaule* Aellen (2n = 2x = 18). Wild quinoa has developed through an adaptation process in three areas:
  - South America: *C. hircinum* and *C. philippianum* as bridge species, with relatives (progenitors) of quinoa.
  - Northeast America: *C. bushianum* and *C. macrocalycium*.
  - Northwest America: *C. berlandieri*.
- Undata, *C. murale*, 2n = 2x = 18.
- Grossefoveata includes wild species of worldwide distribution (Giusti, 1970).

1.1.3.2 Botanical Description

Chenopodium quinoa is an annual herbaceous plant that develops in an erect position and has a pivotal deep and highly branched root system (Figure 1.1a). The stem may be branched or unbranched (Figures 1.1b and 1.1c), striated or channelled, green or red, with variable height depending on the genotype, climate and soil fertility. The stem typically reaches to between 0.5 and 1.5 m in height, but it may reach up to 2.5 m height in the inter-Andean valleys. Leaves are simple, smooth and pinnately veined with alternate phyllotaxes (Figure 1.1d).

The lamina is polymorphic rhomboid triangular in shape, 3–15 cm in length, with variable colours from red and purple, to yellow. Flowers are small, sessile and disposed in glomerulus (Figure 1.1e). The perianth has five tepaloid segments.

The androecium is composed of five stamens, short filaments bearing basifixed anthers. The gynaecium has two to three feathery stigmas. Three types of flowers are typically observed: female, hermaphrodite and androsterile, which may be autogamous

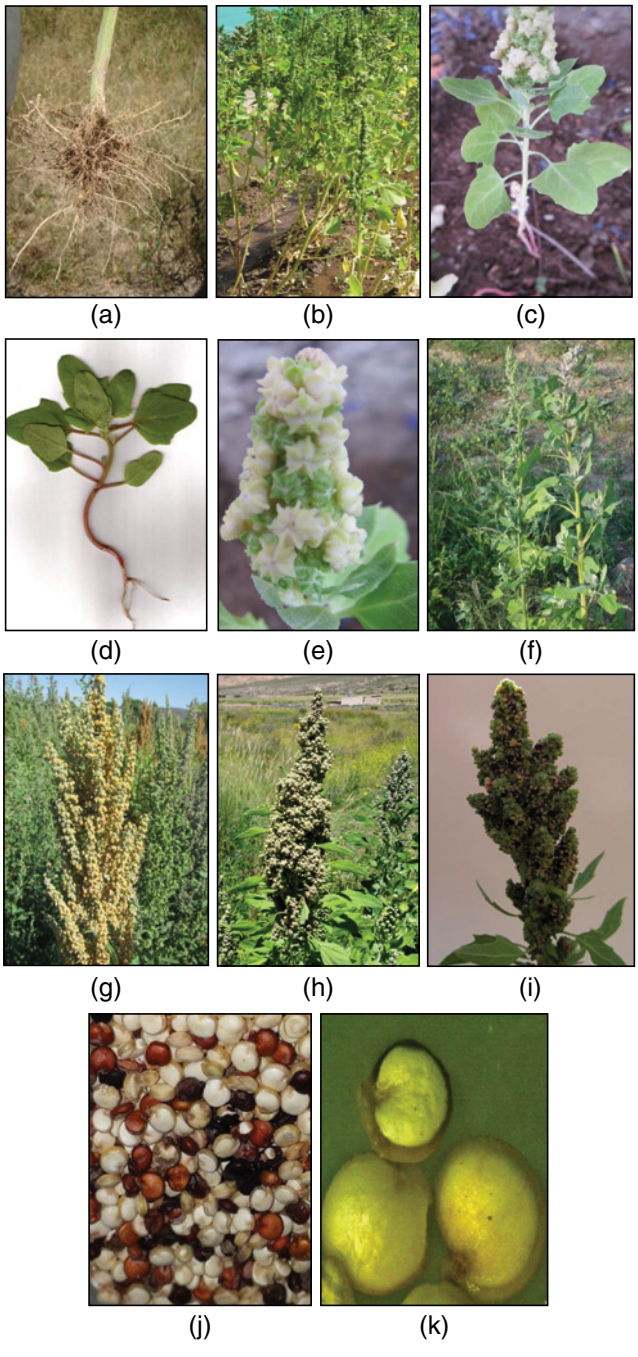


Figure 1.1 Development of quinoa plant: (a) taproot branched; (b) stem branched; (c) stem unbranched; (d) simple leaves; (e) small flowers; (f) panicle in training; (g) panicle amaranthiform; (h) compact panicle ; (i) mature panicle; (j) quinoa seeds; (k) seed. (*See color plate section for the color representation of this figure.*)

or allogamous and are typically arranged in panicles (Heisser and Nelson, 1974). Figure 1f shows a panicle in training. The panicle is made up of a central axis, secondary and tertiary branches and pedicels that support the glomerulus; it may be amaranthiform (Figures 1.1g) or compact (Figure 1.1h), with intermediate formations. The panicle's physiological maturity shows in Figure 1.1(i). The fruit is an indehiscent achene derived from a superior unilocular ovary, and it is cylindrical-lenticular in shape. The ventral part of the achene has a scar from the insertion of the fruit in the floral receptacle. The membranous perianth covers the achene, which easily detaches from the plant. The seed corresponds to the campylotropous type; the embryo is peripheral and has a basal body (Figures 1.1j and k). The areas of food reserves in seeds are: perisperm, a peripheral embryo and a one to two-cell layered endosperm surrounding the hypocotyl-radicle axis of the embryo.

Starch grains occupy at the cells of the perisperm, while the lipid bodies, protein bodies with globoid crystals of phytin, and proplastids with deposits of phytoferritin, are the storage components of the cells of the endosperm and embryo tissues. These globoid crystals contain phosphor, potassium and magnesium (Prego *et al.*, 1998). The quinoa seeds measure 1.5 to 2.5 mm in diameter. The episperm has four layers. There is an outer layer, which is rough and fragile – this contains the saponin. The second layer is narrow and smooth. The third layer is yellow, thin and opaque. The fourth layer is translucent and comprises a single stratum of cells. The embryo is formed of two cotyledons. The radicle is gemmule and curved with peripheral layers enveloping the perisperm. The perisperm is white in colour and serves as a compartment for nutrient storage.

1.1.4 Cultivation

1.1.4.1 Growth and Development

Phenological phases of the quinoa crop are readily recognized. Mujica and Quillahuaman (1989) has proposed 12 stages:

1) *Emergence:* 7–10 days after sowing, the cotyledons are visible above soil surface.
2) *Two true leaves:* 15–20 days after sowing; the epicotyl grows upward and gives rise to true rhomboid leaves with alternate philotaxis.
3) *Four true leaves:* 25–30 days after sowing; cotyledon leaves; two true leaves and the second pair of leaves is growing.
4) *Six true leaves:* 35–45 days after sowing. Three pairs of leaves are visible; alternate philotaxis. The cotyledon leaves will turn yellow.
5) *Branching with eight true leaves:* 45–50 days after sowing; the cotyledon leaves will abscise and fall. Inflorescence develops protected by leaves, which cover the panicle.
6) *Panicle initiation:* 55–60 days after sowing, inflorescence emerges from the shoot apical meristem, surrounded by numerous small leaves, which cover three-quarters of its surface. Basal leaves will turn yellow and the stem will become thick and long.
7) *Panicle formation:* 65–70 days after sowing, inflorescence emerges above the leaves and the glomerulus, at the base of which the flower buds are found.
8) *Beginning of flowering:* 75–80 days after sowing, the apical hermaphrodite flower will open, and stamens will be seen standing separately.
9) *Anthesis:* 90–100 days after sowing, 50% of the flowers will be open in the morning until midday. Then, they will close in the evening. The lower leaves will abscise and fall.

10) *Milky grain stage:* 100–130 days after sowing, the fruit is formed and, when pressed, a milky white fluid appears.
11) *Dough grain stage:* 130–160 days after sowing, the fruit present a dough-like texture when pressed.
12) *Physiological maturity:* 160–180 days after sowing, the fruit exhibits resistance when pressed. Leaves have turned yellow and this is followed by defoliation.

1.1.4.2 Climatic Requirements

Due to its wide genetic diversity, the quinoa plant has the ability to adapt to different environments. It can be grown in desert, hot and dry, cold and dry, mild and rainy climates, on high plateaus and in high Andean areas. The plant readily proliferates at temperatures between 15 °C and 20 °C, and can resist from 38 °C to −8 °C. Temperatures above 38 °C may cause flower abortion and senescence of stigmas and stamens. The plant also grows in high plateaus with 40% humidity, and in very wet regions of Chile. It can tolerate soil water deficit but a supply of 200–250 mm of annual rainfall ensures good development.

Photoperiod and radiation. The different genotypes may adapt to short-day length or long-day length, or be neutral, in relation to light conditions. In the South American Andes (Figure 1.2a), the quinoa plant responds well to a 12 daylight photoperiod. Radiation regulates crop distribution and reaches extreme values in high areas (Frere *et al.*, 1975).

1.1.4.3 Soil and Crop Management

Soil characteristics. The ideal soil for optimum growth should be well drained, preferably of loamy texture and with organic matter. The plant requires nitrogen and calcium, a small amount of potassium and phosphorus. It also grows well in sandy-loam, sandy or clay-loam soils with the essential nutrients for proper crop development. The plant tolerates a wide range of soil pH, growing well at pH 9 as well as in acid soils at pH 4.5. However, the quinoa plant prefers soils with near-neutral pH (Mujica *et al.*, 1997). The quinoa plant is generally not tolerant to flooded soils. Young plants are particularly sensitive to excessive humidity.

The plant displays fair tolerance to salinity. The critical period starts with germination. Jacobsen *et al.* (1997) assessed salt tolerance and observed a stimulation of the germination rate at low salt concentrations. When salt concentrations were increased to 350 mM, germination rate decreased. At a salt concentration of 700 mM, germination rate was so low that it could be regarded as the limit for salt tolerance.

Genotypes differ according to their tolerance to extreme soil salinity.

The Bolivian southern high plateau has soils of volcanic origin. The presence of considerable amounts of volcanic ash contributes to lower density and higher water holding and phosphate fixation capacity. These clay minerals in the soil retain and exchange cations, anions and water.

Water requirements. In both the Bolivian southern Altiplano and northwestern Argentina, technologies are applied to store water and genotypes resistant to water deficit conditions are grown. Moisture equivalent as a measure of the field capacity of the soil exceeds the amount of water needed for commercial quinoa production. Producers typically forecast high yields in dry years, and the opposite occurs for rainy years. In Peru's coastal region, the quinoa plant grows in deserts and sandy soils that have a field capacity of around 9%. In the Peruvian high plateau, where clay-loam soils are the rule,

field capacity reaches up to 22%. In the south of Chile, the *Mapuches* produce the quinoa with around 2000 mm of annual rainfall, but specific genotypes that are adapted to the region are grown. Irrigation may be applied by simple gravity (e.g. furrow irrigation, flooding), dripping or sprinkler irrigation systems.

Traditional tillage is practised in the Altiplano and the inter-Andean valleys. The labour is carried out with manual tools (Figure 1.2b), including *tankan*, to prepare the soil; *taquiza* or *liukana*, to sow in holes; *azadon*, to harvest the crops, and *huaktana*, to conduct the threshing.

Mechanized tillage. A disc plough pulled by tractors was introduced as a tool to stir, loosen, and aerate the soil, and increase humidity and water storage. In the medium term, negative results of this practice were observed: the structure was lost and became compacted, drainage capacity, water infiltration, oxygenation and organic matter decreased. The soil was eroded and loss of soil fertility occurred. Radicular development of the plant decreased and yields dropped. The disc plough turned over the upper layer of the soil; small humus particles were exposed to the wind, and soil degradation took place. Consequently, a technological change in the soil preparation brought about the use of a plough called *Qhulliir* (Aimará).

Preparation of the block. Proper soil conditions include the slope or the terrain, good, fertile soil and the absence of flooding. If the previous crop was *Solanum tuberosum* L. (i.e. potato) or any kind of grass, manure must be incorporated, so that nutrients are available for the following rotation. Sandy soils, with low organic matter contents, benefit from a nitrogen, phosphorus, and potassium application, according to the needs and projected yields.

A mouldboard plough is typically employed for soil preparation. The machine works by burying weeds and the remnants of the previous crop. Then, a harrow is run in crossed passes for destroying and breaking up the soil capillarity and retaining rainfall water. In this case, the implement must be a double-action disc harrow with sharp edge discs and rigid arms. The equipment called *Qhulliri* is used today. The machine avoids soil erosion but it cannot be used in abrupt or pronounced slopes. Tillage preserves soil structure, thereby avoiding mixing or turning over of the soil. In addition, natural cover crops remain on the surface and erosion is prevented. This tool with fixed teeth loosens the soil; its blades cut the weed and a horizontal shovel levels the field surface.

Traditional sowing. In the dry southern Altiplano, sowing is conducted in holes by a special tool. This work is carried out with a *taquiza*, which produces a space of 1.20 m between the holes and the furrows, and 10 to 15 cm of depth. The holes are filled with a mixture of seeds and manure, and then the soil is packed down. When the seeds germinate, only four plants are left in each hole. Three kilogrammes of seeds per hectare are sown. This system works in dry, cold, arid and saline soil environments. In the inter-Andean valleys, sowing is practised in furrows 0.5 m apart. Six to 8 kg of seeds per hectare are placed in rows.

Mechanized sowing. Sowing is carried out depending on environmental conditions, field capacity moisture and the genotype characteristics. In Jujuy, Argentina, direct sowing takes place on irrigated soil in mid-February. In the Calchaqui Valleys, Salta, Argentina, the land is sown from October to December, based on rainfall. Sowing is done in rows. The spacing of 0.40 to 0.80 m between furrows depends on cultivar, and 8 to 10 kg of seeds per hectare are sown. In Salta, Argentina, vegetable seeders (Figure 1.2c) are used. Furrows are 0.50 m apart. In large plots, fine grain seeders have been adapted (Figure 1.2d). The spacing between adjacent furrows ranges from 0.70 to 0.80 m. Seeds should be sown up to 2 cm deep.

Cultural labour. In direct sowing, thinning is used to remove weak or debilitated plants. Weed control is either manual or mechanical. No herbicides are used. When sowing is conducted late, weeds compete with the crop and should be managed by hand-pulling them or using cultivators.

Irrigation. In the Andean region, crops typically rely only on rainfall. In the north of Argentina, the block is irrigated 3 or 4 days before sowing but, from that moment onwards, irrigation frequency will depend on the region and on water availability. The plant will require more water once it begins flowering and setting the fruit crop. Then, irrigation frequencies are reduced towards maturity.

Earthling up. When the plant reaches 0.50 to 0.70 cm high, mounds of soil are drawn up around the stem to allow the plant to continue growing upright once the panicles have developed. The weeds are removed either manually or mechanically.

Fertilization. Fertilization plans for the quinoa plant have to account for nitrogen, phosphorus and potassium needs. Potassium is generally not necessary, as South American soils are rich in potassium. A recommended fertilization formula is equivalent to 80-40-0. In sandy soils with low percentages of organic matter, the formula to be applied is 240-200-80 (Mujica *et al.*, 1997).

Harvest and postharvest. The timing of harvest depends on cultivar, soils characteristics, temperature and humidity. At the onset of ripening, leaves turn into yellow or reddish tones and the fruits develop from the inflorescence, which can be seen as the perianth opens (Figure 1.2e). This process is an indicator of physiological ripeness (Aroni, 2005). The leaves will abscise and fall. Fruit detachment indicates that fruits are ripe and thus ready for harvest. Ripening is verified by gently stroking the panicle, and if grains fall, the harvest must start shortly. Harvest is best practised in the early morning to avoid grain loss.

Under the traditional growing scheme, the ripe panicles are chosen from each furrow or row and the selected plant is pulled and shaken to remove the soil, or is cut with a hoe or a sickle 15 cm above the ground. String trimmers are also used to cut the panicles. The rest of the plant is incorporated as organic matter to the soil. For the same process, wheat combine harvesters adapted for this kind of harvest are used in Salta and Jujuy, northern Argentina (Figure 1.2f). After harvest, the panicles are arranged in piles or stacks forming arches to facilitate grain drying. The panicles are ordered into elongated or round mounds, all of them towards the same direction. When the panicles stand in a circle, inflorescences are placed in the centre. Then they are protected with straw or plastic to avoid loss of humidity. Panicles are left in this position, and, subsequently, after 7 to 15 days, they are threshed. In traditional threshing, the panicles are placed on a blanket, and beaten with an instrument called *huajtana*, a tillage tool from the Inca; then they are aired to separate the grains, which are exposed to the sun for 8 hours to decrease humidity to 12%. Cleaning is done with sieves, which classify the grains as follows: a top-quality grain should have a diameter larger than 1.8 mm and a lesser quality product grain should have a diameter smaller than 1.8 mm. There are threshers that combine the actions of cutting, threshing and airing. Clean grains are packed in polypropylene bags, stored in clean, dry and ventilated areas and placed on pallets at least 15 cm above the ground.

1.1.4.4 Diseases

Mildew. The agent causing mildew is *Peronospora farinosa* f. sp. Chenopodii, an oomycete in the family of Peronosporaceae and an obligate biotrophic parasite. Mildew attacks the entire plant, causes defoliation and affects fruit growth and development.

Figure 1.2 Quinoa cultivation, harvest and diseases: (a) quinoa in the South American Andes; (b) manual tools; (c) vegetable seeders; (d) fine grain seeders; (e) grain maturation; (f) harvest; (g) mildew; (h) abrupt leaf fall. (*See color plate section for the color representation of this figure.*)

The fungus develops optimally in humid environments and produces damage on lower leaves (Figure 1.2g). Then, it spreads to the upper ones. Pale yellow or reddish spots of all shapes and sizes in the upper surface may be observed. The purple-grey mycelium is typically observed in the lower surface of the leaves, followed by abrupt leaf fall (Figure 1.2h). Other symptoms include dwarfism, defoliation and reduction of yield under severe attacks can result in total crop loss (Ortiz *et al*., 1976). Waterlogging should be avoided, as humidity provides a favourable environment for mildew development. It is important to check the presence of piercing and sucking insects (such as aphids) that transmit the infection. Some practical tips to deal with this disease successfully are crop rotation, cultural practices to diminish soil humidity and the use of resistant cultivars or genotypes. The application of copper sulfate is considered an effective preventive measure.

Leaf spot. The agent causing leaf spots is the fungus *Ascochyta hyalospora*, which affects leaves and stems. Such a fungus causes round, sunken spots and dark edges. It is transmitted by infected seeds and plant waste. The fungus cannot grow on the soil surface or survive when the vegetable matter has decomposed. It can be eliminated with a 3- or 4-year crop rotation.

Bacterial spot. The bacterium *Pseudomonas* reaches the leaves due to rain, wind, farm tools and seeds. Infection occurs at sites where humidity levels are high. The bacterium penetrate the stems and leaves through wounds produced by soil tilling or by insects. At the beginning of the infection, irregular water-soaked spots appear on leaves and then they get darker and necrotized, provoking serious lesions. Pycnidia are seen as black dots in the core. To prevent this bacterial infection, it is recommended to use healthy seed and resistant cultivars.

Pests. The quinoa plant ecotypes with a high saponin content are usually not attacked by insects. In addition to this, the high saponin ecotypes act like trap crops for nematodes attacking other rotation crops. The quinoa plant can also be affected by the *Eurysacca quinoae* Povolny moth, typical for the Andean region of South America. There are several species, such as *Eurysacca media* Povolny, *E. melanocampta* Meyrick and the *ticona* complex*: Copitarsia turbata* H.S., *Feltia* sp., *Heliothis titicaquensis* and *Spodoptera* sp. (Saravia and Quispe, 2005), which can cause reductions in yields ranging from 5% to 67%. *Eurysacca melanocampta* Meyrick, develops two generations in the crop, thus the control should be focused on the first stages. First-generation larvae excavate and feed themselves from the parenchyma of the leaves and developing inflorescences. Second-generation larvae affect panicles, destroying milky and ripe grains. This pest has predators and parasitoids that keep natural control: *Copidosoma koehleri* Blanchard, *Dolichostoma* sp., and *Copitarsia turbata* H.S. (Lepidoptera, *Noctuidae*). Such control is done during soil preparation with the tillage that destroys the pupae. The coleopteran *Calosoma* sp. is a predator of the larvae early stages. Contact insecticide with low residual effect can be applied, if necessary.

1.1.5 World Production of Quinoa

In 2012, 102 745 ha were cultivated with quinoa around the world, producing 82 510 tons. Peru and Bolivia are the main producers of quinoa, followed by Ecuador, which usually produces lower volumes (see Table 1.1). The three Andean countries, Bolivia, Peru and Ecuador have taken over the worldwide market. Growth rate of regional

Table 1.1 World production of quinoa.

Year	Country	Production tons	Surface ha	Yield kg/ha
2012	Bolivia	37 500	63 300	595
2012	Peru	44 210	38 495	1161
2012	Ecuador	800	1250	640
Total		82 510 ton	103 045 ha	

Source: Agrofood Division – FAOstat database.

exports have not shown a steady patterns. For example, in the first 10 years, sales increased four times, whereas from 2002 to 2012, sales increased 39 times. The production increased, but the average yield did not. In 2004, the total production of the three countries reached 52 326 ton; in 2012, it was 82 510 ton. The cultivated area in 2004 was 67 243 ha; in 2012, 103 045 ha. Average yield remained steady. In 2004: 771 kg/ha; in 2012: 795 kg/ha.

1.2 Amaranth – *Amaranthus hypochondriacus* L., *Amaranthus cruentus* L., and *Amaranthus caudatus* L. (Amaranthaceae)

1.2.1 Introduction

Amaranthus hypochondriacus L., *Amaranthus cruentus* L., and *Amaranthus caudatus* L., known as amaranths, are grown for grain in tropical regions of Africa, Central and South America and Southeast Asia (especially in India) as well as in warm regions of North America. In America, the producing countries are the United States, Mexico, Guatemala, Ecuador, Peru, Bolivia and, to a lesser extent, Argentina. In the 1980s, these species were rediscovered as promising food crops for food security due to their resistance and tolerance to biotic (pests and diseases) and abiotic (temperature and drought) factors and due to the high nutritional value of seeds.

1.2.2 Origin and History

The three amaranth grain species are annual herbaceous plants domesticated in prehistoric times in the high tropical and subtropical lands of America (Sauer, 1976). Archaeological findings in Tehuacán, Puebla, Mexico show that A. *cruentus* was already cultivated over 4000 years BC, and *A. hypochondriacus* was grown about 500 years AD (Sauer, 1976; Jacobsen and Mujica, 2003). They reached their maximum use when grown by the Aztecs in the valley of Anáhuac. In the fifteenth century, Arizona Indians also grew *A. hypochondriacus*. The earliest archaeological record of *A. caudatus* was found in the north of Argentina (Salta) dating back 2000 years, in an urn, which also contained flowers and pale seeds of amaranth, maize, bean and henopodium (Hunziker and Planchuelo, 1971). Spanish reporters highlighted the nutritional, cultural and religious significance these pseudocereals possessed among pre-Columbian inhabitants. The crop was believed to be sacred in Mexican cultures and its cultivation practices also

had a special nomenclature (Itúrbide and Gispert, 1992). During the conquest there were several factors that acted synergistically to reduce the cultivation of amaranth (Sauer, 1976). Among those factors, it is worth mentioning its replacement by other species of grain introduced from the Old World, a lack of appreciation and religious reasons (Itúrbide and Gispert, 1992).

Sauer (1967) put forward two hypotheses about the origin of amaranth, according to the geographical distribution of its wild relatives, the current cultivated area and their morphological features. Sauer's first hypothesis stated that the three cultivated species might have developed from the domestication of one single species. After a succession of hybridization events with wild subgenus species, other cultivated species arose. Sauer (1967) speculated that *Amaranthus hybridus* gave rise to *A. cruentus*. Then, in the first hybridization event, *A. cruentus* crossed with wild *A. powelli* forming *A. hypochondriacus*. Additionally, he speculated that *A. cruentus* crossed in a second hybridization event with an unknown wild amaranth, giving rise to *A. caudatus*. His second hypothesis suggested that the species may have evolved independently from three different wild species, and was domesticated in both parts of the continent. In this sense, the author proposed that *A. powelli* gave rise to *A. hypochondriacus* for grain crop selection within the current crop area in North America. *A. cruentus* originated from the south of Mexico or Guatemala, in the area of its possible progenitor (*A. hybridus*). Lastly, *A. caudatus* derived from *Amaranthus quitensis* domestication in the Andes.

Recently, Kietlinski *et al.* (2014) have used microsatellites and a more comprehensive sampling of the subgenus wild relatives to understand the phylogenetic relationships of the cultivated species and the relationship between them and the *A. hybridus* complex species. Results from his studies confirm that *A. quitensis* belongs to a different species from *A. hybridus* and it is not the direct progenitor of *A. caudatus*. However, the two of them appear to be hybridizing to some degree in areas where their distribution overlap. *A. hybridus* may consist of two cryptic species or of a single highly variant species from which the three grain amaranths arose. As regards relationship between cultivation and domestication events, he suggested that there is a close phylogenetic relationship between *A. hypochondriacus* and *A. caudatus*, although they are geographically separated. According to this relationship, he proposed two hypotheses for the origin of *A. hypochondriacus* and *A. caudatus*. The first hypothesis refers to a single domestication event occurring in Mesoamerica or the Andes in which *A. hybridus* was followed by geographic divergence. The second hypothesis consists of a dual linage domestication, in which *A. hybridus* lineage, with a broad distribution, was domesticated independently from Mesoamerica to the Andes. Finally, he pointed out that *A. cruentus* may have originated from a secondary distribution in the geographical area of *A. hybridus* across Guatemala and Central Mexico because this is a more distinct species and has a great genetic variability.

1.2.3 Botanical Characteristics / Species / Varieties

It is estimated that there are about 21 germplasm collections worldwide, and the most important ones are stored in the American continent, China and India (Mujica and Jacobsen, 2001). Other minor collections may be found in the United States and Argentina. Most collections include seeds of species grown at the expense of wild relatives, leaving important gaps in current collections.

Cytogenetic studies conducted in varieties of cultivated species show that all species are diploid and have a variable number of chromosomes. The number for *A. hypochondriacus* and *A. caudatus* is 2n = 32; the number for *A. cruentus* is 2n = 34 (Bonasora *et al.*, 2013).

Grain amaranth is an annual herbaceous plant, which can grow to significant heights (Figure 1.3a). The leaves are elliptic to lanceolate-ovate, with acute or acuminate apex. The inflorescence consists of large branches of solid green, red, yellow or variable colours, bearing flowers with or without pointed bracts. Stems tend to be more upright or pendulous, depending on the species. Likewise, seeds are extremely variable in colour. Amaranth seeds are able to germinate a few hours after being sown on moist soil. The radicle is the first structure to emerge, giving rise to a vigorous warped root, densely branched and with numerous small roots, which rapidly develops when branches start to grow from the stem.

Stems are cylindrical and angular, with thick, longitudinal striae, which give a channelled appearance. Stem diameter decreases from the base to apex. It reaches a height of 3 to 4 m. They may differ in colouration, which is usually similar to that of the leaves, although sometimes they show striae of different colours. On several occasions, branches originate from the base or from medium height, from each leaf axil. Leaves are petiiolate, and have no stipules. They exhibit an ovate, elliptic outline with entire margin and may be opposite or alternate. Prominent veins are seen on the reverse. They are smooth or a bit pubescent, green or purple. Size decreases from the base to apex and they are of variable height: from 6.5 to 15 cm (Itúrbide and Gispert, 1992; Mujica, 1992).

Inflorescence. The colourful panicles are amaranthiform (Figure 1.3b), terminal or axillary. They may be fully erect or decumbent. They bloom in colours including yellow, orange, coffee, red, pink or even purple. They reach a height of 0.5 to 0.9 m and take different shapes (Itúrbide and Gispert, 1992; Mujica, 1992). Flowers are unisexual, small, staminate and pistillate. Glomerules consist of dichasial cymes, which bear a terminal male flower that always opens first. Consecutive pairs of lateral branches of female flowers are inserted on the base of male flowers (Hunziker, 1952). Each glomerule may contain 250 female flowers. The percentage of allogamy ranges between 10% and 50%, even within individuals of the same population. Crossing depends on the wind, the number of pollinating insects and pollen production.

The fruit is unilocular, contained in a pyxidium that opens transversely at maturity. The operculum abscises and falls and the seeds inside the urn are exposed (Hunziker, 1952).

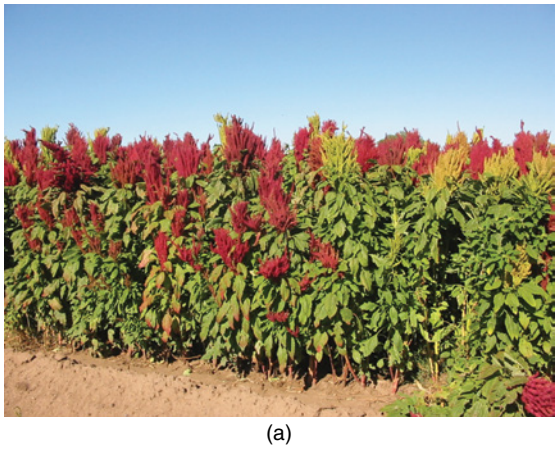
The seeds are small (from 1 to 1.5 mm in diameter) and shiny, slightly flattened, generally white, although sometimes yellowish, golden, red, pink, purple and black; and there are 1000 to 3000 seeds per gram (Figure 1.3c).

The grains contain the episperm, consisting of a very thin layer of cellular tissue; the endosperm; the embryo, made up of protein-rich cotyledon; and the perispern, rich in starch (Irving *et al.*, 1981). In general, seed dormancy has not been observed. Seeds may even germinate where water is scarce.

1.2.4 Cultivation

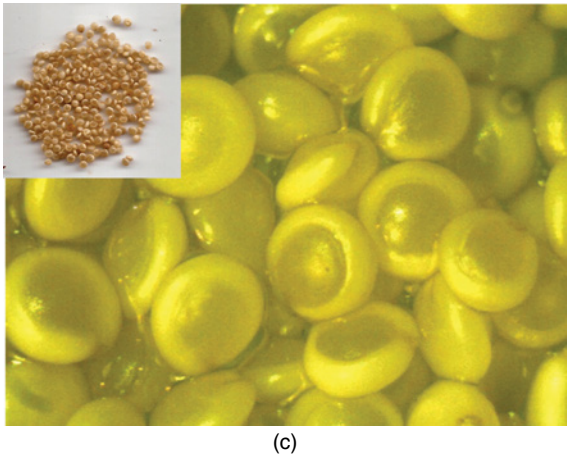
1.2.4.1 Growth and Development

Amaranth phenological characteristics vary extensively according to the cultivated species and the agroclimatic conditions where they are raised. However, generally speaking, sowing date up to 50% of flowering time may vary between 60 and 98 days



(a)

(b)



(c)

Figure 1.3 (a) Cultivation of amaranth; (b) inflorescence of amaranth; (c) amaranthus seeds. (*See color plate section for the color representation of this figure.*)

and, up to maturity, between 130 and 180 days. A description of amaranth phenological stages has been introduced by Mujica and Quillahuamán (1989) and Henderson (1993). Both sources coincide with the phenological stages described as follows:

1) *Emergence (VE).* In this stage, seedlings emerge from the soil, showing their two extended cotyledons. In the furrows, at least 50% of the population going through this stage is observed. All true leaves on the cotyledons are smaller than 2 cm in length. This stage may last from 8 to 21 days, depending on agroclimatic conditions.
2) *Vegetative period (V1Vn).* This stage is determined by counting the number of nodes on the primary stem. Leaves at the nodes may grow at least 2 cm long. The first node matches stage V1; the second one agrees with V2, and so on. As basal leaves senesce, the scar on the primary stem is taken into account in order to determine the corresponding node. The plant starts to branch in stage V4.
3) *Reproductive stage.* The beginning of panicle emergence (R1): the inflorescence apex may be noticed at the stem tip. This stage is observed 50 and 70 days after sowing. The panicle (R2) is at least 2 cm long. The end of panicle emergence (R3): the panicle is at least 5 cm long. If anthesis has already started once this stage has been reached, the plant should be classified as part of the following stage (R4) – here at least one flower is open, showing its separated stamens and the completely visible stigma. Hermaphrodite flowers are the first ones to bloom. Anthesis generally arises from the panicle's central axis to its lateral branches. In this phase, the plant is highly sensitive to frosts and hydrological stress. This stage can be divided into several substages, according to the percentage of panicle central axis flowers that have completed the anthesis stage. For instance, if 20% of central axis flowers have finished their anthesis, the stage will be R4.2; and if the proportion of central axis flowers reaches 50%, the stage will be R4.5. Flowering should be examined at midday as flowers stay closed during early morning or late afternoon hours. During this stage, the plant begins to eliminate older lower leaves, which are also less photosynthetically efficient.
4) *Grain Filling (R5).* At least 95% of the panicle central axis has completed anthesis. According to Mujica and Quihuallamán (1989), this stage can be divided into two stages. The milky grain stage occurs when seeds are squeezed out by pressing them between the fingers, and a milky white fluid appears; the dough-grain stage occurs when the seeds are squeezed out by pressing them between fingers and a whitish doughy substance may be noticed.
5) *Physiological ripeness (R6).* A definite criterion to determine physiological maturity has not been established yet. However, the change in panicle colour serves as the most commonly used indicator. Green panicles change their colour to golden yellow, and red panicles change to reddish-brown. Besides, seeds are hard, and it is not possible to dig nails into them. In this stage, when the panicle is shaken, ripe seeds will fall out.
6) *Harvest maturity (R7).* Leaves senesce and fall and the plant looks dry and coffee coloured. It is expected that autumn frost strikes in order to reduce seed humidity.

1.2.4.2 Climatic Requirements

Amaranth genotypes cultivated in rural agroecosystems of Mexico's central and southern regions are native or creole varieties. However, there exist a small number of improved varieties of two species: *A. hypochondriacus* L., which is grown in places with mild weather at an altitude from 1500 to 2200 m.a.s.l., and *A. cruentus* L., raised in places

with warm weather and at an altitude from 400 to 1500 m.a.s.l. (García-Pereyra *et al.*, 2004). In the case of *A. caudatus*, the crops grow from Ecuador to the northern region of Argentina, in mild areas and inter-Andean valleys, with an altitude ranging from sea level to 3100 m.a.s.l. It is known to be a short-day species, despite its geographic adaptability to diverse environmental conditions. Flowering may occur within day lengths varying from 12 to 16 h. Moisture levels range from 400 to 800 mm; nevertheless, good crops may be grown with 250 mm, although reasonable moisture is essential for germination and flowering. Once established, amaranth is drought tolerant. In subtropical climate zones, harvest may occur twice a year, especially when the plant is watered.

In mild climate zones, cultivated areas mostly depend on the beginning of the temporal season from May to June, receiving 500 to 800 mm of precipitation. Crops raised in areas receiving 1000 mm of annual rainfall have been found. *A. cruentus* L. is sensitive to frost. Branching may withstand temperatures up to 4 °C and resist highest temperatures ranging from 35 to 40 °C.

1.2.4.3 Soil and Crop Management

Amaranth grows best in loam and loamy-sandy soils, with high organic matter content and good drainage, even though it may adapt to different kinds of soils. However, it does not generally bear clay soils. The optimal soil pH is 6–7, despite crops suited to acid soils with 8.5 pH. It is tolerant towards aluminium toxicity (Mujica, 1992; Soto, 2010).

Amaranth is planted either by transplanting in fields called *chinampas* (in the central region of Mexico) or direct sowing. Transplanting is an ancient method still widespread in some areas. It consists of raising seedlings for later transplanting to the field. Direct sowing is more common in southern Mexico. It is carried out in the back (upper border) of the furrow, on streaming, at the beginning of rainy season. Then plants are pruned when they reach a height of 10 to 15 cm. Generally, cultural practices are similar to corn growing: earthing up, two-staged fertilization and weed control. Harvest in those crop areas is like that in the Mexico Valley. From September to October, panicles are cut and, once all the stem leaves are dried, they are all arranged in piles and they are beaten to separate the seeds. Northeastern Mexico *A. cruentus* and *A. hypochondriacus* genotype tests show variable yields reaching from 800 to 2300 kg/ha, although it is possible to increase these values by sowing a larger volume and by using fertilizers (García Pereyra *et al.*, 2009; Kaur *et al.*, 2010).

In the Andes of Peru, Bolivia, Ecuador and Argentina, *A. caudatus* is cultivated in a traditional way and sowed in unirrigated lands, without fertilizers. Other cropping systems such as direct sowing, irrigated or unirrigated transplanting, associated with corn, intercropping, trap cropping, horticultural sowing next to housing, smallholding and larger areas may be used. The seeds are very small, so soil preparation jobs such as breaking up of clods and shaking up are needed. For that reason, it is recommended to plough, then to harrow and make the furrows either in a traditional manner by using a yoke or mechanically. Sowing is often associated with corn and, in the case of a single crop, is done in furrows separated by a distance of 80 cm, on continuous streaming. When the plant is 20 to 25 cm high, the first weed control is implemented. Then thinning follows when seedlings are crowded or should be transplanted to soils with higher moisture levels (Mujica, 1992).

Weed control is conducted manually. In some cases (when harvest time is close), roguing – that is identifying and removing plants with undesirable characteristics – is recommended. Earthing up should be done immediately after weed control is carried out because it improves crop stability when the plant is more than 1.5 m high. Amaranth

crops generally grow in dry lands. However, in irrigated lands soil should be prepared by heavily irrigating the land. Then soil should be moderately irrigated when sowing and at the beginning of flowering, and lightly irrigated during the vegetation development. In this stage, the amount and frequency of irrigation vary according to soil characteristics and weather conditions. In case of shortage of rain, irrigation will be necessary every 30 days and especially at the flowering and grain filling stages (Rojas *et al.*, 2010).

Harvest is done before full maturity to avoid grain shedding. It consists of cutting the plants 50 cm above soil with sickles. They are gathered as small sheaves on furrows until they dry. Then they are hit with sticks while they are laid on extended clothing or tamp soil for threshing and sifted to separate seeds from dead leaves. Crop improvement consists of adequate soil preparation and direct sowing with a density of 4 to 6 kg/ha of selected seeds, in 80 cm furrows, using fertilizers according to the amount of soil nutrients. Cultural work consists of weeding once or twice and a quick earthing up to avoid falling over caused by inflorescence weight (Soto, 2010).

Yield varies from 2000 to 5000 kg/ha in Peru and 900 to 4000 kg/ha in Ecuador.

1.2.4.4 Diseases

Pythium spp. and *Fusarium* spp. are the most frequent diseases that affect seeds. Fungal diseases such as *Sclerotinia* spp. and *Alternaria* spp. cause stem and root rot. The most common pest is *Diabrotica* spp., known as *loritos*, which may harm the plant during emergence. Other pests are *Agrotis* spp. and *Eupicata* spp. In crops in Buenos Aires, the attack of the blister beetle (*Epicauta adspersa*) and the red weed caterpillar (*Loxostege bifidalis*) was noticed. They caused severe defoliation in upper leaves. These pests were controlled by using 1.5% of diatomaceous earth. Under the same growing conditions, panicle damage caused by isolated individuals of spotted maize beetle (*Astylus atromaculatus*) was also detected. It was controlled by spraying with chlorpyrifos (600 cm^3) and pyrethrins (150 cm^3) (Jacquelin *et al.*, 2011).

1.2.5 World Production of Amaranth

In the business environment, amaranth has no specific harmonized tariff but it is included in the 'other cereals' (1008.90.10 and 1008.90.90, 11 digits) and 'other cereal flours' (1102.90.00.900D) categories. Although there are no worldwide official sources that specifically show the volume of production of amaranth, the increase in 'other non-milled cereals' world exports (the category where amaranth is included) showed a general growing trend from 2007 to 2012, probably as a consequence of an increase in the production volume. The two main exporting countries were Peru and Bolivia, with exported values per ton ranging from USD 360 (the lowest in 2009) and USD 640 (the highest in 2011). Within the same period, Germany, France, Lithuania, Poland and China were the most relevant countries as to business transaction volume (Ministerio de Agroindustria, 2013).

1.3 Buckwheat – *Fagopyrum esculentum* Moench

1.3.1 Introduction

Fagopyrum esculentum Moench, known as 'buckwheat', is cultivated in Russia, Hungary, Poland, the Czech Republic, Denmark, France and Germany. In America, the producing

countries are the United States of America, Canada and Brazil. The development of this species is considered not only as an agricultural activity that protects the environment but also as a significant food resource due to its nutritional benefits.

1.3.2 Origin and History

Native to the steppes of Central Asia and Siberia, the first crops were raised in the southern region. Then known as 'buckwheat', this species spread to the West along trade routes and due to invasions. The first records date back to the ninth and tenth centuries in China. Later, buckwheat was introduced to Turkey, Poland through Russia, and then was brought to France, Italy, Switzerland and Austria. The expansion of the crop originated from the seventeenth and eighteenth centuries, reaching Great Britain, the United States of America and Canada.

Buckwheat has been grown in the northeast and central north United States since colonial times, reaching its peak in 1866 due to demand for the seed to make flour and use of the fruit as animal breeding food. As a consequence of immigration flows, it was taken to Chile and Brazil. Ukrainian and Polish immigrants came to America in 1897 and settled down in the province of Misiones, Argentina, and they grew this species for their own consumption. According to Ukrainian tradition, milk, honey and buckwheat cannot be absent from the New Year's meal, as it is a good omen.

Buckwheat is a short season crop, the fruits ripening in the course of 3 months. It has a remarkable adaptability to different kinds of soils, including poor soils with low fertility. For that reason, it was cultivated in the sixteenth century by low-income European people.

It is thought that this plant was brought to North America by Dutch immigrants, who called it *wheat of writings*. In Europe, as well as in Asian countries, buckwheat has been a staple food since ancient times as it is a source of high biological value protein of vegetable origin. It is used for making flour due to its starch content. As it contains no gluten, buckwheat can also be eaten by people with coeliac disease. Between 2% and 3% of rutin (*quercetin-3-O-rutinoside*) is obtained from its leaves, reaching 5% to 8% of this component in improved varieties. In order to extract it, the harvest is gathered when the plant is still green (Oplinger *et al*., 1989). This active ingredient is used for patients who suffer from venous and lymphatic insufficiency, for symptomatic treatment of hair fragility disturbances, haemorrhoids and for visual acuity and visual field disorders of vascular origin (Bruneton, 2001).

1.3.3 Botanical Characteristics / Species / Varieties

Hlásná Cvepková *et al*. (2009) cites 77 accessions. In *Fagopyrum esculentum* Moench, Oplinger *et al*. (1989) express the view that the majority of cultivated buckwheat accessions in the United States are diploids.

Buckwheat is an annual short-season herbaceous plant with many branches. It grows 60 to 70 cm high and has a primary root and an erect smooth stem. Its leaves are simple (Figure 1.4a), entire, and sagittate (arrow shaped). Lower leaves are petiolate, and the upper leaves are sessile, with a length ranging from 5 to 10 cm. They present a smooth edge, a cuspidate apex, palmate venation, developed leaf axil called *ocrea*, alternate phyllotaxis. Its flowers are pink or white and the hermaphrodite is small (Figure 1.4b). They present actinomorphic symmetry, calyx of five sepals, corolla of five petals, androecium of nine stamens of two whorls: one of six stamens and the other one of

three, with shorter filaments; upper gamocarpelar gynoecium, with three carpels, capitate stigmas, hardly fimbriate, trigonous unilocular and uniovulate ovary; orthotropic ovule and basal placentation. Flowers are arranged in corymbose paniculate clusters (Figure 1.4c).

Reproduction occurs by means of crosspollination, presenting heterostyly, different-length stamens and styles. The fruit is a triquetrous achene (Figure 1.4d), with a wooden pericarp and one triangular lenticular seed that ripens irregularly, occurring in the perisperm, the embryo being antitropal peripheral, axial and curved. It has a mealy endosperm (Parodi, 1972).

1.3.4 Pseudocereal Culture

1.3.4.1 Growth and Development

Buckwheat's early crops complete the cycle from sowing to seed ripening within 80 to 90 days. Crops with longer cycles will do it within 100 to 110 days. Once the sowing has been done, the emergence of cotyledons can be observed on the second or third day (Figure 1.4e).

This stage lasts from 6 to 10 days, depending on weather conditions. After emergence, the vegetation period takes place: the epicotyl starts to develop, the first leaves begin to appear and the growth in length occurs in the place where the leaves are inserted, giving rise to internodes (Figure 1.4f). On the stem, leaves are formed at the nodes and the branching begins its development (Figure 1.4g). The reproductive stage occurs 20 or 30 days after sowing, when the paniculate corymbose clusters (Figure 1.4h) start to develop. This stage takes 2 months. Meanwhile, lower leaves abscise and fall. In this stage, the plant is sensitive to hydrological stress and frosts. During physiological maturity, the ovary becomes the fruit and the seminal rudiment turns into the seed. This stage takes 60 to 70 days; the growth is indeterminate. At the same time, the plant has both flowers and immature green fruits and mature fruits. Fruits reach harvest maturity within 75 to 80 days. In this stage, lower leaves abscise and fall and the fruit changes its colour from green to dark brown.

1.3.4.2 Climatic Requirements

For the plant to reach physiological maturity, the sowing season should be determined considering that buckwheat thrives in cool, moist climates and that it is not frost tolerant. During flowering and seed formation, plant development is affected by unfavourable weather conditions, dry climate and high temperatures. In Cantabria, Spain, experimental trials have been conducted in unirrigated soils located in different climatic conditions and at various altitudes such as: (i) the coastal area of Cóbreces at 80 m.a.s.l., (ii) Soba at 574 m.a.s.l., (iii) Valderredible at 730 m.a.s.l. and (iv) Celada at 925 m.a.s.l. Better agronomic behaviour was observed in the coastal area of Cóbreces, characterized by its lower altitude, cool climate and moderate temperatures (García Méndez *et al.*, 2014). Rainfall characteristics and frequency must be considered in order to attain good plant development and flowering, thus achieving a good yield from unirrigated crops.

1.3.4.3 Soil and Crop Management

Buckwheat can be grown in a wide range of soil types with different fertility levels. Better yields are produced from fertile, well drained soils (Tkachuk *et al.*, 1996). It is a

very coarse species that tolerates acid soils. Buckwheat tolerates acid better than other species producing grain; it is effective in extracting phosphorous from low-phosphorous soils. This species does not thrive either in soils with tosca layers near the surface or with high limestone content or in wet, heavy soils. The coating formed on clay soils makes the plant's emergence difficult (Oplinger, 1989). Well drained medium-textured loam, sandy loam and silt loam soils are best suited to grow this crop. The cultivable soil layer must be deep and it must not be flattened because this is not a flood-tolerant species. Before starting with the preparatory work, the plot should be checked in its longitudinal section for impermeable soil layers that could hinder drainage. The necessary corrections should be made when surplus surface water does not percolate rapidly. When tilling takes place, the destruction of soil structure by excessive clearing of arable profile should be avoided. The formation of compacted soil layers in depth strata should also be prevented. Tilling should take soil texture into account. In irrigated crops, plots should be levelled for an even water distribution. Levelling blades are used to achieve the necessary slope (Figure 1.4i). In dry climate soils, the organic matter represents less than 5% of the solid phase.

Compost should be added to reach an adequate fertility level and to improve the soil texture and structure as well. Organic matter allows the addition of particles, which in turn form more porous structures. It also increases the capacity of cationic exchange as well as of water retention in soils. Organic matter in the form of compost can be added either manually or mechanically. In case the crop is rotated with vegetable crops to which manure was added, the nutrients then provided will be available during the buckwheat crop development.

The plot is prepared by tilling the soil with a mouldboard plough or a disc plough. This work is done when residues of the previous crop, green manure and weeds are still in the plot, in order not to affect the seeder machine work. Early tilling allows the nutrients available from the previous crops to be stored in the soil. It also improves the soil's physical condition. The crop residues must have no influence during sowing; burning them is not advisable. If prior to buckwheat some other cereal has been grown in the plot, weed tilling should be carefully performed so as to avoid the formation of a surface layer of straw that could hamper sowing and buckwheat emergence (Napoli *et al.*, 1994). In extensive unirrigated crops located in the northern hemisphere, buckwheat is used for rotation in temporary grasslands, the soil being prepared in April. In the southern hemisphere, tilling is done in June, after the harvest of the grasslands or crops. Seeds of the weeds remain 2 cm deep of the soil superior layer and germinate after rain. When weeds emerge, a disc harrow is drawn (Figure 1.4j), dispersing all the green material. Then a second ploughing is done and the plot is ready for sowing.

Fertilization. The need for nutrients is calculated according to the soil characteristics, the availability of the elements found in the soil and the irrigation system. The next crop is also considered because it will extract nutrients from the soil. The use of manure and / or fertilizers requires a prior soil analysis to add the necessary nutrients. Adding high nitrogen levels results in a great vegetative development that, in turn, causes lodging of the plant and its greater susceptibility to cryptogrammic diseases.

Napoli *et al.* (1994) state that for every 1600 kg of seed produced per hectare, the crop extracts from the soil 47 kg of nitrogen, 22 kg of phosphorous and 40 kg of potassium. Phosphorous is needed for growth and production of flowers. If it is not found in the soil in sufficient quantities, it is added as diammonium phosphate at the moment of sowing acid soils. At a higher pH, monoammonium phosphate is preferable.

Direct sowing. Rows are spaced apart about 15–17 cm; sowing depth is of 4 cm; a fine grain drill is used and seeds should remain in contact with the wet soil. Each hectare takes 60 to 70 kg of seeds. If less is used, the plants will branch out and there will be a significant vegetative development, which will in turn cause lodging of the plant (Napoli *et al.*, 1994). If the soil has been tilled previously, pneumatic precision seeders for vegetables could be used, thus consuming less seeds. To protect the soil structure, tilling should not refine the land in excess. Seeds germinate at temperatures ranging from 20 to 25 °C. In each geographical site, the appropriate sowing date should be considered for the vegetative and the reproductive cycles not to be affected by frost. In Aragón, Spain, located in the northern hemisphere, it is advised that sowing is done during June / July –according to trials carried out in Valderredible by García Méndez (2014). In this area, a higher yield was observed in the plots that had been sown during the summer, with a

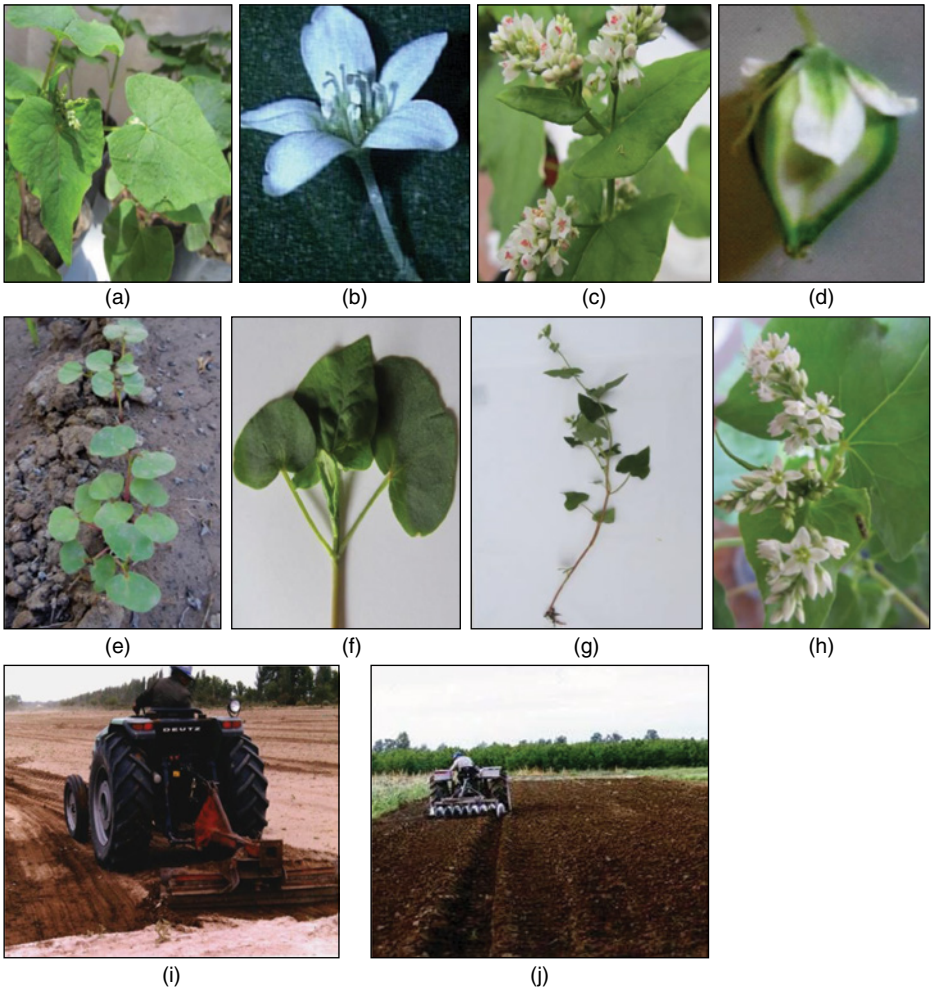


Figure 1.4 Buckwheat: (a) simple leaves; (b) hermaphrodite flower; (c) inflorescence; (d) fruit achene; (e) emergence; (f) first leaves; (g) branches begin; (h) corymbose; (i) levelling; (j) soil preparation; (k) crop uniformity; (l) forms the fruits; (m) seed is mature; (n) harvest; (o) clean fruit. (*See color plate section for the color representation of this figure.*)

Figure 1.4 (Continued)

production of 1400 kg/ha. In the southern hemisphere, the trials carried out by Dionisi (2012) in the province of Córdoba and by Napoli *et al*. (1994) in the province of Misiones, Argentina, proved that sowing must be done after all risk of frosts is over.

Irrigation and cultural labour. In irrigated crops plots, if there is pumping equipment at the exploitation site, the plants are watered during their emergence. After sowing, no cultural work is done given the closeness of the cultivated rows and the fast vegetative growth of the plant, conditions under which weeds find no appropriate growth environment. In a short time, the crop reaches a high plant density and the plants compete with the weeds (Napoli *et al.*, 1994). Figure 1.4k shows the crop uniformity and the density reached in a buckwheat plot. Figure 1.4l shows the fruit.

Harvest – yield. Harvest takes place when 75% of the seed is mature (Figure 1.4m). From the sowing to the harvest, 75 to 80 days go by for short-cycle varieties, and 120 days for long-cycle varieties. Harvesting is done in the morning when the crop is wet with dew, thus decreasing shattering losses. To reach all flowering levels, plants are cut in their lower stem. The harvest equipment cuts and puts the cut plants into rows (Figure 1.4n).

Vegetal biomass is left in the field to dehydrate and when it reaches a humidity of 14–16%, it is threshed. Then, it is cleaned using sieves to remove dirt and vegetable waste. In the storage section, the clean fruit (Figure 1.4o) is stored at 14% moisture in bags that are placed on pallets raised 15 cm above the ground. The environment must be kept clean and pest control for weevil, woodworm and rodents must be carried out. The yield is highly variable and it fluctuates between 600 and 2500 kg/ha.

1.3.4.4 Diseases and Pests

The research carried out in Cantabria, Spain, by Garcia Menendez (2014) revealed the existence of neither diseases nor pests. In the trial conducted in Córdoba, Argentina, by Dionisi (2012), the infections detected had no major impact on production. In crop trials carried out in Cerro Azul, Misiones, Argentina, Napoli *et al.* (1994) observed the following diseases, which occasionally affected the crops in northeast Argentina:

- *Rhizoctonia* sp., a basidiomycete fungus that develops in winter time. It attacks primarily the roots, neck and hypocotyls of plants and leaves in contact with wet soil. In adult plants, it causes damping off, root rot and stem canker. Blight is observed in the lower leaves near the soil. Plants die soon after emerging, mainly in wet soils. Control is conducted with antagonistic fungi *Trichoderma harzianum* (Agrios, 1996).
- *Ramularia* sp., a fungus that forms conidia. It develops in humid environments at 20 °C and does not thrive in temperatures above 27 °C. The leaves show white spots that turn to light brown. A late infection does not affect the yield; early attacks cause defoliation and production losses due to photosynthetic activity reduction. The infection and its development are observed under constant rainfall conditions.
- Aster yellow is a mycoplasma-like organism that leads to bast necrosis with growth interruption. If the plant survives the infection, the flowers show an abnormal ramification phenomenon and calyx hypertrophy; the petals turn greenish or stunt growth; the stamens become sterile and the carpels gain foliaceous structure. It is passed on by vectors: major epidemics are related to the presence of wild plants as reservoirs and to the proliferation of cicadellidae vectors. Control involves eliminating reservoir plants and increasing parasitoids, such as hymenoptera from the *dryinidae* and *mymaridae* families.
- *Pests*. It has been observed that, before the harvest takes place, crops – especially lodging plants – can be attacked by ants, aphids and worms. They can also be damaged by birds and rodents. Control must be enhanced by increasing the activity of natural enemies of the pests that affect the crops, among which there are other insects, fungi, bacteria and pathogenic viruses (Lampkin, 2001).
- *Ants*. Major damage could be caused mostly in times of drought because buckwheat is the only crop that continues growing. Preventive control of ants' nests should be done in the plot to be cultivated and in the outlying strips.
- *Aphids*. Biological pest control is advised, favouring the development of grub and adult coccinellidae, microhymenopterae, carabidae and grub chrysopidae, syrphidae and mantidae nymphs, all of which are voracious natural enemies that attack aphids, butterfly eggs and lepidopter caterpillars.

1.3.5 World Production of Buckwheat

According to a study conducted by Fantasía (2009), the world's buckwheat production reached 3 000 000 tons with annual fluctuations. Buckwheat-producing countries are also the largest consumers: China produces 55% of the world's total production; Russia, 20%; Ukraine, 15%, and Poland, 3%. American producing countries such as the United States of America, Canada and Brazil are exporters.

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2

Structure and Composition of Kernels

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2.1 Introduction

The three major groups of pseudocereals distributed worldwide are amaranth, buckwheat and quinoa. Amaranth and quinoa were widely used in Mesoamerica throughout the pre-Hispanic period and were part of the diet of the Aztecs, Mayas, Incas and other pre-Colombian civilizations. However, after the Spanish conquest their cultivation was discouraged due to their association with the traditional cultures and religions (De la Cruz Torres *et al.*, 2008).

The genus *Amaranthus* L. contains more than 60 species. The main amaranth species being cultivated for their seeds and most used for human nutrition are *A. caudatus* in Peru and other Andean countries, *A. cruentus* in Guatemala and *A. hypochondriacus* in Mexico (Bressani, 2003). Quinoa belongs to the Amaranthaceae family and is a close relative of the amaranths. Quinoa (*Chenopodium quinoa*) was a staple food of the ancient civilizations of the Andes of South America, and is nowadays mainly grown in the Andean Countries of Peru and Bolivia. Buckwheat (*Fagopyrum* spp.) is one of the traditional crops cultivated in Asia, Central and Eastern Europe. Two species of buckwheat are cultivated for food consumption, *Fagopyrum esculentum* (common buckwheat) and *Fagopyrum tartaricum* (tartary buckwheat) (Ikeda, 2002; Mazza and Oomah, 2003). Common buckwheat is the most common cultivated buckwheat species and it is primarily consumed in Asian countries (Wijngaard and Arendt, 2006; Vojtíšková *et al.*, 2012).

Unlike true cereals such as wheat (*Triticum* spp) or rice (*Oryza sativa*), pseudocereals are dicotyledonous species that produce grainlike seeds with function and composition that resemble of those formed by cereals. Pseudocereals are essentially starchy crops that may contain significant quantities of protein and oil. These constituents determine the suitability for a specific end use (Baltensperger, 2003).

The botanical classification of pseudocereals is shown in Table 2.1.

2.2 Gross Structural Features

Pseudocereal grains are a good source of proteins, amino acids, vitamins, minerals and polyunsaturated fatty acids (Alemayehu *et al.*, 2015). In amaranth and quinoa the

Pseudocereals: Chemistry and Technology, First Edition. Edited by Claudia Monika Haros and Regine Schoenlechner.

Table 2.1 Botanical classification of cereals and pseudocereals.

	CEREALS							PSEUDOCEREALS				
Name	**WHEAT**	**RYE**	**BARLEY**	**OAT**	**RICE**	**CORN**	**SORGHUM**	**MILLET**		**AMARANTH**	**QUINOA**	**BUCKWHEAT**
Class	*Monocotyledoneae*										*Dicotyledoneae*	
Order	*Poales*										*Caryophyllales*	
Family	*Poaceae*									Amaranthaceae		Polygonaceae
Subfamily	*Pooideae*				*Bambusoideae*		*Panicoideae*			*Amaranthoideae*	*Chenopodioideae*	*Polygonoideae*
Tribe	*Triticeae*			*Poeae*	*Oryzeae*	*Andropogoneae*		*Paniceae*		*Amarantheae*	*chenopodieae*	*Fagopyreae*
Genus	*Triticum*	*Secale*	*Hordeum*	*Avena*	*Oryza*	*Zea*	*Sorghum*	*Pennisetum*	*Panicum*	*Setaria*	Paspalum	*Amaranthus*	*Chemopodium*	*Fagoryrum*
Species	*T. aestivum*, *T. aestivum spp. spelta*, *T. durum*	*S. cereale*	*H. vulgare*	*A. sativa*	*O. sativa*	*Z. mays*	*S. bicolor*	*P. glaucum* (pearl millet)	*P. miliaceum* (proso millet)	*S. itálica* (foxtail millet)	*P. scrobiculatum* (kodo millet)	*A. caudatus*, *A. cruentus*, *A. hypochondriacus*	*Ch. quinoa* Willd, *Ch. pallidicaule* Aellen (kanigua/kanihua/canihua), *Ch. nuttalia* Safford	f.tartarum f.esculentum Moench

Source: Adapted from Berghofer and Schoenlechner (2007) and Moreno *et al.* (2014).

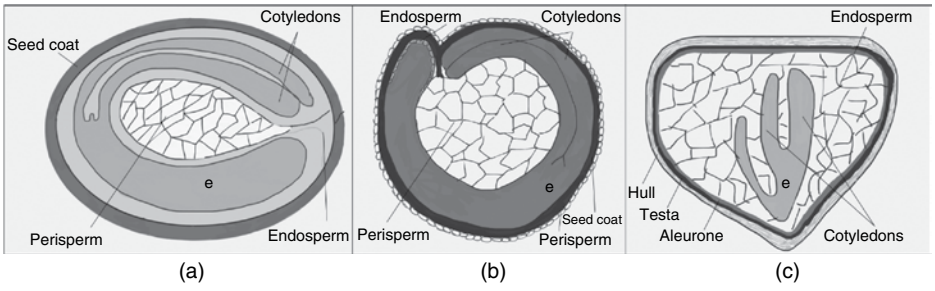

Figure 2.1 Longitudinal sections of seed structures of the three major groups of pseudocereals: (a) amaranth, (b) quinoa, and (c) buckwheat; **e**, embryo. Adapted from Prego *et al*. (1998) and Valcárcel-Yamani *et al*. (2012).

percentage of bran fraction (which is formed by a seed coat surrounding a starch-rich perisperm, and a campylotropus embryo) is higher in comparison with common cereals (Bressani, 2003). This characteristic explains why higher levels of protein and fat are present in these seeds (Figure 2.1).

The main parts of buckwheat kernels (where perisperm is absent) include: the hull (that may be glossy or dull, brown, black, or grey), the testa, the protein-rich aleurone layer, the central part of the starchy endosperm that occupies the major portion of the seed, and the embryo, embedded in the centre of the endosperm and includes the two cotyledons (Figure 2.1).

2.3 Physical Properties

The physical properties of seeds, such as size, surface area, and volume, are required in different handling and processing operations and are also needed as input parameters for the prediction of transport properties and drying rates of grains through simulation models (Abalone *et al.*, 2004). The knowledge of the morphology and size distribution of kernels is essential to design effectively the equipment for cleaning, grading, and separation (Vilche *et al.*, 2003). Taking into account the gravimetric properties of kernels is important when designing equipment related to aeration, drying, storage and transport (Vilche *et al.*, 2003). Bulk density determines the capacity of storage and transport systems, while true density is useful for separation equipment. Seed porosity determines the resistance to airflow during aeration and drying of kernels.

Table 2.2 gives a tabulation of known physical properties of pseudocereal kernels comparing to wheat. It is known that most of the properties vary with differences in moisture content and from variety to variety, year to year, and region to region of production (Watson, 1991; Parde *et al.*, 2003; Vilche *et al.*, 2003; Abalone *et al.*, 2004; Babić *et al.*, 2011). Compared with cereal grains, such as wheat and corn, pseudocereals have shorter size and completely diverse shapes (Figure 2.2), as well as different physical and chemical properties (Tables 2.2–2.5).

Due to the smallness of pseudocereal grains, conventional drying systems are not suitable for the characteristics of these seeds. Proper postharvest handling is critical for producing high quality grain and appropriate technology should be developed (Abalone *et al.*, 2004).

Table 2.2 Physical properties and geometrical dimensions of wheat and pseudocereal seeds.

Parameter	Units	*Amaranthus cruentus*[a]	*Chenopodium quinoa* Willd[d] L/M/S[j]	Buckwtheat[e] varieties Kt/Kb/Ma[l]	Wheat[i] varieties S/D/N[m]
Moisture	% dm	7.7–43.9 9.5–43.6	4.6–25.8 15.0	14.8–17.9/14.8–17.9/13.0–17.0[k]	15.8/15.8/16.4
1000-seed mass	g	0.79[b], 1.2[c]	2.5–3.1	20.7[f], 24.2/25.3/27.0[gk]	46.2/45.9/40.0
Specific volume	m^3/kg	$0.78–1.10\times10^{-3}$	n.r.	n.r.	n.r.
Bulk density	kg/m^3	840–720 820–867[b]	747–667 n.r.	603–584/594–603/608–593 652/705/704[gk]; 722–801[h]	791/789/732
True density[a,d,i]/compacted density[e]	kg/m^3	1390–1320	928–1188	612–590/601–601/606–594	1104/1151/1076
Porosity	%	0.40–0.45	0.194–0.438	n.r.	0.283/0.315/0.320
Length	mm	1.35–1.50	2.045/1.889/1.691[j]	n.r.	5.46/5.37/5.38
Width	mm	1.22–1.37	2.015/1.885/1.689[j]	n.r.	2.56/2.47/2.62
Thickness	mm	0.81–0.93	0.930/0.980/0.973[j]	n.r.	2.12/2.18/2.43
Equivalent diameter	mm	1.10–1.24	1.394–1.607	n.r.	3.09/3.06/3.24
Sphericity		0.81–0.83	0.77–0.80	n.r.	0.57/0.57/0.60
Volume	mm^3	0.55–0.76	n.r.	n.r.	n.r.
Equivalent sphere area	mm^2	3.26–4.04	n.r.	n.r.	30.07/29.64/33.20
Oblate spheroid area	mm^2	3.59–4.43	n.r.	n.r.	n.r.
Solid of revolution area	mm^2	3.60–4.47	n.r.	n.r.	n.r.

(Continued)

Table 2.2 (Continued)

Parameter	Units	*Amaranthus cruentus*[a]	*Chenopodium quinoa* Willd[d] L/M/S[j]	Buckwtheat[e] varieties Kt/Kb/Ma[l]	Wheat[i] varieties S/D/N[m]
Coefficient of friction		n.r.	0.211–0.265	0.26–0.31/0.32–0.29/0.21–0.19	n.r.
Plywood		n.r.	0.145–0.240	0.25–0.29/0.28–0.28/0.18–0.16	0.359/0.325/0.357
Galvanized iron[d]/steel[e]/metal sheet[i]		n.r.	n.r.	0.38–0.43/0.40–0.40/0.25–0.26	n.r.
Concrete					
Angle of repose	degrees	22.7–30.6[b]	18–25	23.6–26.7/22.5–24.7/21.3–25.1	n.r.
Thermal velocity	m/s	n.r.	0.6–1.02	n.r.	n.r.

a) Data from Abalone *et al.* (2004);
b) Ogrodowska *et al.* (2011);
c) Brust *et al.* (2014);
d) Vilche *et al.* (2003);
e) Parde *et al.* (2003);
f) Brust *et al.* (2014) of Tartary buckwheat[i]
g) Stempińska and Soral-Śmietana (2006), varieties Panda/Kora/Luba, moisture: 11.4/11.4/11.3%, respectively;
h) Zhu *et al.* (2013), moisture range: 11.1–17.1% in wet basis;
i) data from Babić *et al.* (2011);
j) L//M/S: Large > 2.0 mm (27.4%) / medium 1.7–2.0 mm (72.3%) / small < 1.7 mm (0.3%);
k) percentage wet basis;
l) Kt/Kb/Ma: Simonida/Dragana/NS40S varieties of *Fagopyrum esculentum* Moench;
m) S/D/N: Simonida/Dragana/NS40S varieties of *Triticum aestivum*, n.r.: not reported.

Table 2.3 Chemical composition of wheat and pseudocereals.

	Units	Amaranth	Quinoa	Buckwheat	Wheat
Protein	% d.b.	14.0(f:5.85)[b], 14.0–14.8(f:5.85)[g], 14.6(f.5.8)[f], 14.9(f:5.70)[c], 15.2[e], 16.5(f:5.85)[a],	11.0(f:5.70)[d], 12.8–13.5(f:5.77)[g], 13.3[e], 13.8(f:5.8)[f], 16.5[h]	10.9[e], 11.3–14.6(f: 5.7)[i], 11.9–14.2(f.6.25)[k], 12.3/15.2(f:5.70)[j], 12.5(f:5.70)[a],	11.6(f:5.70)[c], 11.7[e], 14.3(f:6.25)[h],
Lipids	% d.b.	5.6[c], 5.7[a], 5.9–6.0[g], 6.0[b], 8.0[e], 8.8[f],	4.1–5.8[g], 5.0[f], 5.2[a], 6.3[h], 7.5[d], 7.5[e]	1.3–2.3[i], 2.1[a], 2.1–2.6[k], 2.7[e], 3.0–3.4[i]	1.7[c], 2.0[e], 2.3[h]
Starch	% d.b.	55.1[f], 61.4[a], 67.3[e]	64.2[d], 66.9–70.4[g], 67.4[f], 69.0[e]	58.5/69.4[j],58.9[a], 67.2[e]	61.0[e], 78.4[h]
Dietary Fiber	% d.b.	11.1[f], 20.6[a],	3.8[h], 6.72[d], 12.9[f], 14.2[a], 14.6–19.7[g]	6.7–9.9[i], 29.5[a]	2.8[h], 6.5[g]
Ash	% d.b.	2.8[a], 2.4[b], 2.9[c], 3.3[f], 2.4–2.6[g]	2.7[a], 2.7[d], 3.8[h], 3.3[f], 2.3–2.5[g]	1.4–1.9[k], 2.1[a], 3.9/1.7[j],	1.4[c], 2.2[h]

d.b. dry basis; f: nitrogen to protein conversion factor used.

a) Data from Alvarez-Jubete *et al.* (2009);
b) Sanz-Penella *et al.* (2013) of *A. cruentus*;
c) García-Mantrana *et al.* (2014) of *A. cruentus* and *T. aestivum* L.;
d) Iglesias-Puig *et al.* (2015);
e) Souci *et al.* (2000) of *A. cruentus*, abrased quinoa, *F. escutentum* and *T. aestivum* L.;
f) Valcárcel-Yamani *et al.* (2012);
g) own measurements from *Amaranthus* spp., real quinoa and wheat;
h) Koziol (1992),
i) Izydorczyk *et al.* (2014) of whole groat buckwheat;
j) Wronkowska and Haros (2014) of *F. escutentum* (common buckwheat) with/without hulls;
k) Mazza (1993) of dehulled buckwheat cultivars.

2.4 Kernel Structures

Structurally the seeds of amaranth, quinoa and buckwheat are composed of three main parts including the endosperm, embryo, and seed coat. The endosperm is the primary starch storage portion that also contains proteins. The embryo is the oil-storage portion, high in protein and minerals. The seed coat, also called pericarp or bran, consists mainly of cellulose and hemicellulose with some protein and lignin (Baltensperger, 2003). Relative proportions of the three components vary among the different pseudocereals.

The amaranth seed is smooth, shiny and slightly flattened with a lens-shaped form. The size varies between 1.3 and 1.7 mm in length and 0.9 and 1.3 mm in width while the weight is in the usual range between 0.6 and 1.0 mg. Depending on the species the colour can be white, yellow, pink, brown, red or black. In size seeds are smaller than common cereal grains or pseudocereal seeds, such as wheat, corn or buckwheat (Figure 2.2, Table 2.2).

The fruit of quinoa is an achene. It produces small, circular-shaped seeds similar to a smoothed sphere, with diameters that vary between 1.0–2.6 mm, and 250–500 seeds

Table 2.4 Mineral composition an phytic acid concentration in wheat and pseudocereal kernels.

Chemical compound	Units	Amaranth	Quinoa	Buckwheat	Wheat
Macroelements					
Ca	mg/100 g d.b.	180[a], 204[b]	32.7[e], 32.9[a], 49.7[m], 148.7[f]	14.8[m], 18.1–22.1[g], 60.9[a]	30.8[m], 34.8[a], 48.0[h], 50.3[f]
Mg	mg/100 g d.b.	269[b], 279[a]	207[a], 230[m], 250[f], 270[h]	173.6[m], 200–210[g], 203[a]	78.3[m], 96.4[a], 152[h], 169.4[f]
P	mg/100 g d.b.	530[b]	384[f], 442[m]	260–360[g], 279[m]	204[m], 387[h], 468[f]
Na	mg/100 g d.b.	0.82[b]	3.7[m], 11.5[h]	1.1[m]	2.0[m], 4.0[h]
K	mg/100 g d.b.	470[b]	555[m], 927[f]	402.3[m], 410–440[g]	400[m], 578[f]
Microelements					
Zn	mg/100 g d.b.	1.6[a], 4.2[b]	1.8[a], 3.3[m], 4.4[f], 4.8[h], 5.0[e]	1.0[a], 1.9[m], 2.2–2.3[g]	1.2[a], 1.8[m], 3.3[h], 4.7[f]
Fe	mg/100 g d.b.	8.2[b], 9.2[a]	4.7[e], 5.4[m], 5.5[a], 13.2[f]	2.1–2.5[g], 2.9[m], 4.7[a]	2.7[m], 3.3[a], 3.8[f], 4.6[h]
Cu	mg/100 g d.b.	0.69[b]	0.77[m], 3.7[h], 5.1[f],	0.37–0.46[g], 0.51[m]	0.4[m], 0.6[h], 0.7[f]
Mn	mg/100 g d.b.	3.66[b]	1.35[m], 33.0[a]	1.00–1.02[g], 1.18[m]	2.34[m]
Phytic acid	μmol/g d.b.	4.8/6.7[i], 7.6–8.8/8.2–9.4[j], 13.3[c], 21.1[b]	9.3[e], 13.4[l], 15.2[k], 20.3[m]	9.6[m]	7.5[c], 11.7[m]

d.b. dry basis;
a) Data from Alvarez-Jubete *et al.* (2009);
b) Sanz-Penella *et al.* (2013) of *A. cruentus*;
c) García-Mantrana *et al.* (2014) of *A. cruentus* and *T. aestivum* L.;
e) Iglesias-Puig *et al.* (2015);
f) Koziol (1992);
g) Mazza (1993) of dehulled buckwheat cultivars;
h) Repo-Carrasco *et al.* (2003);
i) Colmenares de Ruiz and Bressani (1990) of *A. cruentus*/*A. caudatus*, respectively;
j) Teutonico and Knorr, 1985 of *A. cruentus*/*A. hypochondriacus*;
k) Ruales and Nair (1993a);
l) Cook *et al.* (1997);
m) Hager *et al.*, 2012 of commercial whole flours.

Table 2.5 Vitamin concentration of wheat and pseudocereal kernels

Vitamin	Units	Amaranth	Quinoa	Buckwheat	Wheat
β-Carotene (A)	mg/100 g d.b.	n.r.	0.39[b]	0.21[f*]	0.02[b]
Thiamine (B_1)	mg/100 g d.b.	0.07–0.10[e]	0.29–0.36[d], 0.38[b], 0.40[c]	0.46[f]	0.55[b]
Riboflavin (B_2)	mg/100 g d.b.	0.19–0.23[e]	0.20[g]; 0.30–0.32[d], 0.39[b]	0.14[f]	0.16[b]
Niacin (B_3)	mg/100 g d.b.	1.17–1.45[e]	1.24–1.52[d], 1.60[b]	1.80[f]	5.88[b]
Pantothemic acid (B_5)	mg/100 g d.b.	n.r.	n.r.	1.05[f]	n.r.
Pyridoxine (B_6)	mg/100 g d.b.	n.r.	0.487[d]	0.73[f]	n.r.
Total Folates (B_9)	µg/100 g d.b.	0.053–0.073[a], 0.102[g**]	0.08[g**]; 0.13[a], 0.18[d]	0.025[a]	0.014[a], 0.040[g**]
Ascorbic acid (C)	mg/100 g d.b.	3.36–7.24[e]	0.18[d], 4.0[b], 16.4[c]	5.00[f]	0.0–1.5[b]
Total tocopherols (E)	mg/100 g d.b.	4.5[g***], 5.7[j], 10.0–12.9[h***]	8.7[j]	5.5[f,j,l]	1.03[l]
α-Tocopherol (E)	mg/100 g d.b.	0.30–1.57[i***], 24.8[k]	2.6[c], 5.37[b]	0.085[l]	0.61[l], 1.15[b]
β-Tocopherol (E)	mg/100 g d.b.	n.d.[i], 54.6[k]	n.r.	n.d.	0.42[l]
γ-Tocopherol (E)	mg/100 g d.b.	n.d.[k]	5.3[c]	5.14[l]	n.d.[l]
δ-Tocopherol (E)	mg/100 g d.b.	0.8[k]	n.r.	0.24[l]	n.d.[l]
α-Tocotrienols (E)	mg/100 g d.b.	n.d.[k]	n.d.[c]	n.d.[l]	0.11[l]
β-Tocotrienols (E)	mg/100 g d.b.	n.d.[k], 0.50–1.15[i***]	0.3[c]	n.d.[l]	2.37[l]
γ-Tocotrienols (E)	mg/100 g d.b.	n.d.[k], 0.10–0.87[i***]	n.r.	n.d.[l]	n.d.[l]

d.b. dry basis, n.r.: not reported, n.d.: not detected

a) Data from Schoenlechner *et al.* (2010) of commercial whole flours of *Amaranthus* spp.; *Chenopodium quinoa*, *Fagopyrum esculentum* and *Triticum aestivum*;
b) Koziol (1992);
c) Ruales and Nair (1993a);
d) Abugoch (2009);
e) Becker *et al.* (1981);
f) Wijngaard and Arendt (2006) of common buckwheat,
g) Schoenlenchner *et al.* (2007);
h) Bruni *et al.* (2002) *of A. caudatus*;
i) Lehmann *et al.* (1994) of *Amaranthus* spp;
j) Alvarez-Jubete *et al.* (2010);
k) Leon-Camacho *et al.* (2001) expressed in mg/100g of oil of *A. cruentus*;
l) Zielinski *et al.* (2001);
* Carotenoids;
** Folic acid;
*** Unit: mg/100g of seeds

Figure 2.2 (a) Amaranth; (b) quinoa; (c) buckwheat; (d) wheat.

per gram (Valencia-Chamorro, 2003; Vilche *et al.*, 2003). The major dimensions of the seed, the length and the width, are approximately equal due to the round longitudinal section (Vilche *et al.*, 2003; Table 2.2). There are hundreds of varieties of quinoa and the pericarp ranges in colour from white, yellow, orange and red, through to brown and black (Figure 2.3; Saturni *et al.*, 2010). According to Jacobsen and Stølen (1993), wild species often have a black pericarp.

The buckwheat kernel is in the form of an achene, being a single seed enclosed in an indehiscent pericarp that fits tightly around the seed. The achene is three-angled 4–9 mm long, the angles being acute, and has the form of a pyramid with the base rounded (Baltensperger, 2003; Izydorczyk *et al.*, 2014). The buckwheat hull or pericarp varies from silver gray to brown or black in colour and is hard and thick, with the surface polished and shining, glossy or dull. It separates readily from the mealy endosperm. The relatively large embryo, rich in proteins, is central, dividing the soft, white endosperm into two parts, the cotyledons being broad. The surrounding testa is membranous and light yellowish-green in colour (Baltensperger, 2003; Izydorczyk *et al.*, 2014). The dehulled achenes of buckwheat (groats) vary slightly in shape and size depending on the species and variety (Izydorczyk *et al.*, 2014). Groats of tartary buckwheat are significantly smaller and rounder than those of common buckwheat.

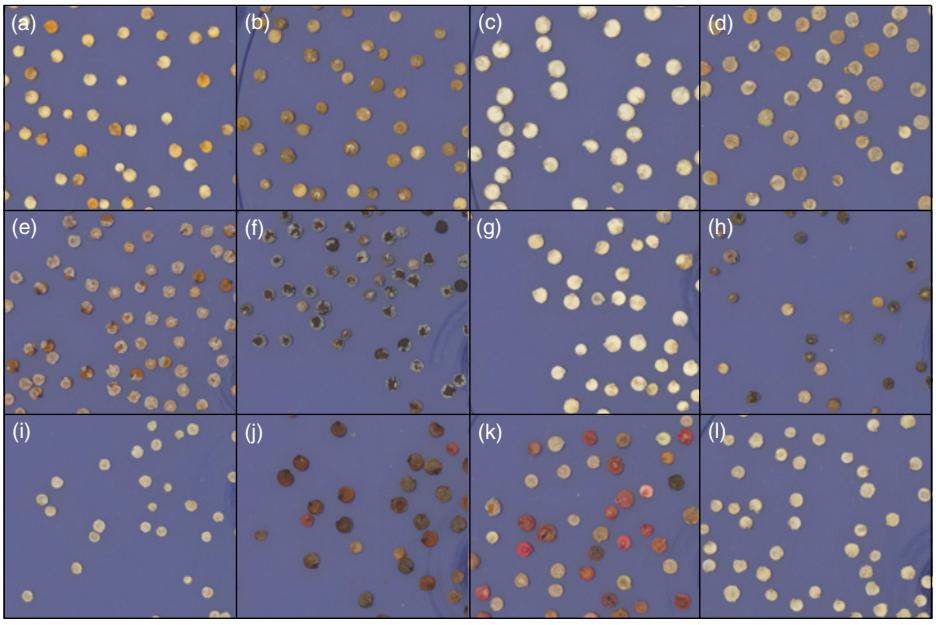

Figure 2.3 Quinoa seeds are diverse in size (1–2.6 mm), colour (green, white, off-white, opaque white, yellow, bright yellow, orange, pink, red vermilion, cherry, coffee, gray and others), composition and shape (conical, cylindrical or ellipsoidal). (a) PI 510535; (b) PI 614987; (c) PI 614916; (d) PI 614886; (e) PI 614880; (f) PI 510549; (g) PI 510544; (h) PI 510536; (i) PI 510533; (j) PI 478415; (k) PI 470932; (l) PI 433232; accessions were obtained from the US National Plant Germplasm System (ARS-USDA, United States). (*See color plate section for the color representation of this figure.*)

2.5 Chemical Composition of Kernels

The proximate composition of pseudocereals is shown in Table 2.3. The chemical composition of proteins, lipids, carbohydrates, fibre and bioactive compounds are well covered in Chapters 3–6. This section focuses on the proximate composition of pseudocereals and on compounds less extensively described in Chapters 3–6.

2.5.1 Proteins

The nutritional value of pseudocereals is mainly connected to their protein content (Schoenlechner *et al.*, 2008). Pseudocereal grains are an extremely valuable source of proteins, which have a well balanced amino acid composition, with a particularly high content of lysine and sulfur-containing amino acids. The proteins in amaranth, quinoa and buckwheat are composed mainly of globulins and albumins, and contain very little or no storage prolamin proteins, which are the main storage proteins in cereals, and the toxic proteins in coeliac disease (Wijngaard and Arendt, 2006; Alvarez-Jubete *et al.*, 2010).

Usually, amaranth has higher protein content than quinoa or buckwheat (Table 2.3). The essential amino acid content is high and the amino acid composition is better balanced than in most cereals (Ballabio *et al.*, 2011). However, the protein content and amino acid patterns depend on the genotype and growing conditions (Schoenlechner *et al.*, 2008). Approximately 65% of the proteins are located in the germ and seed coat,

and 35% in the endosperm (Saunders and Becker, 1984). The protein composition and amino acid profile are described in Chapter 5.

The protein content of quinoa is higher than cereals (Table 2.3). The nutritional value of quinoa protein is comparable to that of milk protein (Ranhotra *et al.*, 1993). Quinoa has a high biological value (83%) because of its high concentration of proteins, providing all of the essential amino acids (Ruales and Nair, 1992; Abugoch, 2009; Gonzalez *et al.*, 2012). Relative to cereal grains, quinoa proteins are particularly high in lysine, the limiting amino acid in most cereal grains. Their essential amino acid balance is excellent because of a wider amino acid range than in cereals and legumes that includes not only higher lysine contents but also methionine (Ruales and Nair, 1993b; Abugoch, 2009). The protein composition and amino acid profile of quinoa are also described in Chapter 5.

Buckwheat is a highly nutritious pseudocereal known as a dietary source of protein with favorable amino acid composition mainly in the aleurone layer and embryo (Bonafaccia *et al.*, 2003; Izydorczyk *et al.*, 2014). Due to high lysine content, buckwheat proteins have higher biological value than cereal proteins. Its protein composition and amino acid profile are also extensively described in Chapter 5.

2.5.2 Carbohydrates

The most common monosaccharides in kernels are glucose, fructose, arabinose and xylose, whereas the most important disaccharides are sucrose and maltose. In pseudocereals, the content of mono- and disaccharides is somewhat higher than in common cereals, and they are found in small amounts (Berghofer and Schoenlechner, 2007). Kernels are also sources of complex polysaccharides. The polysaccharides present in cereals and kernels are starch, nonstarch polysaccharides and resistant starch. Nonstarch polysaccharides present in kernels consist mainly of cellulose, β-glucans and hemicelluloses, which are included as dietary fibre in conjunction with resistant starch. The dietary fibre content of pseudocereals lies within the range of other cereals (Table 2.3).

Starch is the most important carbohydrate in all plants and occurs typically as granular form of various shapes and sizes (Valcárcel-Yamani *et al.*, 2012). Pseudocereals present starch percentage between 55.1 and 70.4 (Table 2.3). In amaranth, starch comprises the main component of carbohydrates, but is usually found in lower amounts than in cereals (Valcárcel-Yamani *et al.*, 2012; Table 2.3). It is located in the perisperm. The amaranth starch granules (1–3 μm) are smaller than those found in other cereal grains (Berghofer and Schoenlechner, 2007; Valcárcel-Yamani *et al.*, 2012). The amylose content of amaranth starch is lower than cereal starches (0.1–11.1%), and normal and waxy-type starches occur in the same species of amaranth (Stone and Lorenz, 1984; Schoenlechner *et al.*, 2008). It is also reported that there are many differences in the amylose / amylopectin ratio due to cultivation and environmental effects (Stone and Lorenz, 1984).

In quinoa, starch is also the most important carbohydrate in the grain (Table 2.3). Granules of quinoa starch have a polygonal form with a diameter of 1.5–3.0 μm, being smaller than starch of common grains (Koziol, 1992; Vega-Gálvez *et al.*, 2010). The amylose content (11.0–12.4%) is lower than that found in rice, corn or wheat (Koziol, 1992).

Depending on their location on the endosperm, buckwheat starch granules have a round or polygonal shape and are generally much smaller (2–14 μm diameter) than granules of wheat, barley or corn (Izydorczyk *et al.*, 2014). The amylose content is

extraordinarily high, it can reach values up to 50%, especially in *F. esculentum* (Berghofer and Schoenlechner, 2007).

The composition of carbohydrates and dietary fibre is described in Chapters 3 and 4, respectively.

2.5.3 Lipids

Pseudocereal seeds have a similar distribution of lipids, in the form of lipid bodies. The greatest amounts are found in the embryo and the endosperm for amaranth and buckwheat, whereas in quinoa they are found in the embryo and perisperm.

Lipid content in amaranth and quinoa is between two and three times higher than in buckwheat and common cereals such as wheat (Table 2.3; Alvarez-Jubete *et al.*, 2010). In general, pseudocereal lipids present a high degree of unsaturation (between 75% and 86%) (Wijngaard and Arendt, 2006; Valcárcel-Yamani *et al.*, 2012). Linoleic acid is the most abundant fatty acid in pseudocereals (47.5–47.8, 48.2–56.0, and 36.6–39.0%), followed by oleic acid (23.7–32.9, 24.5–26.7, and 35.2–37.0%) and palmitic acid (12.3–20.9, 9.7–11.0, and 15.6–19.7%), for amaranth, quinoa and buckwheat, respectively (Wijngaard and Arendt, 2006; Valcárcel-Yamani *et al.*, 2012). Squalene, a highly unsaturated open-chain triterpene, which is the biochemical precursor of the whole family of steroids, is present in high levels in amaranth (1.9–11.2%). Between 3.4% and 5.8% of squalene was also found in the lipid fraction of quinoa seeds (Valcárcel-Yamani *et al.*, 2012). The lipid composition of pseudocereals is described in Chapter 6.

Amaranth and quinoa lipids are reported to be generally stable against oxidation due to the protective effect of tocopherols, and despite of their high fat content and degree of unsaturation (Alvarez-Jubete *et al.*, 2010). On the other hand, buckwheat flour has a higher risk of deterioration due to the lipid composition (Tomotake *et al.*, 2000).

2.5.4 Minerals

Table 2.4 shows the mineral content of pseudocereals and wheat grains. The pseudocereals are highly nutritious kernels known as a dietary source essential minerals and trace elements such as calcium (Ca), magnesium (Mg), iron (Fe), and manganese (Mn) (Ballabio *et al.*, 2011; Sanz-Penella *et al.*, 2013; Iglesias-Puig *et al.*, 2015; Alvarez-Jubete *et al.*, 2009, 2010).

Coloured amaranth seeds genotypes contained higher Mg and Ca concentrations than white seeds genotypes (Mustafa *et al.*, 2011). However, seed colour had no influence on potassium (K), sodium (Na) and phosphorous (P) concentrations. Although copper (Cu) and Fe are the most variable micro-minerals in amaranth, the seed colour does not have an effect on the concentration of either mineral (Mustafa *et al.*, 2011).

Many minerals in quinoa are found at concentrations greater than that reported for most grain crops (Vega-Gálvez *et al.*, 2010). It was found that the mineral concentrations of quinoa from different sources seem to vary dramatically due to the soil type and mineral composition and / or fertilizer application (Vega-Gálvez *et al.*, 2010). Minerals such as P, K, and Mg are located in the embryo, while Ca and P in the pericarp associated with pectic compounds of the cell wall (Vega-Gálvez *et al.*, 2010).

Buckwheat is a richer mineral source than many cereals (except for Ca) (Wijngaard and Arendt, 2006). Variations in mineral composition between cultivars and growth locations have been reported. Minerals such as P are mainly stored as phytates and Mg, Zn, and Co are bound to phytates in protein bodies. These storage compounds are

generally present in embryo tissues and the aleurone layer (Steadman *et al.*, 2001). Minerals such as Fe, Zn, Mn, Cu, Mo, Ni and Al are primarily localized in both the hull and seed coat, whereas Ca and B are present in hull fractions (Steadman *et al.*, 2001; Bonafaccia *et al.*, 2003; Skrabanja *et al.*, 2004; Wijngaard and Arendt, 2006).

2.5.5 Vitamins

Table 2.5 shows the vitamin content of pseudocereals and wheat grains. Amaranth is a good source of riboflavin, vitamin C, folic acid and vitamin E (Dodok *et al.*, 1994; Gamel *et al.*, 2006; Schoenlechner *et al.*, 2010; Ballabio *et al.*, 2011). It contains α-, β- and δ-tocopherols and β- and γ-tocotrienols (Table 2.5). Among the tocopherols, α-tocopherol, which shows important antioxidant activity, is the most abundant in quinoa seeds according to Lehmann *et al.* (1994), whereas Leon-Camacho *et al.* (2001) reported a higher amount of β-tocopherol than α-tocopherol.

Quinoa also contains more carotene, riboflavin, tocopherols and folic acid than wheat, rice, oats and maize, and can supply the daily requirements of certain vitamins and several minerals for children between 1 and 3 years (Ruales and Nair, 1993a). Like amaranth, quinoa contains more riboflavin than cereals and it is particularly good source of vitamin E (α-tocopherol, γ-tocopherol, and β-tocotrienol) which contributes to the prolonged stability of the oil (Koziol, 1992; Ruales and Nair, 1993a; Schoenlechner *et al.*, 2008).

Buckwheat is also source of vitamins (Bonafaccia *et al.*, 2003). Thiamine is known to be strongly adhered to thiamine-binding proteins in buckwheat seeds (Rapala-Kozik *et al.*, 1999). In general, tartary buckwheat has higher levels of vitamin B and tocopherols than common buckwheat (Kim *et al.*, 2002; Bonafaccia *et al.*, 2003). It has been reported by Kim *et al.* (2002) that γ-tocopherol is the main tocopherol in buckwheat seeds; conversely the results of Przybilski *et al.* (1998) indicated that α-tocopherol is the main component. No tocotrienols have been detected in buckwheat seeds (Zielinski *et al.*, 2001). Differences have been attributed to different cultivars (Wijngaard and Arendt, 2006).

2.5.6 Bioactive Compounds

The presence of bioactive compounds has been found in amaranth, quinoa and buckwheat seeds. Polyphenols are important bioactive compounds associated with the prevention of degenerative diseases including cancer. Polyphenol compounds can be found in buckwheat as glycosides of the flavonols quercetin, apigenin or luteolin, glycosides of kaempferol and quercetin in quinoa or caffeic acid, *p*-hydroxybenzoic acid and ferulic in amaranth seeds (Álvarez-Jubete *et al.*, 2010). In amaranth, seed tocotrienols and squalene compounds have been associated with lower levels of cholesterol and triglycerides (Martirosyan *et al.*, 2007). Similar effects have been described for buckwheat (Tomotake *et al.*, 2000). In buckwheat seeds, fagopyritols (a source of *D*-chiro-inositol) have shown beneficial effects in patients with non-insulin-dependent diabetes (Steadman *et al.*, 2000). In quinoa, the presence of bioactive compounds (including phenolics and antioxidants) has been related to improvements in intestinal health (Carrion *et al.*, 2014). Other bioactive compounds found in the seeds of these pseudocereals, such as phytosterols or saponins (traditionally considered antinutrients), possess anticarcinogenic (Guclu-Ustundag and Mazza, 2007) and cholesterol lowering properties (Moghadasian and Frohlich, 1999).

The bioactive compound composition is widely described in Chapter 4.

2.5.7 Antinutritional Factors

2.5.7.1 Saponins

Saponins can form complexes with proteins and lipids, zinc and iron, and possess a haemolytic effect. They are only absorbed in small amounts, and their main effect is restricted to the intestinal tract (Schoenlechner *et al.*, 2008). They can increase membrane permeability, thus enabling their use for increasing food intake at the intestinal level or even for drug assimilation (Vega-Gálvez *et al.*, 2010). However, as previously mentioned, saponins also have health-promoting effects as anticarcinogenic, antibiotic / fungistatic, hypocholesterolemic, immune modulating, and anti-inflammatory effects (Koziol, 1992; Schoenlechner *et al.*, 2008).

One of the factors that limit the widespread utilization of quinoa is the bitter taste caused by the presence of saponins (Ruales and Nair, 1993b). Saponin concentrations estimated by afrosimetry (ability to produce foam in water), ranged from 0.01% to 5.6% in dry basis (Koziol, 1992). They are located in the outer layers of quinoa seeds for protecting against birds and insects (Ruales and Nair, 1993b, Valencia-Chamorro, 2003). Saponins are triterpene glucosides that consist of a linear arrangement of one to six hexose or pentose glycoside units joined to the sapogenin aglycone, which can be a steroidal or a triterpenoid aglycone (Ruales and Nair, 1993b). Quinoa saponins are soluble in methanol or water. Two major saponins were identified in quinoa seeds and also in quinoa bran. These are present in relatively high amounts (Ruales and Nair, 1993b). Saponin A corresponds to β-D-glucopyranosyl-[β-D-glucopyranosyl-(1-3)-α-L-arabino-pyranosyl-(1-3)]-3-β-23-dihydroxy-12-en-28-oate-30 methyl ester, and saponin-B corresponds to β-D-glucopyranosyl-[β-D-glucopyranosyl-(1-3)-α-L-arabino-pyranosyl-(1-3)]-3-β-23 dihydroxyolean-12-en-28-oate. The process of scrubbing and washing quinoa seeds to remove the bitter taste reduced the saponin A content by approximately 50% whereas saponin B was completely removed (Table 2.6). The saponins appeared to be mainly, but not entirely, in the outer layer of the seeds (Ruales and Nair, 1993b; Valencia-Chamorro, 2003). Another way to reduce saponin content is by breeding so-called sweet (low saponin content) quinoa species, around 0.02–0.04% (Mastebroek *et al.*, 2000; Schoenlechner *et al.*, 2008). On the other hand, amaranth seeds contain rather low amounts of saponins (around 0.09%). The low concentration of saponins in amaranths seeds and their relatively low toxicity guarantee that amaranth-derived products create no significant hazard to consumers (Schoenlechner *et al.*, 2008).

Table 2.6 Content of saponins in quinoa seeds (g/100g dry basis).

Saponin	Raw whole quinoa	Polished and washed quinoa	Bran
Saponin A	0.7	0.3	1.7
Saponin B	0.2	n.d.	0.6

Data from Ruales and Nair (1993b) of *Chenopodium quinoa* Willd, variety Latinreco-40057;
n.d. not detected;
HPLC method was used for the determination of the saponin content in quinoa seeds.

2.5.7.2 Phytic Acid

Whole grains contain significant amounts of phytic acid [*myo*-inositol (1,2,3,4,5,6)-hexakisphosphate, InsP_6] or its salts (phytates). Phytic acid intake has been reported to have favourable effects, such as antioxidant function, prevention of heart diseases and anticarcinogen effect, which it performs through its hydrolysis products (Haros *et al.*, 2009; Kumar *et al.*, 2010). However, it is a well known inhibitor of mineral, protein and trace element bioavailability (Hurell *et al.*, 2003). Phytates are strongly negatively charged and have excellent potential for complexing positively charged multivalent cations such as Ca, Mg, Zn, Cu and Fe. This characteristic has adverse effects on mineral bioavailability, owing to the formation, at physiological pH values, of insoluble complexes, which are nonabsorbable in the human gastrointestinal tract (Sandberg *et al.*, 1996; Lopez *et al.*, 2001). The negative health effects of phytates are more significant in developing countries and in risk populations due to their higher incidence of undergoing mineral deficiencies (Hurrell *et al.*, 2003).

Phytate content in various whole grains of the *Amaranthus* genus has been published, ranging from 4.8 to 21.1 μmol/g (Table 2.4). The high levels of phytates in amaranth grain / whole flours could affect negatively the bioavailability of Zn, Ca and Fe (Sanz-Penella *et al.*, 2013).

Saponins and phytic acid are the two main antinutrients present in quinoa seeds. Phytates in quinoa are mainly present in protein bodies of embryonic cells of the grain, approximately 60% of the total phytates (Ando *et al.*, 2002). The phytate content reported for quinoa seeds showed a wide variation (between 9.3 and 20.3 μmoles of phytic acid/g) (Table 2.4), that can be explained by the fact that the InsP_6 content in grain depends on many factors (Bohn *et al.*, 2008).

Buckwheat seeds generally contain higher amounts of phytic acid than legumes and cereals grains and is mainly concentrated in the bran (Steadman *et al.*, 2001).

Though pseudocereals show a favourable mineral composition, the high phytic acid levels may interfere in the mineral availability. This could be disadvantageous, especially for coeliac patients who often suffer from micronutrient deficiencies (Hager *et al.*, 2012). However, phytic acid can be enzymatically degraded by endogenous and exogenous phytases (*myo*-inositol hexakisphosphate phosphohydrolase), improving the nutritional value of the cereal / pseudocereal products (García-Mantrana *et al.*, 2014; Iglesias-Puig *et al.*, 2015). It was previously demonstrated that cereals / pseudocereals show endogenous phytase activity, which is especially high in wheat and buckwheat (Egli *et al.*, 2002). Under conventional processing conditions such as pasta or bread making, optimal conditions for the degradation of phytate are rarely reached (Hager *et al.*, 2012; Sanz-Penella *et al.*, 2013; García-Mantrana *et al.*, 2014; Iglesias-Puig *et al.*, 2015). However, sourdough fermentation provides optimum pH conditions for phytase activity as alternative for total phytic acid hydrolysis in bread (Zannini *et al.*, 2011; García-Mantrana *et al.*, 2015).

2.5.7.3 Protease Inhibitors

Protease inhibitors are proteins that form very stable complexes with proteolytic enzymes. Trypsin inhibitors are at such low levels in amaranth that they do not present a risk to the nutritional status (Bodroza-Solarov *et al.*, 2008). It was reported that quinoa contains small amounts of trypsin inhibitors, which are much lower than those found in commonly consumed grains and hence do not pose any serious concern (Vega-Gálvez *et al.*, 2010). However, the poor digestibility of buckwheat protein is due to different susceptibility of proteolytic action of buckwheat fractions, and antinutri-

tional components such as tannins and inhibitors (Wijngaard and Arendt, 2006). Several inhibitors were identified in buckwheat seeds such as protease inhibitors and also α-amylase inhibitor (Wijngaard and Arendt, 2006).

2.5.7.4 Oxalates

Grain amaranth can be considered a high oxalate source (178–278 mg/100g of amaranth), however, as most is in insoluble form, and due to its high Ca and Mg concentrations, oxalate absorbability could be low. These results should be confirmed by bioavailability studies (Gélinas and Seguin, 2007).

2.6 Conclusions

Due to the high nutritive value of their seeds, their genetic diversity and excellent adaptability to different environments, pseudocereals such as amaranth, quinoa or buckwheat are considered exceptional crops with the potential of contributing to food security worldwide. One of their most outstanding features is their favourable chemical composition, which includes a high content in functional substances such as proteins, vitamins, lipids and bioactive compounds, all associated with health-promoting effects. Nonetheless, in order to enable future product development (such as gluten-free products) further studies that evaluate their nutraceutical characteristics are needed.

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3

Carbohydrates of Kernels

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3.1 Introduction

Carbohydrates constitute the main fraction of cereals, pseudocereals, legumes, tubers and unripe fruits, accounting for up to 40–80% of the dry matter. Carbohydrates are used widely in many industrial products, for example in sugar and starch products, textiles and fibres. They are very important in nutrition because they are abundant and inexpensive and therefore they are the principal source of energy in the human diet. Carbohydrates are present in plants as structural or storage polysaccharides and as simple sugars or oligosaccharides.

Carbohydrates in kernels could be classified based on their polymeric structure into monosaccharides, oligosaccharides and polysaccharides. In food plants, two kinds of carbohydrates can be found: available and unavailable carbohydrates. The available carbohydrates are those digested and absorbed by humans, which include starch and soluble sugars. The unavailable carbohydrates are not digested by humans. These carbohydrates are the structural polysaccharides of the plant cell walls and other complex polysaccharides (Shelton and Jong Lee, 2000).

The most common monosaccharides in kernels are glucose, fructose, arabinose and xylose. Sucrose and maltose are the most important disaccharides in kernels. The content of these components in pseudocereals is somewhat higher than in common cereals. It is about 3–5% in quinoa and amaranth, whereas in cereals it is about 1–2% (Shelton and Jong Lee, 2000; Taylor and Parker, 2002).

Kernels are excellent sources of complex polysaccharides. Polysaccharides are polymers with more than 20 monosaccharide units (BeMiller and Whistler, 1996). Polysaccharides have interesting chemical and physical properties and these are used in many food products. Starch is the most important polysaccharide present both in common cereals and in pseudocereals. It is the principal source of energy in the human diet. The degree of digestion and absorption of starches is affected by a number of factors. In particular, food composition and processing affect the availability of carbohydrates. The other carbohydrates present in cereals and kernels are the nonstarch polysaccharides and resistant starch, which are classified as dietary fibre. Nonstarch polysaccharides present in kernels consist mainly of cellulose, beta-glucans and hemicelluloses.

Pseudocereals: Chemistry and Technology, First Edition. Edited by Claudia Monika Haros and Regine Schoenlechner.

Andean grains, quinoa (*Chenopodium quinoa*), kañiwa (*Chenopodium pallidicaule*) and kiwicha (*Amaranthus caudatus*) are very nutritious crops. Quinoa (*Chenopodium quinoa* Willd) is a seed crop of the *Chenopodiaceae* family. It was a very important crop for the Incas who called quinoa the 'mother grain', *chisiya mama* in Quechua, the native language of the Incas (National Research Council, 1989). Domestication of quinoa took place at least some 8000 years ago on the high plateau of the Andes near Lake Titicaca (Pearsall, 1992). Nowadays, quinoa is cultivated mainly in the Andean region from Colombia to the north of Argentina, with Peru and Bolivia as the most important producers. There are different types of quinoa (landraces) that have adapted under different environmental conditions. Quinoa can be cultivated at sea level, in Andean valleys, the Altiplano (high plateau) and places like the Bolivian salt flats. The varieties which grow on the Bolivian high plateau resist low temperatures (–8 °C), alkaline soils (pH 8) and salinity of 52 mS/cm (Mujica *et al*., 2004).

Kañiwa (*Chenopodium pallidicaule* Aellen) is closely related to quinoa; in fact it was considered a variety of quinoa until 1929 when it was classified as a different species (Gade, 1970). Kañiwa grows under very harsh environmental conditions, mainly in the Peruvian and Bolivian Altiplano. It is more resistant than quinoa against frost. In its native area, year-round temperatures average less than 10 °C and frost occurs during at least 9 months of the year. The frost resistance of kañiwa is probably due to its special anatomical structure, which protects kañiwa's flowers from damage at low temperatures (Tapia and Fries, 2007). Kañiwa is a very important crop for highland farmers: when other crops fail because of frost, kañiwa still provides food. The most intensive production of kañiwa occurs north of Lake Titicaca in the department of Puno in Peru. The department of La Paz is the main producer of kañiwa in Bolivia.

Domestication of amaranths as grain crops took place only in tropical America. Three species of domesticated grain crops were developed in pre-Columbian America: *Amaranthus caudatus*, *Amaranthus cruentus* and *Amaranthus hypochondriacus*. A crucial step in the evaluation of the domesticated grain amaranths was the selection by unknown ancient farmers of mutant forms in which the normal, wild type dark seeds had been altered to white seeds. This resulted in better flavoured grain with superior popping quality. The most important Andean species is *Amaranthus caudatus* Linnaeus. In Quechua, the local language in Peru, it is called 'kiwicha'. In Ecuador, it is known as 'sangoracha' and 'ataco' and in Bolivia as 'coimi' and 'millmi'. Buckwheat (*Fagopyrum esculentum* Mönch) was domesticated in south-east Asia. Two types of buckwheat are used around the world: common buckwheat (*Fagopyrum esculentum*) and tartary buckwheat (*Fagopyrum tataricum*). Common buckwheat was cultivated widely in Europe until the end of the eighteenth century. After that the cultivation of buckwheat declined drastically. Currently it is mainly cultivated in Russia, China and the Ukraine. Tartary buckwheat (Lin *et al*., 1992) is grown and used in the mountainous regions of southwest China (Sichuan).

3.2 Simple Carbohydrates and Oligosaccharides in Quinoa, Kañiwa, Amaranth and Buckwheat

The green plants can use sunlight to produce sugars, which are further used for the construction of different plant components. These plants supply food to all other forms of life. Most of the sugars are converted into polymers, which serve as energy reserves

for the plants. Low molecular weight carbohydrates can only be found in small amounts in grains in general. D-glucose is the most important monosaccharide. It is classified as an aldose. Another common monosaccharide, which belongs to the ketose group, is the D-fructose. These two monosaccharides form sucrose, the common sugar. Other common disaccharides are maltose and lactose.

Soluble sugars in grains include monosaccharides and disaccharides. They play certain roles in processing, especially in that of bread making. They are important during fermentation, offering a substrate to the yeast to produce carbon dioxide and alcohol. Sugars play a role in the process of bread baking as well because they participate in the Maillard reaction and caramelization at higher temperatures, turning the bread crust to brown and affecting the appearance and flavour of the end product. The presence of sugar in the dough affects the porosity, structure and appearance of breadcrumbs.

Andean grains, quinoa, kiwicha and kañiwa have a higher sugar content than common cereals. Repo-Carrasco (1992) analysed the free sugars in Andean grains. The total sugar content, glucose, fructose, maltose and sucrose content in kañiwa was 6.50, 1.80, 0.40, 1.70 and 2.60% respectively. In quinoa the total sugar content was 6.20% and in kiwicha 3.55%. Gross *et al.* (1989) found the following sugars and oligosaccharides in quinoa: fructose, glucose, sucrose, raffinose, stachyose, verbascose and α-galactosides. The main sugar was sucrose (2.79 g/100 g dry basis). Dini *et al.* analysed (2005) the soluble sugar content in the Kanccolla variety of quinoa. They found 2.93% glucose, 0.30% fructose and 1.85% sucrose.

Ogungbenle (2003) studied the sugar content of quinoa flour. He found that the quinoa flour had a high proportion of D-xylose (120.0 mg in 100 g sample) and maltose (101.0 mg in 100 g sample), and a low glucose content (19.0 mg in 100 g sample) and fructose content (19.6 mg in 100 g sample), suggesting that it would be useful in malted drink formulations. Quinoa flour was low in glucose and fructose; this is related to the low glycaemic index. The importance of the blood glucose response after a meal is often expressed as the glycaemic index. This implies that quinoa flour could be recommended for diabetic patients because low glycaemic index foods improve the metabolic control (Oshodi *et al.*, 1999).

Elgeti *et al.* (2014) analysed the sugar content of quinoa white flour (QF) and its effect on the quality of gluten-free bread. They found that QF was rich in glucose. Sucrose was found to be dominating in the outer grain parts of the quinoa. These results are contradictory to the glucose-fructose-sucrose content and ratio (4.55%, 2.41% and 2.39%, respectively) as reported by González *et al.* (1989) and Ogungbenle (2003). The different analysis techniques, varying ecotypes and origin of quinoa as well as high amylolytic activities may contribute to this variation. The abundance of mono- and disaccharides is of fundamental importance for the baking performance of flours. Upon heating, reducing sugars and amino acids provide the reactants for the nonenzymatic browning, called the Maillard reaction. Additionally, the yeast metabolism depends on the availability of its preferred substrates, which are mono- and disaccharides. The quality of gluten-free bread was improved by adding sugars to the formulation.

An important common response in cultivated plants to certain environmental stress seems to be the increased accumulation of sugars. In quinoa, high total soluble sugar content has been associated with tolerance against frost and drought. It is suggested that the level of soluble sugars may be used as an indicator of frost resistance, as the content of soluble sugars was positively correlated to yield in one study carried out by Jacobsen *et al.* (2003). They found that the quinoa cultivars from the Altiplano had a

higher sugar content than the quinoas from the valleys. This frost tolerance may be partly attributed to an increased level of solutes, which protect and support cellular structures under frost stress.

Miranda *et al*. (2010) studied the impact of air-drying temperature on sugars in quinoa. Sucrose (2.15 ± 0.24% dm was found as the predominant sugar in fresh quinoa. The reducing sugars presented an initial value of 0.15 ± 0.03% dm. and 0.24 ± 0.07% dm, for fructose and glucose, respectively. The major loss of sucrose (56%) was observed at high temperature (i.e. 80 °C) probably due to chemical hydrolysis of the disaccharide.

Gamel *et al*. (2006) analysed the content of total sugars in two amaranth species *A. cruentus* and *A. caudatus*. They found that the total sugar content of these two species ranged from 1.84 to 2.17% dm. Sucrose was found to be the dominant sugar. The other sugars found by these investigators were galactose, fructose, maltose, raffinose, stachyose and inositol. Kiwicha (*Amaranthus caudatus*) was found to have a higher oligosaccharide (stachyose and raffinose) content than other Andean grains (quinoa and kañiwa) by Gross *et al*. (1989).

The effect of germination on the sugar content of the *amaranthus* species has been studied by different authors. Colmenares de Ruiz and Bressani (1990) studied the content of sugars and oligosaccharides in different amaranth species during germination. They found that the reducing sugars, total sugars, and damaged starch increased with respect to germination time, whereas raffinose and stacchyose were not detected until after 48 and 24 hours, respectively. These oligosaccharides can cause flatulence if consumed in high quantities. Balasubramanian and Sadasivam (1989) studied the effect of germination on carbohydrates in *Amararanthus hypochondriacus* grains. According to their study, germinated grains experienced a decrease of starch content from 0 to 192 h and an increase in total sugars during the initial period of germination. However, after 48 h a decreasing trend was noticed. Most of the sugars were present as nonreducing sugars. This may be due to the fact that the product of hydrolysis of starch is converted to sucrose, which will then be used by the developing root and shoot tissues.

Lamothe *et al*. (2015) isolated pectic substances and xyloglucans from quinoa and amaranth. They found that, in general, quinoa and amaranth fibre fractions contain xyloglucans and pectic polysaccharides in varying amounts and structures depending on the fibre fraction. Insoluble fibres from pseudocereals were mainly composed of homogalacturonans containing arabinan and galactan side chains, xyloglucans mainly branched with di- and trisaccharide side chains, and cellulose. The soluble fractions differed slightly between quinoa and amaranth. Quinoa soluble fibre was mainly composed of homogalacturonans and arabinans. Amaranth soluble fibre was predominately composed of branched xyloglucans with a majority of di- and trisaccharide side chains, as well as pectic polysaccharides.

The composition of buckwheat grain carbohydrates is the following; 0.4% sugars, 84.5% of starch and 2.1 of nonstarch polysaccharides (Lunn and Buttriss, 2007). About 40% of the soluble carbohydrates of buckwheat are alpha-galactosides. D-*chiro*-inositol has been found in buckwheat. The content of this compound found by Steadman *et al*. (2000) in buckwheat groats ranged from 20.7 to 41.7 mg 100 of dry weight. Most of the D-*chiro*-inositol in buckwheat is in the form of fagopyritols (Horbowicz *et al*., 1998). Fagopyritols with other soluble carbohydrates such as sucrose, are mainly localized in buckwheat embryos (71.4%) (Arendt and Zannini, 2013). D-*chiro*-inositol and fagopyritols lower the elevated plasma glucose and thus buckwheat concentrate has been suggested as a natural product in treating diabetes (Arendt and Zannini, 2013).

3.3 Complex Carbohydrates / Starch / Nonstarch Polysaccharides

3.3.1 Quinoa and Kañiwa

The proximal composition of quinoa and kañiwa grain is presented in Table 3.1. The principal components in their kernels are carbohydrates and the main carbohydrate in both grains is starch. In quinoa, the starch content is approximately 58.1–64.2% of the dry matter (Repo-Carrasco *et al.*, 2003). The content of starch in quinoa and other grains can be appreciated in Table 3.2. Quinoa starch is located mainly in the perisperm and it occurs both as small individual granules and larger compound ones, which are composed of hundreds of individual granules (Berghofer and Schönelechner, 2002). The individual granules are polygonal with a very small diameter (1.0–2.5 μm) and the compound granules are oval, with a diameter of 6.4–32 μm (Atwell *et al.*, 1983). Starches having small sized starch granules have unique applications such as dusting starches, for example, in cosmetics, candy dusting, and as flavour carriers (Ahamed *et al.*, 1996).

Quinoa starch has a low amylose content as compared to common starches (11–12.2%) (Atwell *et al.*, 1983; Qian and Kuhn, 1999a). However, some researchers have reported a considerable variability in the amylose content of quinoa starch (4–20%) (Praznik *et al.*, 1999; Tang *et al.*, 2002; Lindeboom *et al.*, 2005). The amylose content in different grains is presented in Table 3.3. Quinoa starch is rich in amylopectin and it gelatinizes at relatively low temperatures (57–71 °C). The starch has a high pasting viscosity and single-stage starch swelling in the temperature range 65–95 °C (Ahamed *et al.*, 1996). Quinoa starch has a lower gelatinization temperature as compared to corn starch (85 °C). The gelatinization temperature for other starches is as follows: wheat starch, 65–67.5 °C; potato, 56.7–62.5 °C; tapioca, 62.5–68.7 °C; rice, 58.7–61.2 °C (Ahamed *et al.*, 1996).

Lindeboom *et al.* (2005) characterized the starch of eight quinoa lines. They discovered that quinoa starches varied widely in physicochemical properties, especially with respect to pasting properties and swelling power, which were highly correlated with

Table 3.1 Chemical composition of quinoa and kañiwa grains.

Component	Quinoa[a,b,c,d] (g/100 g)	Kañiwa[e,f,g] (g/100 g)
Protein	11.2–16.7	14.1–16.7
Crude fat	4.0–8.5	4.1–7.8
Crude fibre	1.92–10.5	5.4–10.7
Ash	3.0–2.8	3.5–4.6
Carbohydrates	60–74.7	56.4–66.4

a) Gonzalez *et al.* (1989);
b) Wright *et al.* (2002);
c) Dini *et al.* (1992);
d) Koziol (1992);
e) White *et al.* (1955);
f) Repo-Carrasco *et al.* (2003);
g) Gross *et al.* (1989)

Table 3.2 Starch content in Andean grains and common cereals (percentage dry basis).

Grains	Starch content
Quinoa[a, b, c]	55.2–69.2
Kiwicha[d, c]	62–65
Kañiwa[e]	90.1–94.6
Rice[c]	76.8 ± 0.8
Barley[f]	65–68
Corn[g]	69.1–86.0
Red sorghum[h]	41.33 ± 1.06
White sorghum[h]	42.58 ± 2.25
Wheat[i]	64

a) USDA (2005);
b) Mundigler (1998);
c) Nascimento *et al.* (2014);
d) Singh and Singh (2011);
e) Steffolani *et al.* (2013);
f) Quinde *et al.* (2004);
g) Mendez-Montalvo *et al.* (2005);
h) Bustos-Vásquez *et al.* (2010);
i) Kent (1987).

amylose contents. However, not all variation in starch characteristics was due to amylose content, for example the freeze-thaw stability of the starches, where no correlation with amylose content was detected and large differences between lines were observed. Due to the large differences in amylose content and physicochemical properties among quinoa starches, the authors suggest a wide variety of food and nonfood applications, and the possibility of undertaking a systematic breeding programme to develop quinoa lines.

Valdes *et al.* (2013) studied the viscosity properties and gelatinization of starch of three quinoa varieties. The results of thermal characteristics of these starches are presented in Table 3.4 and the curves of differential scanning calorimeter (DSC) are presented in Figures 3.1, 3.2 and 3.3. The temperatures of gelatinization of the starch of the three quinoa varieties were in accordance with the temperatures reported by Qian and Kuhn (1999a) and Youa and Izydorczyk (2007), with relatively low gelatinization temperatures. Gelatinization temperatures correlate positively with amylose content (Lindeboom, 2005; Youa and Izydorczyk, 2007). Lower enthalpy values are related to increased levels of amylose. White quinoa (Hualhuas variety) starch presented a lower level of gelatinization enthalpy (8.66 J/g) with a higher amylose content (13.63%). Quinoa starches of the varieties Rosada Huancayo and Pasankalla had higher gelatinization enthalpy (9.80 and 9.33 J/g) and lower levels of amylose (12.81 and 10.08 J/g, respectively). Furthermore, starches of the three varieties of quinoa showed lower gelatinization temperatures than amaranth starch (T0 = 66.3 °C, Tp = Tm = 74.5 °C and 86.9 °C) (Qian and Kuhn, 1999a).

Quinoa starch has excellent freeze-thaw stability, which is related to the fact that it is rich in amylopectin. This good freeze-thaw stability of quinoa starch suggests applica-

Table 3.3 Amylose and amylopectin content of Andean grains and common cereals (percentage dry basis).

Grains	Amylose	Amylopectin
Quinoa[a,b,c,d,e]	3.5–22.5	77.5
Kiwicha[f]	2–12	
Kañiwa[e]	11.7–18.9	
Rice[g]	7.4–29.8	61.0
Barley[h]	1.0–45.0	
Corn[i]	28.3	71.6
Red sorghum[j]	23.73 ± 6.90	70.39 ± 6.90
White sorghum[j]	29.61 ± 5.49	76.27 ± 5.49
Wheat[k]	25–28	72–75
Buckwheat[l]	18.3–47	

a) Tang *et al.* (2002);
b) Qian and Kuhn (1999a);
c) Tari *et al.* (2003);
d) Lindeboom (2005);
e) Steffolani *et al.* (2013);
f) Singh and Singh (2011);
g) Tukomane and Varavinit (2008);
h) Morrison *et al.* (1986);
i) Betancur-Ancona (2001);
j) Bustos-Vásquez *et al.* (2010);
k) Colonna and Buleon (1992);
l) Qian *et al.* (1998).

Table 3.4 Thermal characteristics of starches of quinoa.

Thermal characteristics	Rosada de Huancayo[d]	Blanca de Hualhuas[d]	Pasankalla[d]	Quinua[a,b,c]
Gelatinization enthalpy ΔH (J/g)	9.80	8.66	9.33	1.66–15
T_0°C	62.45	62.18	59.89	44.6–59,9
T_P°C	68.84	68.08	66.29	54.5–69.3
T_f°C	77.54	75.71	75.74	71.0–86,4

T_0 (onset temperature); T_p (peak temperature); T_f (final temperature);
a) Qian and Kuhn (1999a);
b) Lindeboom *et al.* (2005);
c) Youa and Izydorczyk (2007);
d) Valdez *et al.* (2013).

tions as a thickener in frozen food products. Quinoa starch paste is resistant to retrogradation, suggesting applications not only in frozen food products but in the emulsion type of food products such as salad dressings as well. Other applications where poor retrogradation can be industrially exploited are sauces, cream soups and pie

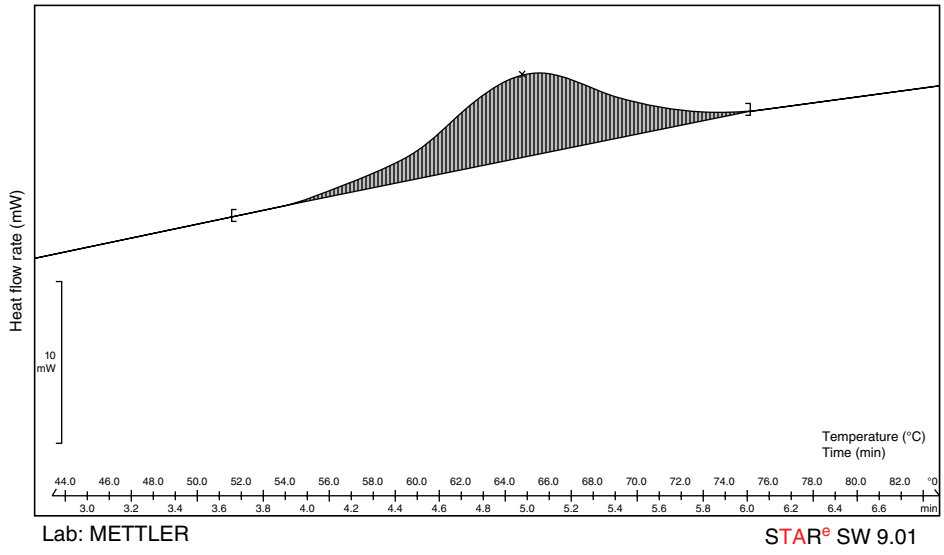

Figure 3.1 Differential scanning calorimetry (DSC) Rosada of Huancayo quinoa starch.

fillings (Ahamed *et al.*, 1996). The opaque nature of quinoa starch is a desirable characteristic for certain types of products such as salad dressing.

Linsberger-Martin *et al.* (2012) studied the effect of hydrostatic pressure on the content of resistant starch (RS) in quinoa, amaranth and wheat starches. The interest in the use of RS in food products is increasing which is mainly due to its potential health benefits. The effects of RS in the gastrointestinal tract are quite similar to the effects of dietary fibre. RS appears to have positive impact on colonic health and exerts a range of

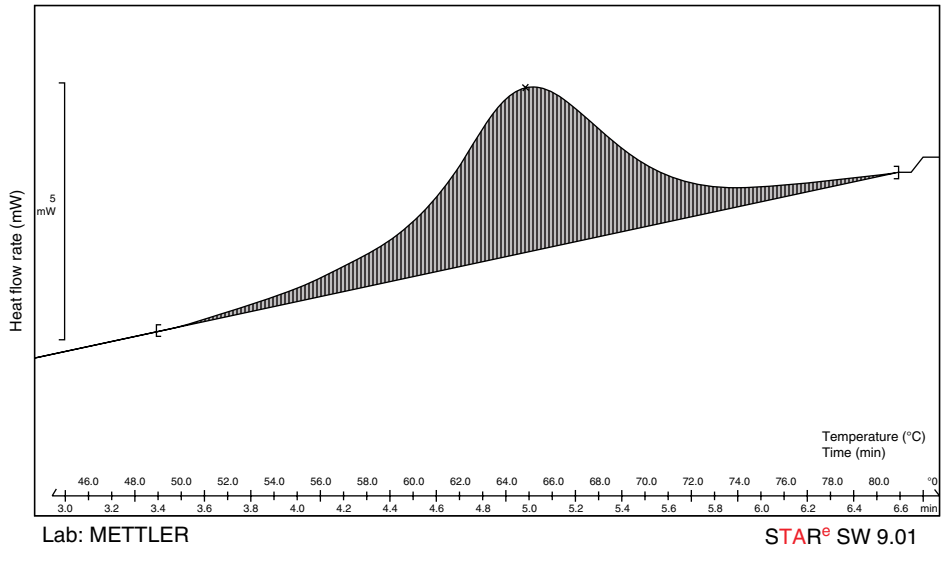

Figure 3.2 Differential scanning calorimetry (DSC) Blanca of Hualhuas quinoa starch.

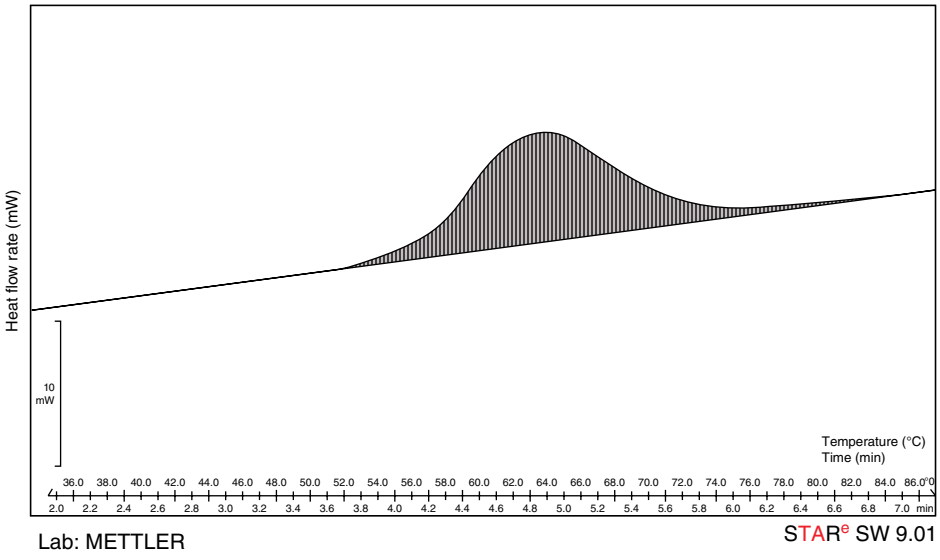

Figure 3.3 Differential scanning calorimetry (DSC) Pasankalla quinoa starch.

further beneficial effects such as the prevention of colonic cancer, reduction of serum cholesterol and triglycerides (Haralampu, 2000; Hylla *et al.*, 1998; Raben *et al.*, 1994). It also lowers the caloric density of food products. In the study of Linsberger-Martin *et al.* (2012), the RS content could be increased by various combinations of pressure, temperature and time in wheat and quinoa starch but not in amaranth starch. The RS content in wheat starch could be increased by a factor of about 10 and in quinoa starch even by a factor of about 18. The aim of this study to increase the content of RS in gluten-free materials by pressure treatments could only be reached with quinoa starch. The authors therefore recommend the use of high-pressure technology to obtain functional ingredients for gluten-free products (bread) and according to their findings quinoa would be a good choice.

Like quinoa, kañiwa is rich in starch. Steffolani *et al.* (2013) compared the physicochemical and functional properties of quinoa and kañiwa starches. In this study, kañiwa showed higher amylose content than quinoa but both have lower content than common cereals or tubers. The amylose content of the kañiwa ecotypes was between 10.70 and 17.44%. Kañiwa starch granules are smaller in average (about 1.45 μm) than the granules of quinoa (about 2.53 μm). In both grains, the granule shape is irregular, polygonal and angular. In the study of gelatinization and retrogradation parameters of quinoa and kañiwa starches, Steffolani *et al.* (2013) discovered that kañiwa starches presented high onset and peak temperatures compared to quinoa starches using a differential scanning calorimeter (DSC). The retrogradation enthalpy and percentage of kañiwa starches were higher than these values of quinoa starches. These values are consistent with a low amylose content of quinoa starch compared with kañiwa starch. Kañiwa starches presented higher values of firmness and lower syneresis than quinoa starches; thus, starches of kañiwa could be used in foods where certain consistency and firmness are required.

In general, the starches with a small granule size, offer unique functional properties and unique uses in the food industry. Commercial sources of small granule starch

Table 3.5 Starch granule size in Andean grains and common cereals (μm).

Grains	Starch granule size
Quinoa[a, b, c, d, e]	0.6–3.5
Kiwicha[c, f]	1–2 0.5 and 2.5
Kañiwa[e]	<2.0
Rice[g]	3–8
Barley[h]	2–3 and 12–32
Corn[i, j]	5–20
Red sorghum[k]	13.89 ± 2.39
White sorghum[k]	13.10 ± 2.47
Wheat[l]	1–30

a) Ruales and Nair (1993);
b) Tang *et al.* (2002);
c) Qian and Kuhn (1999a);
d) Lindeboom *et al.* (2005);
e) Steffolani *et al.* (2013);
f) Singh and Singh (2011);
g) Clédat *et al.* (2004);
h) Lindeboom *et al.* (2004);
i) Jane *et al.* (1994);
j) Betancur-Ancona (2001);
k) Bustos-Vásquez *et al.* (2010);
l) Kent (1987).

include rice, wheat and oat. Potential sources of small granule starch include quinoa, kañiwa, amaranth and buckwheat (see Table 3.5). The starches with a small granule size have many potential industrial uses. They can be used as fat replacement because aqueous dispersions of small starch granules produce a creamy, smooth texture with fatmimetic properties (Malinski *et al.*, 2003). A small granule size increases the level of starch that can be incorporated into biodegradable films (Lim *et al.*, 1992). Araujo-Farro *et al.* (2010) studied quinoa starch in the production of biodegradable films. They concluded that quinoa starch appears to be a very interesting raw material for the preparation of edible films and coatings. The process developed in this study produced colourless films with good mechanical properties and excellent barrier properties. In addition, small starch granules can be combined into interesting and potentially useful porous spheres when spray dried with small amounts of bonding agents. A need exists in the food industry for containment of flavour essences and other components in a manner that will provide oxidative protection and controlled release over a defined period of time (Lindeboom *et al.*, 2004). Recently, Pagno *et al.* (2015) developed active biofilms using quinoa starch containing gold nanoparticles. These active biofilms exhibited a strong antibacterial activity against foodborne pathogens with inhibition percentages of 99% against *E. coli* and 98% against *S. aureus*. The quinoa starch biofilms containing gold nanoparticles are very promising for use as active food packaging for the maintenance of food safety and extension of the shelf life of packaged foods.

3.3.2 Amaranth

Starch is the most abundant component in the amaranth seed, as in all grains. In general, amaranth seeds contain 65% to 75% starch, 4% to 5% dietary fibres, two to three times higher content of sucrose in comparison to wheat grain, and nonstarch polysaccharide components (Venskutonis and Kraujalis, 2013). Marcone (2005) reported a starch content of about 60% among the different amaranth species. The chemical composition of different amaranth species is presented in Table 3.6.

Amaranth starch has received attention because of its extremely small granules (0.75–3 μm) and high water-absorption capacity (Uriyapongson and Rayas-Duarte, 1994). The small starch granules of amaranth provide unique functional properties for food and nonfood applications, including food thickeners, paper coatings, laundry starch, dusting powers, cosmetics and fat replacers (Marcone, 2005).

Wu and Corke (1999) studied the starch of 26 *amaranthus* species. The starch content of these species was between 2–37.6%. The content of amylose was 7.8–34.3% for the same species. Among the samples, there were not only grain amaranths but leaf amaranths, as well. This study indicated broad diversity in the content and properties of starches of different species. They pointed out that assessing the utilization of *amaranthus*, it should be borne in mind that there is no generic or typical *amaranthus* starch from a functional point of view. Uriyapongson and Rayas-Duarte (1994) compared two methods of extraction of amaranth starch: wet and dry-wet milling processes. Dry-wet milling gave a higher starch yield and required less time to isolate starch than wet milling. They also compared the starch of two amaranth species with commercial starches and found that the two cultivars of amaranth showed different properties. The thermal properties, intrinsic viscosity, apparent viscosity, and clarity of cold paste of *A .cruentus* were similar to that of waxy corn starch. The properties of *A. hypochondriacus* X hyb. differed significantly from that of waxy corn. The removal of proteins can enhance the yield. Radosavljevic *et al.* (1998) isolated *Amaranthus cruentus* starch using a diluted alkaline-protease treatment. They developed an improved method for starch isolation that produced starch with low protein content (0.2%) and a high recovery (80%). Their method has been scaled up for pilot plant processing for amaranth starch production. The method

Table 3.6 Chemical composition of amaranth species.

Component species	*A. caudatus* (%)[a]	*A. hypochondriacus* (%)[b]	*A. cruentus* (%)[c]	*A. hybridus* (%)[d]
Protein	15.5	17.9	15.5	13.1
Crude fat	7.6	7.9	7.7	7.5
Crude fibre	4.7	n.d.	4.4	6.8
Ash	3.4	3.3	3.3	2.0
Carbohydrates	68.8	63.6	58.3*	n.d.

n.d. = not determined;
* starch content;
a) Gross *et al.* (1989);
b) Marcone (2005);
c) Berghofer and Schönelechner (2002);
d) Osuntogun and Oke (1983).

requires much less NaOH for the processing, which reduces production costs of the starches.

The gelatinization temperature of the starch of *A. hypochondriacus* is between 62 and 68 °C (Saunders and Becker, 1984). The starch of amaranth is mainly constituted by amylopectin, the amylose content is very low: 5–7% (Becker *et al.*, 1981). However, Marcone (2005) reports slightly higher amylose content in one amaranth species, *A. pumilus*. This amaranth could be used in bread and cake formulations because of its higher amylose content. The starch with low amylose content performs poorly in bread and cake formulations. Gonzales *et al.* (2007) obtained starch-rich fractions of *A. cruentus*. They studied the effect of the high temperature heating on some properties of these starch-rich fractions. The loss of crystalline structure and an increase in degree of gelatinization was observed by increasing the temperature and moisture. According to these findings, the high starch fraction obtained by differential milling of the amaranth grain can be considered as an interesting raw material for production of precooked amaranth high-starch flours having a wide range of hydration properties.

Baker and Rayas-Duarte (1998a) studied the freeze-thaw stability of amaranth starch measuring the percentage of syneresis in centrifugation. The effects of salt and sugars on freeze-thaw stability were also studied. Based on DSC and centrifugation methods, amaranth starch had better stability after freezing and thawing through four cycles than did corn, wheat, and rice starches. Amaranth starch with added salt showed similar stability as compared with a control when measured by centrifugation and showed increased stability when measured by DSC. Adding sugars to amaranth starch gels had varying results, but for the most part they showed similar or increased stability when compared with a control. The stability of starch gels during freeze-thaw cycling enhances its potential in food products. They also studied retrogradation of starch of amaranth at different temperatures (Baker and Rayas-Duarte, 1998b). They found that amaranth starch showed 2–9 times slower retrogradation rates than corn, wheat, and rice starches at low temperatures, and up to 2.8 times lower maximum percentage of retrogradation than the other starches at all three temperatures studied.

Qian and Kuhn (1999a) compared amaranth and quinoa (*Chenopodium quinoa*) starches. They isolated and characterized these starches using rapid Visco analysis (RVA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and X-ray diffractometry (XRD). Amylose content measured enzymatically was 7.8 and 11.2% for amaranth and quinoa starch, respectively. Quinoa starch was much more viscous than amaranth starch and gelatinized at a lower temperature as determined with RVA. DSC demonstrated a wider gelatinization temperature range for amaranth starch (20.6 °C) than for quinoa starch (11.1 °C). SEM observation revealed polygonal shape of starch granules, and XRD suggested a typical A type diffraction pattern for both the starches in question. A crystallinity of 45.5% for amaranth and 35.4% for quinoa starch, respectively, was also determined from the XRD collected data. Thermal properties of different grains are presented in Table 3.7.

Kong *et al.* (2012) studied the effect of acid hydrolysis on thermal and rheological properties of amaranth starches with varying amylose content. They concluded that, with an increase in amylose content, the effects of acid hydrolysis on gelatinization temperatures became less pronounced. Nevertheless, prolonged acid hydrolysis caused the starch pastes to become more liquidlike. The acid hydrolyzed amaranth starch characteristics showed that they could be used in the candy industry and as stabilizers in sausages and dressings. With prolonged hydrolysis they might also be employed in

Table 3.7 Thermal properties of starches in kernels.

Starches	Gelatinization enthalpy ΔH (J/g)	T_0°C	T_P°C	T_C°C
Quinoa[a, b, c, e, f, j]	1.66–15	44.6–62.5	54.5–69.3	71.0–86.4
Kiwicha[a, d]	2.58	66.3 60–77	74.5	86.9
Kañiwa[e]	7.49–9.32	58.39–59.18	66.12–66.68	
Barley[f]	14.8	66.4		
Corn[g, h]	1.9 a 4.7 10.3	62.3	66.3	72.9
Red sorghum[i]	11.06 ± 0.89	68.37 ± 0.27	71.43 ± 0.18	75.47 ± 0.14
White sorghum[i]	11.06 ± 0.88	66.19 ± 0.43	71.00 ± 0.50	75.49 ± 0.63

T_0 (onset temperature); T_p (peak temperature); T_c (final temperature);
a) Quian and Kuhn (1999a);
b) Lindeboom *et al.* (2005);
c) Youa and Izydorczyk (2007);
d) Singh and Singh (2011);
e) Steffolani *et al.* (2013);
f) Lindeboom *et al.* (2005);
g) Mendez-Montalvo *et al.* (2005);
h) Betancur-Ancona (2001);
i) Bustos-Vásquez *et al.* (2010);
j) Valdez *et al.* (2013).

parenteral food and instant beverages. Amaranth starch has been reported to have high digestibility (Caselato-Sousa and Amaya-Farfan, 2012). Chaturvedi *et al.* (1997) studied the effect of amaranth, wheat and grain preparations in the glycemic index (GI) of non-insulin-dependent diabetic patients. *A. esculentum* L. was used in the form of 'popcorn' (popped) and was prepared with different proportions of wheat flour to create unleavened bread (chapattis). In the amaranth–wheat combination, a GI of 91.7 was observed for a proportion of 50:50 and a GI of 105.7 was observed for a proportion of 25:75. For a combination of popped amaranth and unsweetened milk, a GI of 136.2 was observed. They concluded that due to the high starch digestibility, the isolated ingestion of amaranth grains should not be recommended to diabetic patients.

Capriles *et al.* (2008), have compared the in vitro digestibility of the starch of amaranth seeds and white bread. Raw seeds resulted in a rapidly digestible starch content of 30.7% db and a predicted GI of 87.2. The cooked, extruded and popped preparation forms were digested similar to white bread (92.4; 91.2; and 101.3, respectively), and the seeds in the form of flakes or toasted showed a higher GI (106 and 105.8, respectively). Cooking and extrusion did not alter the digestibility of the seed content. The authors concluded that amaranth is a high-GI food, probably due to the small size of its starch granules and its tendency to completely lose the crystalline and granular structure of the starch during the heat treatment. In addition to this, amaranth cannot be considered as a good source of resistant starch, the RS/total starch proportion in raw amaranth seed was 0.86%. Crops containing more than 4.5% RS are considered to be a good source of RS.

Urban *et al*. (2012) produced cyclodextrins from *A. cruentus* starch. All the commercially important α-, β-, and γ-cyclodextrins were detected chromatographically after the hydrolysis of the starch and the authors concluded that amaranth starch is an excellent substrate for producing cyclodextrins because of the high dispersibility, high starch-granule susceptibility to amylases, and the exceptionally high amylopectin content. Starch derivatives (succinylated, acetylated, and phosphorylated) have proved effective encapsulating agents when used in the spray drying of flavours, pigments and probiotics. Different cereal starches have been used for this purpose, with special emphasis on maize, rice and wheat starch. However, this range is expanding – in particular, the pseudocereals are an interesting novel source of starch. Falfán Cortés *et al*. (2014) evaluated the use of modified amaranth starch as a shell material for the encapsulation of probiotics. Succinylated and acetylated amaranth starches had the best survival of cells of *L. casei* ATCC 334 at 4 °C and an aw-value of 0.355. A good applicability of derivative starches containing probiotics in a food system based on commercial precooked oatmeal was obtained.

3.3.3 Buckwheat

Starch is the main carbohydrate in buckwheat kernel endosperm. The content of total carbohydrates in buckwheat is 68–73% of which 54.5% was found to be starch (Li and Zhang, 2001; Steadman *et al.*, 2001). The percentage of starch (57.4 ± 0.12%) in tartary buckwheat is slightly higher than in common buckwheat.

From a chemical point of view, starch comprises two polymers of D-glucose: amylose and amylopectin. Amylose is linear (only lightly branched) and completely amorphous. Amylopectin is a highly branched polymer and provides partial crystallinity to the starch granule. The ratio of amylose to amylopectin is of technological relevance especially in connection with bread staling, but is also an important nutritional feature of starch (Hager *et al.*, 2012). The starch of buckwheat has a relatively high amylose content 18.3–47% (Qian *et al.*, 1998, Yoshimoto *et al.*, 2004, Wolter *et al.*, 2013). There do not seem to be consistent differences between apparent amylose percentages of common and tartary buckwheat (Li *et al.*, 1997). Qian *et al*. (1998) found that buckwheat amylose forms complexes with lipids. These complexes can decrease the swelling power and solubility of buckwheat starch thus affecting the functional properties of the starch.

Yoshimoto *et al*. (2004) detected the presence of long chain amylopectins in buckwheat starch. These long chain amylopectins affect the gelatinization properties of the starch increasing the viscosity. Buckwheat starch exhibits a higher peak viscosity than common cereal starches and its pasting behaviour resembles more closely that of root and tuber starches (Qian *et al.*, 1998; Arendt and Zannini, 2013). These high viscosity values can be partly explained by the high granule swelling and gelling tendency of buckwheat starch (Yoshimoto *et al.*, 2004). The peak gelatinization temperature differs between the cultivars ranges from 57 to 70 °C (Li *et al.*, 1997; Noda *et al.*, 1998; Qian *et al.*,1998).

The water-binding capacity of buckwheat starch (109.9%) is higher than the water-binding capacity of wheat and corn starch (Qian *et al.*, 1998). This can be explained by the small size of the buckwheat starch granules (2.9–9.3 μm) (Qian and Kuhn, 1999b). The buckwheat starch granule has pores and due to these pores and the small granule size, this starch is more susceptible to fungal α-amylase than corn and wheat starch (Qian *et al.*, 1998). Wolter *et al*. (2013) found that the buckwheat starch granules have a

diameter in average of 5 μm and that the granules occur in aggregates and singly with the same range of diameter (3–8 μm), possessing a spherical shape.

Buckwheat starch has a relatively high resistant starch (RS) content; according to Skrabanja and Kreft (1998) the content of RS in buckwheat groats is about 35%. Enzymes do not digest this starch. This undigested starch can be considered as part of dietary fibre and thus can have positive nutritional effects. Factors that limit starch digestion include granule size, amylose content, starch-protein interactions, and starch-lipid complexes. Starch that is resistant to digestion passes to the large intestine, where it may be fermented by colonic microflora. Processing can affect the content of resistant starch in buckwheat. Autoclaving decreased the RS in buckwheat but, on the other hand, the content of retrograded starch can be increased by autoclaving or cooking (Skrabanja and Kreft, 1998). Retrograded starch is one form of RS and can present the beneficial effects of RS. In general, high amylose / amylopectin ratios result in increased levels of resistant starch upon heating.

Steadman *et al.* (2001) studied the carbohydrate composition of milling fractions of common buckwheat. They separated 11 milling fractions and compared the composition of these fractions. Soluble carbohydrates were most concentrated in bran (up to 7% dry weight). Buckwheat flour contained the highest concentration of starch (65–76%). By contrast, bran contained less than 18% starch. In general, an inverse relationship between the concentration of starch and the concentration of protein, lipid, ash and soluble carbohydrates among milling fractions was found.

Wronkowska and Haros (2014) studied the properties of starch fraction of wet-milled buckwheat. Starchy materials obtained were characterized by determining starch extraction efficiency, particle size distribution and microstructure. The pasting (RVA) and thermal properties (DSC) were also analysed. The mean particle diameter of pure starch isolated from buckwheat with or without hull was about 18 μm. Microstructure characteristics analysed by SEM showed that buckwheat starch isolated using the wet-milling method had a polygonal and irregular shape and often aggregated. DSC analysis of buckwheat flour revealed a gelatinization starch temperature range from 68 to 81 °C with a peak at 74 °C. These temperatures are higher than those of wheat. The buckwheat starch has good water absorption during gelatinization and viscosity increases quickly during heating and decreases during cooling (Biacs *et al.*, 2002). Qian *et al.* (1998) determined the water-binding capacity of buckwheat starch and found that it was higher than that in wheat and corn starch. The water-binding capacity of buckwheat starch was 109.9%. In general, it can be said that buckwheat starch has its own unique characteristics; some properties correspond to tuber starches (high viscosity values) and others correspond more to cereal starches (shape and composition) (Wijngaard and Arendt, 2006).

Li *et al.* (1997) studied the physiochemical properties of common and tartary buckwheat. Starch colour differed greatly between tartary and common buckwheat, indicating that the removal of yellow pigments from tartary buckwheat flour may be problematic during starch isolation. The peak gelatinization temperature in water was 63.7 °C for wheat starch, 66.3–68.8 °C for common buckwheat and 68.8–70.8 °C for tartary buckwheat. A comparison of pasting characteristics of common and tartary buckwheat starches to wheat starch indicated similar peak viscosity, higher hot paste viscosity, higher cool paste viscosity, smaller effect of NaCl on peak viscosity, and higher resistance to shear thinning. Praznik *et al.* (1999) found that buckwheat starch with a viscosity of 230 mPa.s at 95 °C shows no acid resistance and is unstable upon shearing but performs very well in freeze / thaw experiments.

Qian and Kuhn (1999b) compared the pasting behaviour of starches of different cultivars of buckwheat. These results showed that the most starches started to gelatinize from around 60, 70 and 80 °C measured with DSC, RVA and Brabender viscoamylography (BV), respectively. Buckwheat starch exhibited higher viscosity than cereal starches.

Buckwheat contains water-soluble nonstarch polysaccharides. Salting out and chromatography, ultracentrifugation and electrophoresis have isolated these polysaccharides. The main component found by Marshall and Pomeranz (1982) had a high viscosity in aqueous solution. This polysaccharide consisted of xylose, mannose, galactose and glucuronic acid units.

Lu *et al.* (2013) compared the nutritional composition of groats with husks of ten buckwheat cultivars. The total starch content of 10 buckwheat cultivars exhibited significant genetic variation, ranging from 61.2% to 76.8%. They studied the starch digestibility of cooked and raw buckwheat groats and found that cooked buckwheat groats were digested more slowly during enzyme incubation compared with raw groats. This is probably due to the higher RS content of cooked buckwheat groats than that of raw buckwheat groats.

High-amylose starch causes only a mild rise in the glycaemic index (GI = the blood glucose elevation compared to standard, normally D-glucose or white wheat bread) (Whistler and BeMiller, 1997). As buckwheat starch has a relatively high amylose content, it is expected that the glycaemic index of buckwheat is low. The content of RS has influence on GI by decreasing it. Non-native buckwheat starch (hydrothermally processed starch) has been suggested as an ingredient for low glycaemic index foods (Arendt and Zannini, 2013). In comparison to white wheat bread (GI = 100), boiled buckwheat groats had a GI of 61.2 and buckwheat bread baked with 50% buckwheat groats had a GI of 66.2 (Skrabanja *et al.*, 2001; Arendt and Zannini, 2013). Wolter *et al.* (2013) compared different gluten-free bread formulations in their predicted glycaemic load (pGL) and found that the bread made with buckwheat flour had the lowest pGL. Buckwheat flour contains compounds such as tannins, phytic acid, and proteinaceous inhibitors that can act against human saliva amylase (Ikeda *et al.*, 1994; Skrabanja *et al.*, 2001) and affect the level of digestible starch. It would be interesting to know what the relative contribution of these various factors on the digestibility of starch is, when designing low GI products (Wijngaard and Arendt, 2006).

Buckwheat noodles have been studied by Kreft and Skrabanja (2002) to identify the possibility of reduced starch hydrolysis rate and glucose release after the ingestion of buckwheat meals, in comparison to the wheat-based meals. The rate of starch hydrolysis and the resistant starch formation in boiled buckwheat noodles, boiled wheat noodles, boiled buckwheat groats, and white wheat bread were evaluated *in vitro*. The highest content of RS (total starch basis) was found in boiled buckwheat groats. The rate of *in vitro* amylolysis was significantly reduced in both studied buckwheat products in comparison to the reference white bread. This study confirms that buckwheat products have a potential in diets designed in accordance with the dietary recommendations for diabetic patients and for healthy subjects.

3.4 Conclusion

The main carbohydrate in quinoa, kañiwa, amaranth and buckwheat is the starch. The starch of these pseudocereals has a very small granule size and thus has many potential industrial uses, such as fat replacement, as well as in biodegradable films and coatings.

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4

Dietary Fibre and Bioactive Compounds of Kernels

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4.1 Introduction

Amaranth, kañiwa and quinoa are very nutritious pseudocereals of Andean origin, whereas buckwheat is from the Chinese gene centre (Biacs *et al*., 2002). Quinoa (*Chenopodium quinoa* Willd) is a seed crop of the *Chenopodiaceae* family. It was a very important crop for the Incas. Kañiwa (*Chenopodium pallidiaule* Aellen) is closely related to quinoa. Kañiwa grows under very harsh environmental conditions, mainly in the Peruvian and Bolivian altiplano. The most important Andean amaranth species is *Amaranthus caudatus* Linnaeus, called kiwicha. Buckwheat (*Fagopyrum esculentum* Mönch) was domesticated in south-east Asia. It was cultivated widely in Europe until the end of eighteenth century, and nowadays, it is mainly cultivated in Russia, China and Ukraine. There are many species of buckwheat in the world and, for the most part, there are nine species that have agricultural value. Generally, there are two types that are used around the world: common buckwheat (*F. esculentum*) and tartary buckwheat (*F. tataricum*). Common buckwheat is widely grown and used, whereas tartary buckwheat is primarily grown in mountainous regions (Krkoskova and Mrazova, 2004).

4.2 Dietary Fibre

Traditionally, dietary fibre was considered to be the portion of plant foods that is resistant to digestion by human digestive enzymes; this includes polysaccharides and lignin. More recently, the definition has been expanded to include oligosaccharides, such as inulin, and resistant starches. Dietary fibre has been classified into two categories: soluble, such as viscous or fermentable fibres (such as pectin), which are fermented in the colon, and insoluble fibres, such as wheat bran, that have bulking action but may only be fermented to a limited extent in the colon (Anderson *et al*., 2009).

Many definitions of dietary fibre exist worldwide, with some based on analytical methods and others that are physiologically based. According to AACC (2001), dietary fibre is the edible parts of plants or analogous carbohydrates that are resistant to digestion and absorption in the human small intestine, with complete or partial fermentation in the large intestine. Dietary fibre includes polysaccharides, oligosaccharides, lignin,

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and associated plant substances. It promotes beneficial physiological effects, such as laxation, blood cholesterol attenuation, and / or blood glucose attenuation.

Functional fibre consists of isolated, nondigestible carbohydrates that have beneficial physiological effects in humans (Slavin, 2003). Total fibre is the sum of dietary fibre and functional fibre. The generally used classifications for dietary fibre are: total, soluble and insoluble fibre. There has been a trend to assign specific physiological effects, either to soluble or insoluble fibres. This approach makes it difficult to evaluate the effects of fibre provided by mixed diets. Dietary fibre provided by mixed diets is two-thirds to three-quarters insoluble, although the exact distribution between soluble and insoluble is very dependent on the method of analysis. Furthermore, some fibres are placed in one category or another when, in fact, they may have major benefits attributable to both soluble and insoluble fibres, for example, psyllium seed husk, oats and oat bran (Slavin, 2003). The recommendation is to discontinue the use of the terms soluble and insoluble fibre, making current fibre values in nutrient databases obsolete. Since these changes are still in the proposed stage, the existing dietary fibre data, including total dietary fibre, soluble fibre, and insoluble fibre, are still consistent.

It is generally accepted that the consumption of food naturally rich in dietary fibre is beneficial to the maintenance of health. However, the intake of fibre in many diets is inadequate and nutritionists recommend a higher intake of fibre-rich whole grain cereals as opposed to refined grains. It is recommended that the bulk of carbohydrate-containing foods consumed have a low glycaemic index (GI), i.e. slowly digested carbohydrates.

4.2.1 Dietary Fibre in Andean Grains

The content of dietary fibre in quinoa is similar to that of common cereals; however, there are varietal differences in the content of dietary fibre in quinoa (Table 4.1). In fact, this is common in grains. Gebruers *et al*. (2008) found substantial variation in the content of dietary fibre between different wheat types and varieties. Similar results were obtained for oat and barley types and varieties (Anderson *et al*., 2008; Shewry *et al*., 2008). Some of this variation may relate to environmental conditions, such as soil nutrient status and water availability. Furthermore, interactions between the genotype and environment may occur, resulting in different impacts on the concentrations of components (Shewry, 2009).

Some authors report relatively low dietary fibre content for quinoa: 7.8–14% (Guzman-Maldonado and Paredes-Lopez, 1998; Alvarez-Jubete *et al*., 2009; Vidueiros *et al*., 2015). This could be due to the different varieties, as well as differences in handling and processing the seed. Eliminating the bitter substances, saponins, of quinoa, decreases the fibre content. Quinoa grains analysed in the study of Alvarez-Jubete *et al*. (2009) were preprocessed by washing, centrifuging and drying.

The other Andean grain, kañiwa is an excellent source of dietary fibre. The content of total, soluble and insoluble dietary fibre in kañiwa is about 26–27, 4.1–4.4 and 22–24%, respectively (Glorio *et al*., 2008). It has more dietary fibre than common cereals and other Andean grains. The perigone, which covers the grain, contains mainly cellulose, contributing to the high dietary fibre content of kañiwa. The dietary fibre content of kañiwa, quinoa, kiwicha and some common cereals is presented in Table 4.1.

Repo-Carrasco (1992) studied the dietary fibre content of kiwicha (*A. caudatus)*. In this study, kiwicha was found to be a rich source of dietary fibre, especially the insoluble fraction. The insoluble fibre of amaranth is composed primarily of lignin and cellulose.

Table 4.1 Dietary fibre content in Andean grains and cereals (g/100 g).

Species/variety	IDF	SDF	TDF	Reference
Quinoa				
La Molina 89	14.4	2.5	16.9	Glorio *et al.* (2008)
Blanca de Juli	12.2	2.4	14.6	Glorio *et al.* (2008)
Sajama	12.0	2.5	14.5	Glorio *et al.* (2008)
Kcancolla	12.7	2.3	15.0	Glorio *et al.* (2008)
Salcedo INIA	23.5	3.1	26.5	Glorio *et al.* (2008)
Kiwicha				
Centenario	14.9	2.4	17.3	Glorio *et al.* (2008)
Kañiwa				
Cupi	23.5	4.1	27.6	Glorio *et al.* (2008)
LP1	21.9	4.4	26.3	Glorio *et al.* (2008)
Ramis	23.1	4.2	27.3	Glorio *et al.* (2008)
Oat	n.d.	n.d.	10-23	Shewry (2009)
Barley	n.d.	n.d.	15-24	Andersson *et al.* (2008)
Wheat	n.d.	n.d.	10-18	Gebuers *et al.* (2008)

n.d. = not determined;
IDF = insoluble dietary fibre;
SDF = soluble dietary fibre;
TDF = total dietary fibre.

Guzman-Maldonado and Paredes-Lopez (1998) studied the dietary fibre in two *Amaranthus* species. The total dietary fibre of *A. hypochondriacus* consists of 75% insoluble dietary fibre (IDF) and 25% soluble dietary fibre (SDF), while *A. cruentus* was higher in insoluble fibre and, consequently, lower in soluble fibre (86% IDF and 14% SDF).

Lamothe *et al.* (2015) studied the dietary fibre content and composition in quinoa and kiwicha (*Amaranthus caudatus*). They found that quinoa and amaranth have a dietary fibre content that is in the same range as common cereal grains. Total dietary fibre content was 10% for quinoa and 11% for amaranth. For both pseudocereals, 78% of the dietary fibre was insoluble. Insoluble fibre (IDF) from quinoa and amaranth was mainly composed of galacturonic acid, arabinose, galactose, xylose and glucose. Linkage analysis indicated that IDF was composed of homogalacturonans and rhamnogalacturonan-I with arabinan sidechains (55–60%), as well as highly branched xyloglucans (30%) and cellulose. For both pseudocereals, 22% of total dietary fibre was soluble, which is a higher proportion than that found in wheat and maize (15%). The soluble fibre (SDF) was composed of glucose, galacturonic acid and arabinose; for amaranth, xylose was also a major constituent. Xyloglucans made up 40–60% of the SDF and arabinose-rich pectic polysaccharides represented 34–55%. Given that quinoa and amaranth have higher proportions of SDF than do common cereals, and that the composition of their fibres resembles that of fruits, vegetables and leguminous seeds instead of cereals, it would be of interest to investigate the functionality and fermentable properties of their dietary fibre isolates. The compositional and structural characteristics of dietary fibres from these pseudocereals suggest a good potential for favourable function in the colon.

Processing grains affects the content and composition of the dietary fibre. Repo-Carrasco-Valencia (2011) studied the effect of extrusion on the dietary fibre, phytates, phenolic compounds and the radical scavenging capacity in two kiwicha varieties. The total dietary fibre content in the extruded kiwicha was similar to the content found by Plate and Areas (2002): 8.20% for *A. caudatus*. In both varieties, the content of total and insoluble dietary fibre decreased during the extrusion process. In the case of the Centenario variety, the soluble dietary fibre content increased from 2.45 to 3.06% during the extrusion process. However, in the Oscar Blanco variety, the amount of soluble dietary fibre decreased slightly (from 1.65 to 1.46%).

Gualberto *et al.* (1997) investigated the effect of extrusion on dietary fibre and phytic acid in cereal brans. They found also a decrease in the content of insoluble dietary fibre during extrusion cooking and an increase in the content of soluble fibre. This could be due to shear stress caused by high screw speed or high temperature. The exposure to shear stress and high temperature causes chemical bond breakage, creating smaller particles that are soluble. There is a transformation of some insoluble fibre components into soluble fibre during extrusion.

Repo-Carrasco-Valencia *et al.* (2009b) studied the effect of the extrusion process on the dietary fibre of two kañiwa varieties (Ramis and Cupi). There was a significant decrease in the total and insoluble dietary fibre content of both varieties of kañiwa. Frochlich and Hestangen (1982) analysed the total dietary fibre content in rye grains, as well as in extruded rye. They observed a decrease of total dietary fibre from 16.8% to 12.7%. The content of soluble dietary fibre was also significantly decreased in both varieties, according to the analysis of variance. Björck *et al.* (1984) obtained similar results in the extrusion of wheat flour; the content of soluble dietary fibre decreased from 2.3% to 1.7%. The lignin content of the Ramis and Cupi varieties decreased in both cases. Benchaar *et al.* (1994) also found a decrease in lignin content, from 2.3% to 1.1% for raw and extruded horse beans, respectively. The content of betaglucans in extruded kañiwa was insignificant.

Repo-Carrasco-Valencia and Astuahuaman (2011) studied the effect of extrusion on dietary fibre in quinoa varieties. There were no significant differences in the content of total dietary fibre (TDF), insoluble dietary fibre (IDF) and soluble dietary fibre (SDF) between the varieties. In all cases, the contents of total and insoluble dietary fibre decreased during the extrusion process; however, this decrease was significant only in the Sajama variety. At the same time, the content of soluble dietary fibre increased during the extrusion process. The increase in the content of soluble dietary fibre was statistically significant in the Blanca de Juli, Kcancolla and La Molina 89 varieties. Gualberto *et al.* (1997) also found a decrease in the content of insoluble dietary fibre and an increase in the content of soluble fibre during extrusion cooking. Rinaldi *et al.* (2000) studied the effect of extrusion on the dietary fibre of wheat extrudates enriched with wet okara, and these results support the results of Repo-Carrasco-Valencia and Astuahuaman's (2011) study. Extrusion of the formulations resulted in decreased insoluble fibre and increased soluble fibre contents of the products. Extrusion cooking of white wheat flour has also been found to cause a redistribution of insoluble to soluble dietary fibre (Björck *et al.*, 1984).

Lue *et al.* (1991) investigated the extrusion cooking process, with the expectation that mechanical rupture of the glycosidic bonds will lead to an increase of soluble fibre. In some cases, an increase of insoluble fibre was observed (Unlu and Faller, 1998). Esposito *et al.* (2005) studied the effect of extrusion on the dietary fibre of durum

wheat. The data showed that the extrusion cooking process did not have an effect on the amount of soluble dietary fibre, independent of the fibre typology of the different samples. This difference in fibre solubilization during processing could be explained by the variability in the raw material composition, as well as by different experimental conditions, for example, screw share forces and pressure in the extrusion. The high mechanical stress during extrusion may cause the breakdown of polysaccharide glycosidic bonds, releasing oligosaccharides, therefore, resulting in an increase in soluble dietary fibre. Ruales and Nair (1994) determined the content of dietary fibre in raw and processed quinoa samples. They found a total of 13.4% of total dietary fibre in raw quinoa. The content of total dietary fibre was decreased only in cooked quinoa, while in autoclaved and drum-dried samples, it remained the same. Some soluble fibre was lost during cooking, and in autoclaved samples, it was probably lost due to depolymerization of fibre components.

Extrusion can affect the content of resistant starch in grains. In the study of Repo-Carrasco-Valencia *et al.* (2009b), the content of resistant starch in two kañiwa varieties increased during the extrusion process. Huth *et al.* (2000) also found an increase in resistant starch in barley during the extrusion process, especially under high temperatures (170 °C). The increase of resistant starch during the extrusion process can be explained by the modification of the amylose structure.

Gonzalez-Soto *et al.* (2006) studied the effect of extrusion on the resistant starch content of corn. The content of resistant starch in corn was between 1.97% and 2.05%. It was reported that the content of resistant starch decreased when the screw velocity increased. This is probably due to the increase in shear stress, which causes the structure of resistant starch to rupture. Resistant starch acts as a soluble fibre in the colon. It is fermented by the intestinal microflora, resulting in the formation of short chain fatty acids, which protect the colonic mucosa.

Konishi *et al.* (2000) studied the physiological effects of quinoa fibre. They reported that a diet supplemented with 3% quinoa pericarp significantly decreased serum and liver cholesterol levels in mice. It has been suggested that the hypocholesterolemic effect of the quinoa pericarp can be attributed to the water-soluble dietary fibre content, such as in oat, rice bran or other fibres.

Grajeta (1999) studied the effect of amaranth and oat bran on the lipids of the blood serum and liver in rats. Amaranth and oat bran added to the diet provided 4–4.5% of the dietary fibre. Amaranth significantly decreased the level of total cholesterol in rat blood serum (by 10.7% in the case of a diet containing lard and by 14% with sunflower oil) and in the liver (by 20% in the case of a diet with lard and by 23% with sunflower oil). Similarly, oat bran decreased the level of total cholesterol in the blood serum by 19% in the diet containing lard and by 22% with sunflower oil, as well as in the liver by 22 and 27%, respectively. Amaranth and oat bran did not influence HDL-cholesterol in the blood of rats. High fibre fractions can be obtained by differential milling of amaranth (Tosi *et al.*, 2001). These fractions contained 21.7 and 37.2% dietary fibre.

Guzman-Maldonado and Paredes-Lopez (1998) reviewed the studies regarding the effects of amaranth grains on serum cholesterol level in rats. In several studies, the cholesterol lowering effects of amaranth grain were confirmed. The cholesterol-lowering properties are assumed to be due to the SF fraction of the grains, such as oats. Since amaranth contains only small amounts of soluble fibre, the authors suggest that the hypocholesterolemic effects associated with amaranth are attributable to components other than those of SDF.

4.2.2 Dietary Fibre in Buckwheat

Dziedzic *et al.* (2012) studied the components of dietary fibre in buckwheat. According to their research, buckwheat grains contained 6.79% of lignin, 2.22% of hemicellulose and 10.64% of cellulose. This study shows that buckwheat fibre has a low SDF/IDF ratio (0.5–0.28). Dietary fibre exhibits the most effective physiological action at a SDF/IDF ratio of 1 : 2 (Jaime *et al.*, 2002). The authors recommend the combination of buckwheat fibre with fruit and vegetable fibre, which is characterized by a much higher ratio of the SDF/IDF fractions.

Steadman *et al.* (2001) studied the TDF, SDF and IDF in buckwheat seed milling fractions. According to this study, the whole groats of buckwheat contain 55% starch, 12% protein, 4% lipid, 2% soluble carbohydrates, 7% TDF, 2% ash, and 18% other components (organic acids, phenolic compounds, tannins, phosphorylated sugars, nucleotides and nucleic acids, and unknown compounds). Buckwheat bran is a rich source of TDF and SDF – particularly bran with hull fragments (40% TDF, of which 25% is SDF), while bran without hull fragments has 16% TDF, of which 75% is SDF. Total dietary fibre in buckwheat bran milled without hulls is similar to that of oat bran (17%) (Lee *et al.*, 1992).

The content of the dietary fibre components depends on the buckwheat species (Krkoskova and Mrazova, 2004). Bonafaccia *et al.* (2003) compared the content of TDF, IDF and SDF in common and tartary buckwheat flour and bran. This study showed that common and tartary buckwheat contain similar amounts of total dietary fibre. The soluble fraction was found, especially in the bran, at levels of around 1%. A higher proportion of soluble fibre was found in tartary buckwheat than in common buckwheat.

Zhu *et al.* (2014) studied the dietary fibre content in buckwheat hulls and the effect of micronization technology on physicochemical and antioxidant properties of dietary fibre from buckwheat hulls. The TDF content of the buckwheat hulls was 86.83%. SDF increased from 16.00% to 26.60%, while IDF decreased from 70.27% to 56.63% after ultrafine grinding, suggesting that ultrafine grinding causes a redistribution of fibre components in TDF. The results of this work suggest that mini-type airflow pulverization instruments could effectively reduce the particle size of buckwheat hull and redistribute fibre components from insoluble to soluble fractions, yielding a kind of healthy DF with higher SDF content. The micronization in buckwheat hull DF could be an alternative to producing functional foods and nutraceuticals.

Stringer *et al.* (2013) studied the efficacy of a food product made from buckwheat to modify glucose metabolism in both healthy people and those with type 2 diabetes mellitus (T2DM). Healthy participants or those with T2DM consumed either buckwheat or rice crackers. Blood samples were collected at baseline and 15, 30, 45, 60, 120 and 180 minutes after consumption. In a second phase of the study, participants consumed one serving of buckwheat crackers daily for one week; fasting blood samples taken on day one and day seven were analysed. The researchers concluded that although the buckwheat cracker did not modify acute glycaemia or insulinaemia, it was sufficient to modulate gastrointestinal satiety hormones. The identity of the active component in buckwheat that is responsible for the higher levels of satiety hormones observed in this study remains unknown. Certain soluble fibres can influence gastrointestinal hormone secretion and satiety feelings in the overweight population (Parnell and Reimer, 2009). Buckwheat contains several nonstarch polysaccharides that consist of xylose, mannose, galactose and glucuronic acid, and it is possible that short-chain fatty acids produced

from fermentation of these nonstarch polysaccharides stimulated secretion of several gastrointestinal satiety hormones (Stringer *et al*., 2013).

The physiological effect of dietary fibre depends first of all on its origin, proportions of individual fractions, and the applied thermal processes. The insoluble fraction of dietary fibre that activates intestinal peristalsis is capable of binding bile acids and water. Dietary fibre exhibits a varied capacity in terms of the sorption of bile acids. This is connected first with the varying content of its individual fractions (Dziedzic *et al*., 2012). Lignin fraction, found most frequently in the outer layers of cereals, shows some influence on the bile acid binding, whereas the cellulose fraction has no properties of this type. Dziedzic *et al*. (2012) studied the potential capacity of buckwheat milling fractions and roasted kernels, before and after roasting, for bile acid sorption. They found that in buckwheat hulls, lignin and cellulose fractions were predominant, while the hemicellulose fraction dominated in broken groats. Hull and bran bound bile acids to the highest degree, while broken buckwheat groats bound them to the lowest degree. The researchers recommend the use of buckwheat hulls and bran for enriching food products because of the significant sorption ability of bile acids.

4.3 Bioactive Compounds

Bioactive compounds are phytochemicals present in plants that can promote health but they are not essential for life. Oxidative stress, which releases free oxygen radicals in the body, has been implicated in a number of disorders, including cardiovascular malfunction, cataracts, cancers and rheumatism (Arendt and Zannini, 2013). Phytochemicals in fruits and vegetables can act as antioxidants, protecting the cells. In plants there are different types of antioxidants, such as vitamins A, C and E. Polyphenol compounds have been extensively researched recently for health promoting properties, such as in the prevention of degenerative diseases, including cancer and cardiovascular disease. Flavonoids are very efficient antioxidants and are present in most plants. Recently, plant bioactive peptides have received attention as health-promoting compounds.

4.3.1 Bioactive Compounds in Amaranth

Amaranth contains various compounds that have potential health-promoting properties. The different amaranth species are good sources of phenolic compounds. Repo-Carrasco-Valencia *et al*. (2009a) analysed the content of total phenolic compounds in two kiwicha (*Amaranthus caudatus*) varieties. Kiwicha contained 0.99–1.13 mg gallic acid/g of sample, dry basis. Guzman-Maldonado and Paredes-Lopez (1998) reported levels of 2–4 mg/g of total phenolic compounds in amaranth. This difference could be due to different amaranth species and to different growing conditions. Kiwicha has more total phenolic compounds than do oats. Emmons *et al*. (1999) analysed the total phenolic compounds in different milling fractions of oat and found the content of these compounds to be between 8.9 and 34.2 mg GAE/100 g of sample. The content of total phenolic compounds in kiwicha was lower than in bran-enriched wheat milling fractions, 130–530 mg/100 g, as found by Trust *et al*. (2005). Del Pozo-Insfran *et al*. (2007) analysed the content of total phenolic compounds in three genotypes of corn, two blue genotypes and one white. The content of total phenolic compounds was between 410 and 3430 mg/100 g calculated as gallic acid equivalents. Dykes *et al*. (2005) determined

the total phenolic compounds in sorghum varieties. Grain sorghum is very high in these compounds (201–910 mg gallic acid/100 g).

Klimczak *et al.* (2002) determined the antioxidant activity of ethanolic extracts of amaranth seeds. They also analysed the total phenolic content and free phenolic acids in *A. caudatus* and *A. paniculatus.* The total phenolic content was 107 μg/g of seed for *A. caudatus* and 296 μg/g of seed for *A. paniculatus.* Both species showed appreciable antioxidant activity in the model system compared to β-carotene and linoleate. Gorinstein *et al.* (2007) studied the effect of phenolic substances on the antioxidant potentials of some cereals and pseudocereals, such as buckwheat, amaranth and quinoa. They concluded that, based on high levels of polyphenols, flavonoids and antioxidant activities, these pseudocereals can substitute for cereals in common and atherosclerotic diets, as well as in cases of allergies.

The composition of polyphenols in amaranth has been studied. De la Rosa *et al.* (2009) isolated three polyphenols, rutin, nicotiflorin and isoquercetin, from different amaranth (*Amaranthus hypochondriacus)* varieties. Rutin was present at the highest concentration, followed by nicotiflorin. Several health effects have been related to the uptake of the aglyconic groups of these polyphenols. Rutin and its metabolites could have implications in the prevention of different pathologies by inhibiting the formation of the glycation end products (AGE) (Pashikanti *et al.*, 2010). Quercetin can act as a protective defence against oxidative damage *in vivo* (Meyers *et al.*, 2008). Nicotiflorin seems to have a protective effect on reducing memory dysfunction (Huang *et al.*, 2007). Klimczak *et al.* (2002) and Repo-Carrasco-Valencia (2010) analysed the free phenolic acid content of *Amaranthus caudatus* seeds. Barba de la Rosa *et al.* (2009) published information concerning the phenolic acid content of a different amaranth species (*Amaranthus hypochondriacus*). According to their data, amaranth seed flour contained soluble 4-hydroxybenzoic acid (0.17–0.22 mg/100 g), vanillic acid (0.15–0.18 mg/100 g) and syringic acid (0–0.08 mg/100 g).

Amaranth contains betalains, which are a class of red and yellow indole-derived pigments found in certain plant species, where they replace anthocyanin pigments. Cai *et al.* (2003) determined the antioxidant activity of amaranth betalains. They also investigated the relationship between the chemical structure and activity of the betalains. This study demonstrated that the amaranth betalains have very strong antioxidant activity, as compared to typical antioxidants (ascorbic acid, rutin and catechin), suggesting that these betalains may become a useful source of both natural antioxidants and natural colorants. This study also revealed that antioxidant activity of different betalains generally depended on their chemical structures. The free radical scavenging activity of the betalains increased with the number of hydroxyl groups and amino groups in the molecule. The C-5 position of the hydroxyl group on aglycones in the betalain molecules significantly improved activity, and more glycosylation of aglycones clearly reduced activity.

Amaranth has several minor constituents that may possess positive or negative effects. The phytic acid content of amaranth (0.34–0.61%) is higher than that found in rice, but lower than those reported in maize and wheat. Trypsin and chymotrypsin inhibitors have been found in amaranth seeds. Tamir *et al.* (1996) isolated and characterized the thermostable protease inhibitor from amaranth seeds and studied its effect on trypsin- and chymotrypsin-like proteases, as well as the possible role in modulating tumorigenic behaviour in human breast cancer cells *in vitro*. They found that this inhibitor, AmI, affects trypsin and chymotrypsin from the digestive system of insects, such as

Tribolium castaneum and *Locusta migratoria*, supporting the hypothesis that inhibitors may have evolved as defence mechanisms of seeds against insects. AmI was found to inhibit the anchorage-independent growth of MCF-7 breast cancer cells, suggesting that AmI may have anticarcinogenic activity.

Lectins are another minor component found in amaranth. One lectin, called amaranthin, has been isolated from *A. cruentus*. According to Guzman-Maldonado and Paredes-Lopez (1998), its concentration ranges from 1.6 to 1.7 mg/g. Amaranthin has been used as a histochemical probe for proliferating cells in sections of human colonic tissues. Experimental data suggest that amaranthin may be useful for identifying abnormal proliferation in colorectal cancer syndromes (Boland *et al*., 1991).

Amaranth proteins are mainly globulins, representing about 20% of the total seed protein. These globulins are composed principally of amaranthin (11S fraction of globulins). It has been suggested that 11S globulins have cholesterol-lowering effects (Guzman-Maldonado and Paredes-Lopez, 1998). Active peptides were found in amaranth proteins with 12 main activities: antiamnestic, antithrombotic, immunomodulating, opioid, regulating, antioxidant, ligand, activating ubiquitin-mediated proteolysis (AUMP), immunostimulating, embryotoxic, protease inhibiting, and antihypertensive (Hartman and Meisel, 2007). Silva-Sanchez *et al*. (2008) studied bioactive peptides in *Amaranthus hypochondriacus*. They detected the presence of lunasin in *A. hypochondriacus* seeds. Lunasin is a unique 43 amino acid peptide whose cancer-preventive properties have been demonstrated in a mammalian cell-culture model and in a skin-cancer mouse model against chemical carcinogens, oncogenes, and inactivators of tumour-suppressor proteins (De Lumen, 2005). The presence of lunasin has been detected in barley and wheat suggesting the possibility that lunasin or lunasin-like compounds could be found in other grains (Silva-Sanchez *et al*., 2008). The total lunasin concentration in amaranth, as found by Silva-Sanchez *et al*. (2008), was similar to that found in barley (5.9 to 8.7 µg/g of protein), where no significant differences were reported among cultivars studied. In conclusion, their study showed that amaranth-seed proteins could be an alternative source of lunasin or lunasin-like isoforms. Amaranth seeds are also a potential source of other bioactive peptides with biological functions that could be beneficial to health, particularly antihypertensive activity.

4.3.2 Bioactive Compounds in Quinoa and Kañiwa

Quinoa and kañiwa are good sources of various bioactive compounds. Several researchers have studied the content of total phenolic compounds in quinoa (Pasko *et al*., 2009; Miranda *et al*., 2010; Repo-Carrasco-Valencia and Astuahuaman, 2011). These researchers found that the total phenolic compound content was 1.59–374 mg GA/100 g in different quinoa varieties. Repo-Carrasco-Valencia *et al*. (2009b) and Repo-Carrasco-Valencia and Asuahuaman (2011) analysed the total phenolic compound content in kañiwa and quinoa varieties, finding that kañiwa varieties are higher in phenolic compounds than quinoa. The content of phenolic compounds was 2.54 and 2.43 mg of gallic acid equivalents (GAE)/g for Cupi and Ramis, respectively. This content is higher than in oat, buckwheat, quinoa and rice (Trust *et al*., 2005). There were significant differences between the quinoa varieties in the total polyphenol content. The total polyphenol content in the four quinoa varieties ranged from 1.42 to 1.97 mg GAE/g. Pasko *et al*. (2005) defined the total polyphenol content in quinoa to be 3.75 mg GAE/g by using a two-step extraction process, first with methanol and then with acetone. As Repo-Carrasco-Valencia and

Astuahuaman (2011) used methanol only, some polyphenols may not have been included in the extract. Yawadio *et al.* (2008) analysed the total phenolic compounds in quinoa and amaranth (*A. hypochondriacus, A. cruentus*) and found a level between 94.3 and 148 mg/g of tannic acid equivalents.

The composition of phenolic compounds in Andean grains has been studied. Repo-Carrasco-Valencia *et al.* (2010) compared the composition and content of phenolic acids in Andean grains (kiwicha, kañiwa and quinoa). The total content of phenolic acids varied from 16.8 to 59.7 mg/100 g in the samples analysed and the percentage share of soluble phenolic acids varied from 7% to 61% (Table 4.2). There were several differences in the phenolic acid composition of the three different grains (quinoa, kañiwa and kiwicha). The samples of the *Chenopodium* species contained caffeic acid, ferulic acid, p-coumaric acid, p-OH-benzoic acid and vanillic acid. In addition to these, sinapinic acid and protocatechuic acid were detected in Amaranthus samples. There was a statistically significant difference in the content of ferulic acid in quinoa, kañiwa and kiwicha, with kañiwa having the highest and kiwicha the lowest. Of the *Chenopodium* species, kañiwa samples contained less vanillic acid but more caffeic and ferulic acids than did the quinoa samples. The total phenolic acid content was higher in quinoa than in kiwicha but much variation existed between the samples. In quinoa varieties, the proportion of soluble phenolic acids was high (mean 39±11%). In kañiwa and amaranthus varieties, the mean values were 21 ± 9% and 10 ± 3%, respectively.

Peñarrieta *et al.* (2008) identified vanillic and ferulic acids in whole plants of *Chenopodium pallidicaule* (kañiwa). The results for vanillic acid were of the same magnitude, whereas the lower level of ferulic acid found was comparable to Repo-Carrasco-Valencia *et al.*'s (2010) results. This difference probably arises from sample differences (seeds versus whole plants), as well as different methodologies. However, Peñarrieta *et al.* (2008) also found much variation between samples (ecotypes).

According to Repo-Carrasco-Valencia *et al.* (2010), Andean cereals contained lower levels of phenolic acids compared with common cereals like wheat (*Triticum* spp.) and rye (*Secale cereale*). In these cereals, the phenolic acids accumulate in bran where their levels are as high as 419 and 453 mg/100 g in rye and wheat bran, while the whole grain flours of these grains contain 137 and 134 mg/100 g, respectively (Mattila *et al.* 2005). However, according to Mattila *et al.* (2005), the phenolic acid content of other cereals, like oat (*Avena sativa*), barley (*Hordeum vulgare*), corn (*Zea mays*), rice (*Oryza sativa*), millet (*Panicum miliaceum*) and buckwheat (*Fagopyrum esculentum*), is of the same magnitude (25–60 mg/100 g) as in the Andean grains studied by Repo-Carrasco-Valencia *et al.* (2010). Gallagher *et al.* (2010) demonstrated that the total phenol content increased during sprouting of the quinoa grains.

Quinoa and kañiwa seeds are abundant sources of flavonoids, consisting mainly of glycosides of the flavonols kaempferol and quercetin (Peñarrieta *et al.*, 2008; Alvarez-Jubete *et al.*, 2010; Gallagher *et al.*, 2010). Kañiwa is exceptionally rich in resorcinols, compounds that are not very common in plants (Peñarrieta *et al.* 2008). Of the major cereals, resorcinols have been reported in high levels in wheat, rye and triticale, and in low amounts in barley, millet and maize. Cereal alkylresorcinols (ARs) have been reported to have anticancer and antimicrobial effects, as well as the ability to inhibit some metabolic enzymes *in vitro*. Cereal ARs have also been reported to have antioxidant activity (Ross *et al.*, 2003).

Peñarrieta *et al.* (2008) analysed extractable flavonoids in the whole plant of *Chenopodium pallicaule* and found mainly quercetin and kaempferol. De Simone *et al.*

Table 4.2 Total contents (mg/100 g) phenolic acids in quinoa, kaniwa and kiwicha grains.

Sample	Caffeic acid	Ferulic acid	p-Coumaric acid	p-OH-benzoic acid	Vanillic acid	Sinapic acid	Protocatachuic acid	Total
Quinoa samples								
Ccoito	0.95 ± 0.04	15.3 ± 0.5	6.46 ± 0.18	3.87 ± 0.07	8.97 ± 0.01	n.d.	n.d.	35.6 ± 0.4
INIA-415 Pasankalla	0.61 ± 0.03	20.0 ± 0.2	27.5 ± 0.4	2.44 ± 0.02	9.19 ± 0.36	n.d.	n.d.	59.7 ± 0.5
Roja de Coporaque	0.50 ± 0.03	13.9 ± 0.6	4.07 ± 0.01	2.60 ± 0.08	11.0 ± 0.3	n.d.	n.d.	32.1 ± 1.0
Witulla	1.47 ± 0.21	14.9 ± 0.7	2.26 ± 0.08	2.46 ± 0.09	9.20 ± 0.28	n.d.	n.d.	30.3 ± 0.6
03-21-0093	0.86 ± 0.02	16.6 ± 0.5	8.72 ± 0.02	2.80 ± 0.13	10.7 ± 0.5	n.d.	n.d.	39.7 ± 1.1
Salcedo INIA	0.25 ± 0.01	12.3 ± 0.9	8.02 ± 0.36	3.17 ± 0.02	14.6 ± 0.2	n.d.	n.d.	38.4 ± 1.5
Commercial 1.	0.57 ± 0.02	18.6 ± 1.7	2.84 ± 0.14	3.38 ± 0.24	11.9 ± 0.3	n.d.	n.d.	37.2 ± 1.9
Commercial 2.	0.87 ± 0.03	14.3 ± 0.1	2.60 ± 0.03	3.88 ± 0.04	10.3 ± 0.1	n.d.	n.d.	32.0 ± 0.1
Huaripongo	0.37 ± 0.04	12.0 ± 0.1	4.01 ± 0.06	2.65 ± 0.02	12.4 ± 0.1	n.d.	n.d.	31.4 ± 0.2
03-21-1181	0.59 ± 0.07	13.7 ± 0.7	9.50 ± 0.36	1.92 ± 0.08	10.7 ± 0.5	n.d.	n.d.	36.3 ± 1.2
Kañiwa samples								
Kello	1.10 ± 0.01	26.1 ± 1.9	1.34 ± 0.12	1.77 ± 0.09	4.34 ± 0.30	n.d.	n.d.	34.7 ± 2.4
Wila	2.16 ± 0.02	29.8 ± 0.2	1.00 ± 0.01	1.77 ± 0.04	3.61 ± 0.08	n.d.	n.d.	38.3 ± 0.3
Guinda	2.37 ± 0.12	26.0 ± 0.8	1.74 ± 0.19	1.55 ± 0.08	3.04 ± 0.18	n.d.	n.d.	34.7 ± 1.3
Ayara	7.04 ± 0.11	23.4 ± 1.2	0.70 ± 0.04	1.97 ± 0.19	6.95 ± 0.21	n.d.	n.d.	40.1 ± 1.7
Commercial sample	1.10 ± 0.09	12.0 ± 0.4	0.37 ± 0.02	1.54 ± 0.13	3.23 ± 0.38	n.d.	n.d.	18.3 ± 0.8
Kiwicha samples								
1	0.85 ± 0.01	8.32 ± 0.70	0.81 ± 0.04	3.16 ± 0.02	6.67 ± 0.03	0.32 ± 0.04	12.8 ± 0.4 (0%)	32.9 ± 1.3
2	0.87 ± 0.02	6.46 ± 0.64	0.99 ± 0.09	1.97 ± 0.15	4.28 ± 0.42	0.09 ± 0.01	6.28 ± 0.42	20.9 ± 1.4
3	0.70 ± 0.07	6.21 ± 0.09	0.80 ± 0.05	3.19 ± 0.02	6.38 ± 0.40	0.09 ± 0.01	n.d.	17.4 ± 0.6
4	1.13 ± 0.04	6.57 ± 0.01	0.98 ± 0.02	3.68 ± 0.10	4.35 ± 0.26	0.09 ± 0.01	n.d.	16.8 ± 0.4

n.d. = not detected. Reference: Repo-Carrasco-Valencia (2011).

(1990) and Zhu *et al.* (2001) characterized flavonol glycosides in quinoa (*Chenopodium quinoa* Willd) seeds. Zhu *et al.* (2001) isolated and characterized six flavonol glycosides: four kaempferol glycosides and two quercetin glycosides. In one study, Hirose *et al.* (2010) found large amounts of quercetin and kaempferol glycosides in quinoa grains. Repo-Carrasco-Valencia *et al.* (2010) analysed the flavonoid composition in various ecotypes of quinoa and kañiwa (Table 4.3). They found that the flavonoid content of these species was exceptionally high, varying from 36.2 to 144.3 mg/100 g. The predominant flavonoids in quinoa samples were quercetin and kaempferol, whereas in some varieties, myricetin and isorhamnetin were also found. Kañiwa samples contained mostly quercetin and isorhamnetin, with smaller amounts of myricetin, kaempferol and rhamnetin in some varieties. As in the case of phenolic acids, much variation was found between different samples. There were no statistically significant differences in the content of quercetin, rhamnetin and total flavonoids in quinoa and kañiwa. The content of isorhamnetin was significantly higher in kañiwa compared to quinoa. In the case of kaempferol, the content in kañiwa was significantly lower than in quinoa.

Berries have been considered as an excellent source of flavonols, especially quercetin and myricetin. For example, lingonberry contains 10 mg/100 g fw of quercetin and cranberry contains 10.4 and 6.9 mg/100 g fw quercetin and myricetin, respectively (Mattila *et al.*, 2000). The levels in these flavonoid-rich berries are 5–10 times lower than those found in *Chenopodium* seed samples. When compared on a dry-weight basis, the flavonoid contents in berries and *Chenopodium* samples are of the same magnitude. Quinoa and kañiwa seeds can thus be considered very good sources of flavonoids.

Isoflavones, particularly daidzein and genistein, have been detected in quinoa seeds (Vega-Galvez *et al.*, 2010). These compounds are implicated in plant physiology (protection from pathogens, UV light and nitrogen-limited soils) and can be recognized by α- and β-estrogen receptors in humans. These endoplasmic reticulum-linked receptors are implicated as inhibitors of tyrosine kinase enzymes, and as antagonists of vessel contraction. They also reduce arterial resistance, improve bone density and stimulate osteoprogerin secretion by osteoblasts, in addition to their antioxidant properties.

Quinoa is a rich source of phytoecdysteroids (Kumpun *et al.* 2011). Phytoecdysteroids are polyhydroxylated steroids, structurally related to insect-moulting hormones, which have been implicated in plant defence by deterring insect herbivory, delaying insect development and causing lethality to insect larvae (Graf *et al.*, 2014). Phytoecdysteroids have also shown a wide range of therapeutic effects in mammals (Graf *et al.*, 2014), including anabolic, performance-enhancing (Gorelick-Feldman *et al.*, 2008; Slama and Lafont, 1995), antiosteoporotic (Kapur *et al.*, 2010; Seidlova-Wuttke *et al.*, 2010) and wound-healing properties (Syrov and Khushbaktova, 1996). These molecules are bioactive compounds found in certain traditional herbs in Chinese medicine, and extracts of these plants have been marketed and sold as health products (Graf *et al.*, 2014). Recent literature also suggests that the most prevalent phytoecdysteroid, 20-hydroxyecdysone (20HE,also known as ecdysterone or b-ecdysone) may play a role in the treatment and prevention of diabetes and obesity (Graf *et al.*, 2014). The highest concentration of this compound was found in an extract of spinach leaves (*Spinacia oleracea* L.) (Gorelick-Feldman *et al.*, 2008). Quinoa seeds, however, contain 4–12 times more 20HE by dry weight (184–484 μg/g) (Kumpun *et al.*, 2011) than do spinach leaves (40 μg/g) (Gorelick-Feldman *et al.*, 2008). Graf *et al.* (2014) optimized a method for producing a quinoa leachate (QL) with a high 20HE content and demonstrated that the QL significantly lowered fasting blood glucose in obese, hyperglycaemic mice.

Table 4.3 Contents of flavonoids in quinoa and kaniwa grains (mg/100 g).

Sample	Myricetin	Quercetin	Kaempferol	Isorhamnetin	Rhamnetin	Total
Quinoa samples						
Ccoito	n.d.	38.1 ± 2.3	16.3 ± 1.6	n.d.	n.d.	54.5 ± 4.0
INIA-415 Pasankalla	n.d.	35.7 ± 0.2	0.45 ± 0.11	n.d.	n.d.	36.2 ± 0.3
Roja de Coporaque	0.22 ± 0.04	55.5 ± 4.2	16.9 ± 1.1	n.d.	n.d.	72.6 ± 5.3
Witulla	0.86 ± 0.11	23.5 ± 0.8	44.7 ± 1.2	n.d.	n.d.	69.0 ± 2.1
03-21-0093	0.90 ± 0.13	32.6 ± 0.1	14.2 ± 0.7	n.d.	n.d.	47.7 ± 1.0
Salcedo INIA	n.d.	11.6 ± 0.1	54.2 ± 0.5	n.d.	n.d.	65.8 ± 0.6
Commercial 1.	1.24 ± 0.07	36.8 ± 0.6	10.2 ± 0.3	2.08 ± 0.06	n.d.	50.3 ± 1.0
Commercial 2.	0.51 ± 0.08	47.1 ± 2.4	21.5 ± 1.1	n.d.	n.d.	69.2 ± 3.6
Huaripongo	0.88 ± 0.20	53.2 ± 4.1	14.2 ± 0.8	0.89 ± 0.11	n.d.	69.2 ± 5.2
03-21-1181	0.67 ± 0.12	28.5 ± 2.7	11.5 ± 0.3	1.02 ± 0.10	n.d.	41.7 ± 3.2
Kañiwa samples						
Kello	n.d.	84.3 ± 1.2	n.d.	60.0 ± 1.3	n.d.	144.3 ± 2.5
Wila	n.d.	68.7 ± 5.8	n.d.	14.2 ± 0.8	n.d.	83.0 ± 6.6
Guinda	n.d.	25.1 ± 2.0	n.d.	29.5 ± 1.3	n.d.	54.6 ± 3.3
Ayara	n.d.	21.4 ± 1.4	5.97 ± 0.02	n.d.	18.7 ± 2.0	46.1 ± 3.5
Commercial sample	0.18 ± 0.01	78.6 ± 6.6	2.24 ± 0.33	24.8 ± 2.4	n.d.	105.8 ± 9.3

n.d. = not detected. Reference: Repo-Carrasco-Valencia (2011).

Although commonly considered as antinutrients, quinoa saponins present some health-promoting properties. For instance, saponins can reduce cholesterol levels and they exhibit insecticidal, antibiotic and fungicidal properties (Zhu *et al*., 2002). There is also some evidence that quinoa saponins possess anti-inflammatory activity (Mujica, 1994). Guclu-Ustundag and Mazza's (2007) research has shown that saponins may have anticarcinogenic and cholesterol lowering properties. Other health-promoting properties of saponins include immunostimulatory and antioxidant effects (Guzman-Maldonado and Paredes-Lopez, 1998).

4.3.3 Bioactive Compounds in Buckwheat

The buckwheat grain can be stored for long periods without any chemical changes. This is due to the content of several natural antioxidants, including tocopherols, phenolic acids and flavonoids (Biacs *et al*., 2002). Whole buckwheat contains two to five times more phenolic compounds than do oats or barley, whereas buckwheat bran and hulls have two to seven times higher antioxidant activity than do barley, triticale, and oats (Holasova *et al*., 2002; Zdunczyk *et al*., 2006). Guo *et al.* (2012) compared the milling fractions of tartary buckwheat for their phenolics and antioxidant properties. Tartary buckwheat hull, coarse bran, fine bran and light flour were examined and compared for their free and bound phenolics, flavonoids, phenolic acid composition and antioxidant activity. The results showed that free phenolic contents were much higher than were bound phenolics for each sample, and four samples significantly differed in their phenolic and flavonoid contents, phenolic acid composition and antioxidant activities. According to these authors, tartary buckwheat hull and bran with high amounts of phenolic compounds are considered to be excellent materials for cereal-based food processing, with significant health benefits.

The primary antioxidants in buckwheat are rutin, quercetin, hyperin, and catechins (Morishita *et al*., 2007). The flavonoid content and composition in buckwheat seeds vary in different buckwheat species during growing phases and among growing circumstances. Generally, the flavonoid content in *F. tataricum* (about 40 mg/g) is higher than that in *F. esculentum* (10 mg/g). In *F. tataricum* flowers, leaves and stems, the flavonoid content can surpass 100 mg/g (Li and Zhang, 2001).The principal flavonoids in buckwheat are rutin, orientin, vitexin, quercetin, isoorientin and isovitexin (Biacs *et al*., 2002). The total flavonoid content in buckwheat reported by Oomah and Mazza (1996) was 387–1314 mg/100 g. Buckwheat hulls contained the highest levels of rutin and quercetin (Oomah and Mazza, 1996). Tartary buckwheat is especially rich in rutin (Fabjan *et al*., 2003). Rutin is a very interesting flavonoid because it has been shown to be able to antagonize the increase of capillary fragility associated with haemorrhagic disease of hypertension in man (Biacs *et al*., 2002; Watanabe *et al*., 1997). Other beneficial effects related to rutin are: reduction of high blood pressure, antioxidant activity, and lipid-lowering activity. Rutin is widely present in plants but is relatively rare in their edible parts. Among fruits, vegetables and grain crops, grapes and buckwheat are the most important rutin-containing foods (Kreft *et al*., 2006). According to Zhang *et al.* (2012), buckwheat is the only pseudocereal that contains rutin.

Sedej *et al.* (2010) compared the antioxidant activity and flavonoid content of buckwheat with wheat flour. They identified and quantified rutin, quercetin, and ferulic acid in buckwheat flours, while ferulic acid was quantified in wholegrain wheat flour. Significantly higher levels of phenolics and tocopherols were found in buckwheat than

in wheat flours. Tocopherols in buckwheat flours were present in the order: γ- > α- > δ-tocopherol, and in wheat flours: α- > γ- > δ-tocopherol. Buckwheat flours possessed better scavenging abilities on DPPH•, •OH and O2 •– radicals, as well as better reducing activity, while wheat flours showed better chelating activity on Fe2+, according to IC50 values. The results suggest the possibility of improving the antioxidant properties of wheat-based food products through the addition of buckwheat flour.

Biacs *et al.* (2002) reported therapeutic uses of buckwheat. Daily doses of rutin of between 180 and 350 mg have been reported to have clinically demonstrated positive effects. A daily intake of 100 g buckwheat flour or bran on food would cover 10% of the therapeutic dose of rutin. Rutin is an antioxidant, although quercetin shows higher antioxidant activity than does rutin. Rutin is a glycoside of quercetin and it is generally known that glycolization reduces antioxidant activity (Rice-Evans *et al.*, 1997). Watanabe (1998) detected four catechins with antioxidant activity in buckwheat groats. These catechins were epicatechin, catechin 7-O-β-D-glucopyranoside, epicatechin 3-O-p-hydroxybenzoate and epicatechin 3-O-(3,4-di-O-methyl) gallate. These catechins showed higher antioxidant activity than that in rutin.

It has been demonstrated that intragastric administration of buckwheat concentrate containing D-chiro-inositol (DCI), myo-inositol and fagopyritols lowered serum glucose concentrations in diabetic rats (Kawa *et al.*, 2003). D-chiro-inositol is an inositol isomer that is probably the main mediator of insulin metabolism. It acts by enhancing the action of insulin and decreasing blood pressure, plasma triglycerides and glucose concentration (Fonteles *et al.*, 2000; Ueda *et al.*, 2005; Zhang *et al.*, 2012). D-chiro-inositol has a great potential to be used as an adjunctive drug in the treatment of diseases related to insulin resistance, such as type-2 diabetes.

Qiu *et al.* (2014) isolated and identified cytoprotective agents from nonpolar extracts of buckwheat flour. Three pure compounds were isolated, identified and evaluated for bioactivity. Ferulic acid ethyl ester was the most potent isolate, doubling quinone reductase (QR) specific activity (CD value) at 2.1 μM, whereas furaneol was a moderate QR inducer, with a CD value of 185 μM. Protocatechuic acid was least effective at inducing QR, with a CD value of 2.0 mM. Binary mixtures of the three isolated components acted borderline additively / antagonistically in the QR bioassay. The compounds identified in this study can be added to a growing list of bioactive agents in buckwheat, headed up by quercetin, rutin and additional quercetin glycosides.

Choi *et al.* (2013) investigated the protective effects of tartary buckwheat (TB) and common buckwheat (CB) on amyloid-β-induced impairment of cognition and memory function in vivo in order to identify potential therapeutic agents against Alzheimer's disease (AD) and its associated progressive memory deficits, cognitive impairment, and personality changes. Results of behaviour tests in AD models showed that oral administration of methanol (MeOH) extracts of TB and CB improved cognition and memory function. Furthermore, in groups receiving MeOH extracts of TB and CB, lipid peroxidation was significantly inhibited, and nitric oxide levels in tissues, elevated by injection of amyloid-β, were also decreased. In particular, the MeOH extract of TB exerted a stronger protective activity than did CB against amyloid-β-induced memory and cognitive impairment. These studies imply that the protective role of buckwheat may be related to the quantity of rutin present. Accordingly, TB may provide more protection than does CB due to its higher rutin content.

When buckwheat is processed, flavonoid levels and antioxidant activity can be affected. Heat treatment at 150 °C for 10 min significantly reduced the flavonoid concentration by

about 20% (Arendt and Zannini, 2013). Kreft *et al.* (2006) analysed the content of rutin in buckwheat food materials and products. They discovered that there was much less rutin in noodles (78 mg/kg, dm) than in the dark buckwheat flour (218 mg/kg, dm) from which they were produced. The authors stated that a possible explanation for this was the presence of the rutin degrading enzyme. In raw (uncooked) groats, there was 230 mg/kg (dm) of rutin and in precooked groats, 88 mg/kg (dm). In buckwheat beer and vinegar, there was a negligible content of rutin. Buckwheat leaf flour contained about 2700 mg/kg (dm) rutin, and could thus be a suitable material for enriching different kinds of food products.

Buckwheat protein shows high biological value due to a well balanced amino acid pattern and is rich in lysine and arginine. It has been reported that buckwheat protein has many unique physiological functions, for example decreasing blood cholesterol, inhibiting mammary cancer caused by 7,12-dimethylbenzene, restraining gallstones and others (Tomotake et al., 2000). In humans, consumption of buckwheat is associated with a lower prevalence of hyperglycaemia and improved glucose tolerance in people with diabetes (Zhang et al., 2007). Buckwheat proteins have a high biological value due to a well balanced amino acid composition, although its digestibility is relatively low (Krkoskova and Mrazova, 2004). Buckwheat protein extracts may have strong healing effects on some chronic diseases, such as diabetes, hypertension, hypercholesterolemia and many other cardiovascular diseases (Li and Zhang, 2001). The lysine / arginine and methionine / glycine ratios in buckwheat proteins are lower than those in most other plant proteins. This composition is very similar to the composition in soybeans, implying that buckwheat could have a strong cholesterol-lowering effect, similar to soya (Carroll and Kurowska, 1995). It has been reported that lysine / arginine and methionine / glycine are critical factors that determine the cholesterol-lowering effects of the plant proteins. The lower the lysine / arginine and methionine / glycine ratios are, the better the cholesterol-lowering effect can be. There are several hypotheses to explain the cholesterol-lowering effect, but the mechanism is still not clear (Li and Zhang, 2001). The cholesterol-lowering effect of buckwheat proteins is also attributed to the low digestibility of buckwheat proteins and other dietary fibre-like components in buckwheat (Kayashita, 1997).

Buckwheat protein extract has hypocholesterolemic, anticonstipation and antiobesity properties (Zhang et al., 2012). In addition to these properties, buckwheat protein has a protective effect against induced colon carcinogenesis in rats by reducing cell proliferation (Tomotake et al., 2006). Guo et al. (2010) isolated a novel antitumour protein from tartary buckwheat.

The plant sterols (so-called phytosterols) found in buckwheat seeds, although at a low level, also show positive effects in lowering the blood cholesterol level. Phytosterols show pharmaceutical effects for many chronic diseases. Plant sterols were reported to have antiviral effects, improving the immunological status of the tested subjects (Krkoskova and Mrazova, 2004; Li and Zhang, 2001).

4.4 Conclusions

Andean grains, quinoa, kañiwa and amaranth and the buckwheat are excellent sources of dietary fibre. These grains also contain important amounts of health-promoting bioactive compounds and thus could be used as nutritive ingredients in the food industry.

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5

Proteins and Amino Acids of Kernels

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5.1 Introduction

The nutritional value of pseudocereals is mainly connected to their protein content. Pseudocereals contain similar or sometimes slightly higher protein content than the true cereals (see Figure 5.1). More importantly, the quality of the protein, in particular in amaranth and quinoa, is much higher than in cereals; pseudocereals have a very well balanced content of amino acids.

5.2 Amaranth

Compared to buckwheat or quinoa, amaranth often shows a higher protein content. Most of this protein is stored in the germ and outer seed coat (about 65%), whereas the starch-rich perisperm contains only 35% (Saunders and Becker, 1984). As in all plants, the protein content and amino acid pattern depend on genotype and growing conditions.

The analysis of 48 *A. hypochondriacus* and 11 *A. caudatus* lines revealed that *A. caudatus* lines had a higher protein content than *A. hypochondriacus* lines, whereas the Amaranthus lines with higher colour a*-values and lower 1000-kernel weight, L*- and b*-values had a higher protein content (Kaur *et al.*, 2010). Eight groups of *A. cruentus* and *A. hypochondriacus* grain samples grown in Hungary and Austria were studied and it was found that the difference between the lowest (14.23%) and highest (17.40%) protein content was relatively large, suggesting that breeding might be a potential means for increasing the protein content (Tömösközi *et al.*, 2009).

5.2.1 Storage Proteins

According to the Osborne classification, proteins can be fractionated into four types according to their solubility: water-soluble albumins, salt-soluble globulins, alcohol-soluble prolamins and insoluble glutelins. In most cereals the alcohol-soluble prolamins

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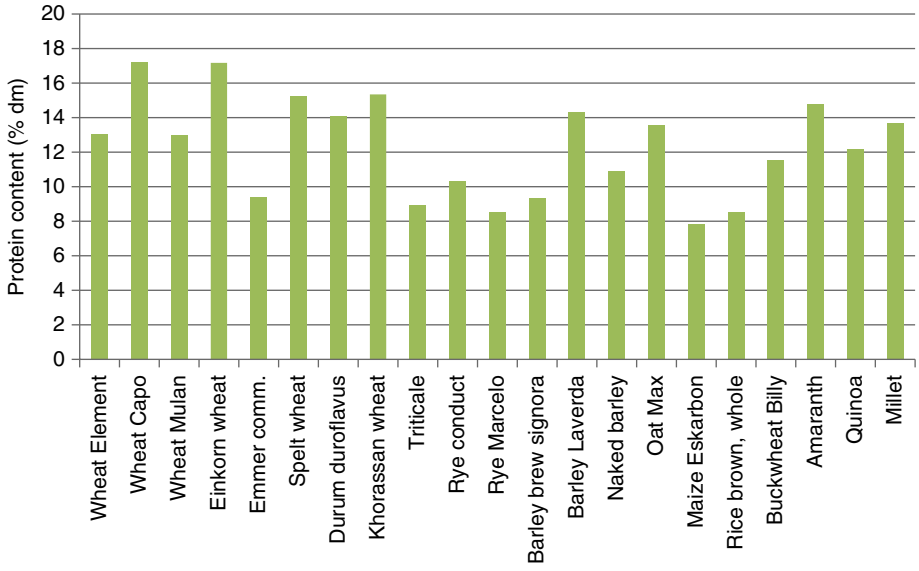

Figure 5.1 Protein content of various cereals and pseudocereals.

represent the major storage proteins, but in dicotyledonous plants the main storage proteins are globulins and albumins (Gorinstein *et al.*, 2002; Drzewiecki *et al.*, 2003). The amaranth proteins consist of about 40% albumins, 20% globulins, 25–30% glutelins, and only 2–3% prolamins (Segura-Nieto *et al.*, 1994; Bucaro Segura and Bressani, 2002, and others). Other authors reported an even lower amount of proloamins: 1.2% were found by Gorinstein *et al.* (1999), who also mentioned that the protein proportions for amaranth were similar to rice. Only 0.48–0.79% prolamins were measured by Muchova *et al.* (2000). Thermal treatment decreased the water-soluble protein fraction (albumins and globulins) and alcohol-soluble fraction (prolamins) (Gamel *et al.*, 2005). The amaranth proteins are similar to seed proteins in other dicotyledonous crops like legumes, and have no relationship to the major prolamins of cereals. According to Gorinstein *et al.* (2001, 2004) the glutelin fraction showed some similarities to maize. Globulins and albumins constitute the principal protein fraction in amaranth isolates (Shevkani and Singh, 2015). According to their sedimentation coefficient, two main classes of globulins can be differentiated: 7S and 11S globulins (Quiroga *et al.*, 2009). The globulin 11S (amaranthin) is the main grain storage protein in amaranth (Condés *et al.*, 2009), while the globulin 7S (conamaranthin) is found in much lower amounts. The molecular mass of 11S globulin is according to Barba de la Rosa *et al.* (1996) 56 kDA. The 7S globulin is formed by 4 subunits of 66, 52, 38 and 16 kDA with a molecular mass near 200 kDA (Quiroga *et al.*, 2009).

Cooking and popping decreased the fraction of albumins + globulins and the fraction, while germination significantly reduced the levels of all fractions except the albumins + globulins (Gamel *et al.*, 2005).

The protein profile and amino acid composition of 11 species (*A. viridis, A. powellii, A. muricatus, A. deftexus, A. blitoides, A. graecizans, A. retroflexus, A. albus, A. blitum, A. cruentus*, and *A. hypochondriacus*) from wild populations (from the south-west of Spain) were studied by gel filtration chromatography and denaturing electrophoresis (Juan *et al.*, 2007, cited in Venskutonis and Kraujalis, 2013). In this study, six main

fractions of around 300, 180 and 120 kDA, between 40 and 50 kDA, 20 and 30 kDA, and below 10 kDA were observed, while the electrophoretic analysis showed peptides grouped into three main fractions, between 50 and 64 kDA, 33 and 37 kDA, and 18 and 25 kDA. The most balanced amino acid compositions were observed in *A. muricatus, A. blitum*, and *A. powellii*, whereas A. *hypochondriacus* and *A. graecizans* showed the most deficient amino acid composition with limitations in five essential amino acids (Juan *et al*., 2007 cited in Venskutonis and Kraujalis, 2013).

Besides these four protein fractions, some other important proteins are present in amaranth. Some of these proteins have inhibitory activities like α-amylase inhibitor or trypsin inhibitor. The overall protein composition and their bioactive peptide sequences, which may prevent certain diseases were reviewed in detail by Montoya Rodriguez *et al*. (2015). They summarize that the 15 main proteins in amaranth seed are 11S globulin, 7S globulin, α-amylase inhibitor, trypsin inhibitor, antimicrobial proteins, nonspecific lipid-transfer-protein-1, superoxide dismutase, ring-zinc finger protein, prosystemin, amaranth albumin 1, glucose-1-phosphate adenyltransferase, glucosyltransferase, polyamine oxidase, granule-bound starch synthase 1, and acetolactate synthase. All proteins showed high occurrence frequencies of angiotensin-converting enzyme-inhibitor peptides (A = 0.161 to 0.362), as well as of dipeptidyl peptidase IV inhibitor (A = 0.003 to 0.087). Other proteins showed antioxidative (A = 0.012 to 0.063) and glucose uptake-stimulating activity (A = 0.023 to 0.042), and also antithrombotic (A = 0.002 to 0.031) and anticancer sequences (A = 0.001 to 0.042). The results of the study of Montoya Rodriguez *et al*. (2015) support the concept that amaranth grain could be part of a 'healthy' diet and thereby prevent chronic human diseases.

Applying two-dimensional gel electrophoresis (2-DE) and LC-MS/MS Maldonado-Cervantes *et al*. (2014) identified proteins in amaranth, which were related to stress and defence responses, metabolic, respiratory, and oxide-reduction processes. Sabione *et al*. (2015) obtained amaranth protein isolates and fractions and evaluated its antithrombotic activity. The glutelin fraction exhibited the highest antithrombotic activity, significantly superior compared to other fractions. As this fraction showed a potential capacity to inhibit coagulation, it might be a promising ingredient for functional foods.

5.2.2 Amino Acids

The three pseudocereals – amaranth, quinoa and buckwheat – have an outstanding amino acid composition, with a high content of essential amino acids. The balanced amino acid composition of amaranth is close to the optimum protein reference pattern in the human diet according to FAO/WHO requirements (Grobelnik-Mlakar *et al*., 2009; Rastogi and Shukla, 2013, both cited in Montoya Rodriguez *et al*., 2015). Methionine, lysine, arginine, tryptophan and sulfur-containing amino acids are found in higher amounts than in other cereals (Matuz *et al*., 2000a; Gorinstein *et al*., 2002). Also Palombini *et al*. (2013) found higher concentrations of leucine, lysine and phenylalanine in two Brazilian cultivars. For amaranth, the sum of essential amino acids has been reported to be 47.65 g/100 g of protein (Drzewiecki *et al*., 2003). Amaranth amino acid composition profile was shown to be generally closer to *Leguminosae* than to cereal grains, except for sulfur-containing amino acids being present in higher amounts in amaranth than in legumes.

Table 5.1 Amino acid composition of amaranth (average of several varieties) (Montoya-Rodriguéz *et al*., 2015).

Amino acids (g/100 g of protein)							
Trp	Met/Cys	Thr	Ile	Val	Lys	Phe/Tyr	Leu
1.3	4.5	3.5	3.6	4.2	5.6	7.3	5.4

Regarding limiting acid, the data in literature are sometimes controversial, depending on the method used for their determination. Most often leucine, isoleucine and valine are mentioned as limiting (see Table 5.1) (Montoya Rodriguez *et al*., 2015). When considering the chemical score, several authors indicated leucine as the limiting amino acid in amaranth (Saunders and Becker, 1984; Abreu *et al*., 1994; Escudero *et al*., 2004 and others), others found valine to be limiting (Aguilar *et al*., 2015), whereas when considering the protein efficiency ratio (PER), threonine was recognized to be the limiting amino acid (Bressani *et al*., 1989). However the limiting amino acids in pseudocereals are not a serious problem, since these are in excess in most common grains (Montoya Rodriguez *et al*., 2015).

Free amino acids that may play some role in the Maillard reaction during thermal treatment of amaranth or other products with amaranth addition were studied by LC–MS/MS and it was determined that their content in *A. hypochondriacus* ranged from 0.61 ± 0.03 for ornithine to 10.7 μg/g for threonine (Nimbalkar *et al*., 2012).

The available lysine content might be reduced by heating amaranth seeds (as with popping); however, differences in initial sugar and moisture contents of grain influencing the rate of potential Maillard reaction may be the reason of some contradictory data published in the literature on this matter (Tömösközi *et al*., 2009). Gamel *et al*. (2004) found that after popping the loss of the amino acid tyrosine was highest, followed by phenylalanine and methionine. Based on the chemical score, lysine was the limiting acid in the popped sample, as previously found by Tovar *et al*. (1989). During germination, the amounts of asparagine acid, serine, and alanine increased, while those of threonine, arginine, and tyrosine decreased (Gamel *et al*., 2005).

5.2.3 Nutritional Quality

The content of amino acid alone does not describe the quality of protein sufficiently. Several parameters are applied to determine the protein quality regarding its bioavailability or digestibility. Protein digestibility, available lysine, biological value (BV), net protein utilization (NPU), protein efficiency ratio (PER), or the protein digestibility corrected amino acid score (amino acid score × protein digestibility, PDCAAS) are widely used as indicators for the nutritional quality of proteins.

Several studies have been undertaken to determine the protein quality from pseudocereals and they demonstrated that the values determined are higher when compared to cereals. Generally, the protein quality of pseudocereals is close to that of casein.

Average protein digestibility of raw amaranth wholemeal flours was determined to be 74.2% (Bejosano and Corke, 1998). Escudero *et al*. (2004) and Gamel *et al*. (2004) determined slightly higher values, 81 and 80–86%, respectively. Heating increased protein digestibility, which was probably due to the fact that the carbohydrate–protein complex

was opened by thermal treatment. Antinutritional factors like trypsin inhibitors or polyphenols (tannic acid) could also have been inactivated (Bejosano and Corke, 1998). Generally, a high correlation was found between the protein digestibility and the presence of polyphenols, whereas only a weak correlation was found with trypsin inhibitors. Fadel *et al.* (1996) demonstrated that heat treatment lowers the activity of trypsin inhibitors, thus improving the nutritive value of amaranth.

Chemical score for amaranth protein was calculated to be 50 to 67 (Correa *et al.*, 1986). Calculated-PER (C-PER) ranged from 1.39 to 1.80 and biological value (BV) from 52 to 68. Similar values have been found by Escudero *et al.* (2004). Yanez *et al.* (1994) measured a C-PER value for amaranth of 1.94 compared to 2.77 in casein and 1.64 in wheat. The net protein ratio (NPR) value ranged from 3.04 to 3.20, compared to a NPR of 4.08 in casein. PDCAAS assessment demonstrated that amaranth wholemeal flour has a higher value (0.64) than wheat (0.40) or oat (0.57), but lower values than sodium-caseinate, which had a value for PDCAAS of 1.03 (Bejosano and Corke, 1998; Escudero *et al.*, 2004). In recent measurements of Aguilar *et al.* (2015) for two new amaranth cultivars the following values were obtained: NPU 33.56–46.04%; true digestibility 68.80–75.40%, BV 44.53–64.28% and PDCAAS 23.69–36.19%. They suggested that the new amaranth flours varieties could be adequate for human consumption and as a complementary protein source.

The effect of processing on protein quality was investigated by some authors. Popping seemed to have no effect on *in vivo* protein digestibility, although the *in vitro* digestibility was slightly higher for the popped seeds compared to raw seeds. But after popping the PER value was reduced by 14–19%, probably due to a loss of essential amino acids (Gamel *et al.*, 2004). Extrusion cooking improved the *in vitro* digestibility of protein in two amaranth varieties (*A. caudatus*) (Repo-Carrasco-Valencia *et al.*, 2009).

5.2.4 Allergy and Coeliac Disease

To date, only a few studies have been performed on amaranth allergy or on toxicity of amaranth proteins to coeliac disease. A study about allergenic reaction to the prolamin fraction of amaranth was undertaken by Matuz *et al.* (2000b). In contrast to wheat, barley, rye, triticale and oat, the prolamin fraction of amaranth showed no reactivity against the rabbit antigliadin (wheat) antibodies. Bergamo *et al.* (2011) investigated millet, tef, amaranth and quinoa grains in intestinal T-cell lines, cultures of duodenal explants from HLA-DQ2+ CD patients and HLA-DQ8+ transgenic mice for signs of activation. Their data indicated that tef, millet, amaranth and quinoa did not show any immune cross reactivity toward wheat gliadin, and therefore confirming their safety in the diet of CD patients. From a tolerability study of 40 amaranth varieties, using both SDS-PAGE-immunoblotting and ELISA, it has been established that their binding affinities for both specific antigliadin antibodies and human IgAs are quite similar, most of them being in a range below 20 μg/g, as measured by ELISA (Ballabio *et al.*, 2011).

In vivo and *in vitro* investigations of general allergic reactions to amaranth revealed that amaranth causes a classical type-1 reaction in sensitized patients (Bossert and Wahl, 2000). On the other hand Hibi *et al.* (2003) found that amaranth grain and its extract inhibited antigen-specific IgE production by augmenting Th1 cytokine responses *in vivo* and *in vitro*. Genetically modified maize with an amaranth 11S globulin (amarantin)

caused no important allergenic reactions to amarantin during *in vitro* investigations (Sinagawa-Garcia *et al*., 2004).

5.2.5 Functional Properties of Proteins

Research has revealed that all pseudocereal proteins are highly soluble and are thus a good source to be applied in functional foods (Bejosano and Corke, 1999; Segura-Nieto *et al*., 1999; Kovacs *et al*., 2001; Salcedo-Chavez *et al*., 2002).

The production and characterization of amaranth protein isolates has been pursued by several research groups, in particular in recent years. Generally, amaranth protein isolates have shown good foaming and film forming properties (Fidantsi and Doxastakis, 2001). The usefulness of amaranth protein isolates, native and thermally treated, in edible films preparation was studied by Condes *et al.* (2013). Films from amaranth native protein isolates showed low water vapour permeability but poor mechanical properties, which were improved by thermal treatment (protein denaturation) of the proteins. Depending on protein and thermal conditions, amaranth proteins are able to form self-supporting gels that could be applied in different gel-like foods (Avanza *et al*., 2005). In addition, Scilingo *et al*. (2002) found that an amaranth protein isolate hydrolysed by papain keeps a high solubility after heating, thus indicating that it could be a suitable ingredient in foods submitted to thermal treatments. Bolontrade *et al.* (2016) analysed the influence of pH and ionic strength on the stability of foams prepared with amaranth protein isolates. They clearly showed that the foams made with amaranth proteins at acidic pH exhibited better stability than those obtained at alkaline pH. Under these conditions more flexible and elastic films were formed. These results suggest the application of amaranth proteins into acid foam-type foods like dessert stuffing or ice cream.

Amaranth globulins were shown to have particularly good functional properties (Segura-Nieto *et al*., 1999). Marcone and Kakuda (1999) found that the functional properties of amaranth globulin isolate are much better than soybean isolate, especially in the vicinity of its electrical point (pH 5–6), showing higher solubility, heat stability, foaming capacity and stability as well as emulsifying activity. The physicochemical behaviour of films made of amaranth 7S-globulin was investigated by Gonzalez *et al*. (2012). They found that isotherms of pure 7S globulin directly deposited on either water or buffer subphases behave similarly. Globulin forms a condensed film made of globular and denature structures. They showed that globulin 7S mixed well with lipid phases, which could be important in food applications as stabilizers or emulsifiers. The studies of the physicochemical properties of 11S globulin suggested that the cumulative effects of many factors are responsible for its high thermal stability, whereas the balance between surface hydrophobicity and hydrophilicity is important for good emulsifying property (Tandang-Silvas *et al*., 2012).

The functional properties of amaranth albumins have been investigated by Silva-Sanchez *et al.* (2004). The maximum solubility values are above pH 6. When comparing these values to the solubility of egg albumins, amaranth albumins showed excellent foaming capacity and foaming stability at pH 5, suggesting that they could be used as whipping agents like egg albumins. Moreover, the water and oil absorption capacities reached their maximum values at an acidic pH.

The physicochemical properties of the glutelin fractions were influenced by the solvent (borate or NaOH) used to extract these glutelin fractions (Abugoch *et al*., 2003), and this in turn may result in different functional properties.

5.2.6 Enzyme Inhibitors

Protease inhibitors (e.g. chymotrypsin or trypsin inhibitors) are found in many food plants. They competitively inhibit the activity of proteolytic enzymes. On the other hand, protease inhibitors can have anticarcinogenic, antioxidative, blood glucose regulatory, as well as anti-inflammatory effects. By heat treatment (e.g. cooking, popping) or germination their activity can be reduced.

Amaranth contains only low amounts of protease inhibitors compared to many cereals (Bressani, 1994; Bejosano and Corke, 1998). Gamel *et al.* (2006) found trypsin inhibitor activity (TIU) ranging from 3.05 to 4.34 TIU/mg, chymotrypsin inhibitor activity (CIU) ranging from 0.21 to 0.26 CIU/mg, and amylase inhibitor activity ranging from 0.23 to 0.27 AIU/mg.

5.3 Quinoa

Quinoa (*Chenopodium quinoa* Willd.) is known as a complete food due to its well balanced composition of nutritive and antinutritive ingredients. It has extraordinary good nutritional properties, especially because of its high protein quality and average content of about 13–15% (Repo-Carrasco *et al*., 2003; Abugoch *et al*., 2009; Hager *et al*., 2012). According to literature a range of 8–22% for the protein content can be found (Prakash and Pal, 1998; Bhargava *et al*., 2007; Rosero *et al*., 2013). Generally, the genetic source causes great variations in the protein content and quality. Environmental and climatic conditions also show a significant influence; the amino acid composition is especially highly affected (Prakash and Pal, 1998; Gonzalez *et al*., 2011; Mickowska *et al*., 2013; Miranda *et al*., 2013). Tillage and fertilization influence crude protein content to a high degree (Kakabouki *et al*., 2014). Prakash and Pal (1998) examined the changes in protein and amino acid content during maturation of seeds. During seed development first a decrease and then a slight increase in the protein concentration was observed (Cocozza *et al*., 2013).

5.3.1 Storage Proteins

The proteins of quinoa are mainly stored within the embryo in order to provide nutrients for growth and development. Beside fats, the seedling consists mainly of proteins, whereas the concentration of proteins in the perisperm is much lower. Ando *et al*. (2002) found protein concentrations of 23.5% in the embryo and 7.2% in the perisperm, whereas D'Amico *et al*. (2015) found higher concentrations of up to 38% in the embryo and less than 5% in the perisperm. The low amount of proteins in the perisperm was also confirmed by Lindeboom *et al*. (2005) and Chauhan *et al*. (1992). However, the low occurrence of polypeptides in the perisperm differs from cereals, where most proteins are stored in the endosperm.

Quinoa shows a distribution of the proteins that is different from cereals, according to the Osborne classification (separation by solubility) . Apart from rye, the main fractions of common cereal proteins are prolamins and glutelins. In contrast, quinoa proteins consist predominantly of albumins and globulins, which account for up to 80% of total protein (Koziol, 1992). An overview about the distribution of Osbourne fractions is given in Table 5.2. The different studies mentioned in this table verified the predominance of albumins and globulins in quinoa, ranging from 60% to 70%. Yet the ratio of albumins

Table 5.2 Distribution of protein fractions (in %) according to Osbourne.

Reference	Albumin	Globulin	Prolamin	Glutelin[b]
Prakash and Pal (1998)	31.0	37.0	12.3**	19.7
Ando *et al.* (2002)	33.1	28.9	6.4*	31.6
Watanabe *et al.* (2003)	28.5	34.1	19.3	18.1
Thanapornpoonpong *et al.* (2008)[a]	13.2–13.4	51.4–60.2	3.2–5.9	23.4–29.3
D'Amico *et al.* (in press)	42.3	27.9	11.1***	21.8

a) Range of two quinoa varieties.
b) Glutelins were mainly calculated based on insoluble proteins.
* Lactic acid soluble fraction.
** Ethanol and alkaline soluble fraction.
*** SDS-soluble fraction.

and globulins varies to a high degree. Two studies (Ando *et al.*, 2002 and D'Amico *et al.*, 2015) revealed the albumins as most abundant protein fraction, whereas three studies showed that globulins occurred in bigger amounts (Prakash and Pal, 1998; Watanabe *et al.*, 2003; Thanapornpoongpong *et al.*, 2008). A unique attribute of seeds from the Amaranthaceae family is the presence of a second albumin fraction, which can be separated by water after an extensive extraction of globulins and albumins (Drezewiecki *et al.*, 2003; Gorinstein *et al.*, 2005). This attribute might be responsible for varying results in respect to the ratio of globulins and albumins. Generally, the portion of prolamins is quite small (see Table 5.2), although some authors reported higher values. This discrepancy can be explained by the different extraction solvents used in the listed studies. The addition of SDS, acids or bases also coextracts glutelins in different amounts. The share of glutelins or insoluble proteins ranges between 18.1% and 31.6%. This variance is quite small considering the coextraction of glutelins by the used extraction procedures. These findings were largely in accordance with the study by Koziol (1992).

Several authors analysed the molecular weight of quinoa proteins by SDS-PAGE. In quinoa, mainly medium-sized proteins with a mass between 10 and 70 kDA were found and only a few weak bands from 70 to 100 kDA were detected (Drzewiecki *et al.*, 2003; Gorinstein *et al.*, 2005; Abugoch, 2009; Hager *et al.*, 2012). The most abundant protein is the so-called globular chenopodin, which is of 11S type and makes up to 37% of the total protein mass. It has a molecular weight between 50 and 55 kDA and is built up by two subunits. Under reducing conditions, the disulfide bonding break down and the size of the subunits can be detected. The acidic subunit has a molecular weight of 30–40 kDA, the basic one of 20–25 kDA (Brinegar und Goundan, 1993; Hager *et al.*, 2012; D'Amico *et al.*, 2015). Chenopodin has low amounts of methionine and cysteine compared to total protein. The second most abundant protein is a 2S-type polypeptide with a relatively small molecular mass of about 9–10 kDA (Brinegar and Goundan, 1993; Hager *et al.*, 2012). This protein is rich in cysteine, arginine and histidine, whereas the concentration of methionine is again quite low (Brinegar, 1997). The two major quinoa proteins vary predominantly in their solubility at pH 5, where the 11S is precipitated while the 2S protein is still soluble (Brinegar, 1997).

A very detailed insight into the protein composition was given by application of RP-HPLC (D'Amico *et al.*, 2015), which is shown in Figure. 5.2. Albumins (water), globulins

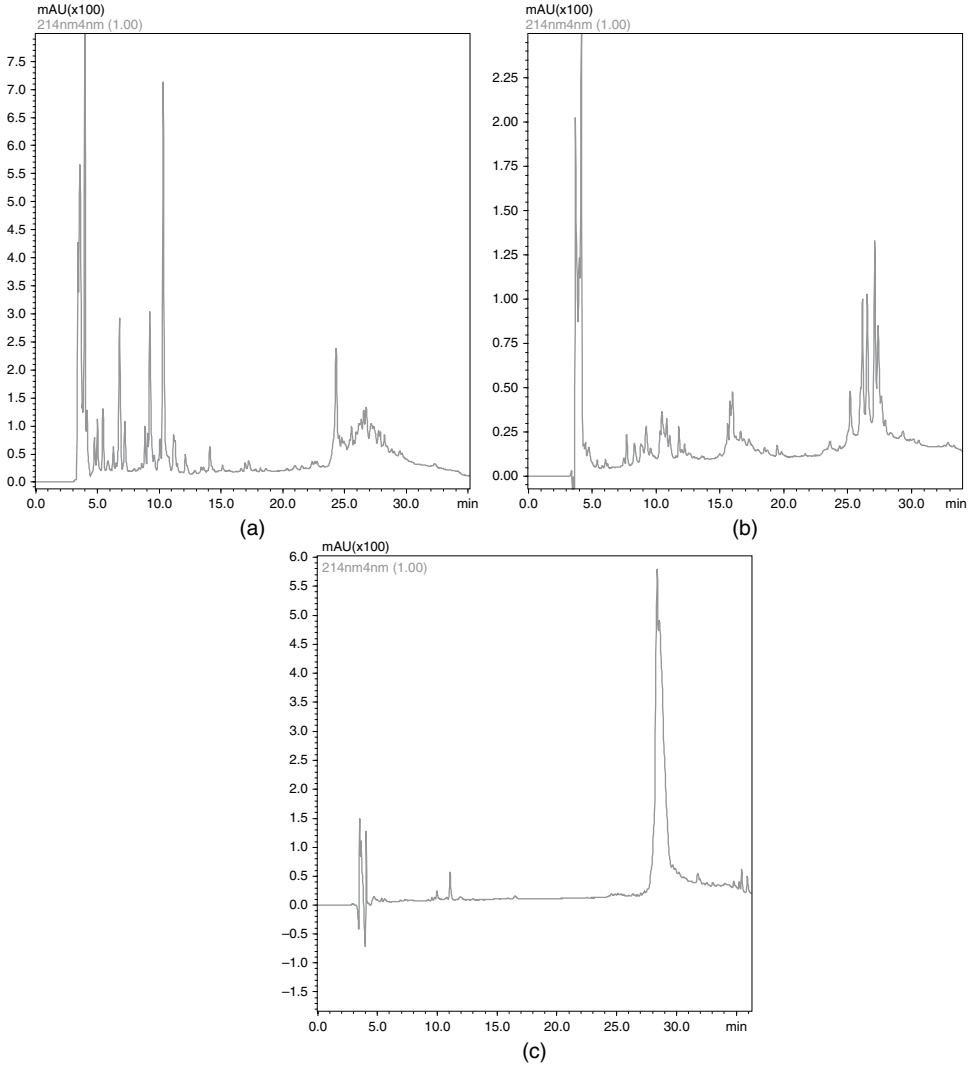

Figure 5.2 Chromatograms of quinoa protein fractions based on solubility, (a) water, (b) 2% sodiumchloride and (c) 1% SDS. Polypeptides were separated on Jupiter (Phenomenex, Germany) using a water/acetonitrile gradient containing 0.05% TFA and detected at 214 nm.

(2% sodium chloride) and prolamins with some glutelins (1% SDS) were successively extracted from whole quinoa seeds. The albumin and globulin fraction could be divided into three subfractions based on retention time, which correlated with the hydrophobicity of these proteins. In the albumin fraction, peaks could be observed mainly in the first subfraction (more polar), whereas in the second and third subfractions only a few peaks of low intensity were detected. The globulins showed a controversial picture. In the first section fewer peak intensities were detected, whereas in the second section more peaks and in the third section the most polypeptides were identified. Considering data from SDS-PAGE measurements and information from literature the agglomeration of peaks in the third subfraction of globulins could be assigned to chenopodin. Due

to the high separation power of RP-HPLC chenopodin was obviously split up further. In the SDS-soluble fraction, which consisted of prolamins and also to a minor degree of coextracted glutelins, only a small number of proteins were detected. This result was confirmed by Mickowska *et al.* (2013), who detected only 2–3 bands by SDS-PAGE in the alcohol soluble fraction of three quinoa varieties.

Little is known about the secondary structure of quinoa proteins. Only one study examined the organization of proteins very detailed by a nonlinear least-squares curve-fitting program based on results of circular dichroic measurements (Drezewieki *et al.*, 2003). Quinoa polypeptides were rather randomly organized. The β-sheet prevailed as ordered structure, whereas the occurrence of α-helices was low. Gorinstein *et al.* (2005) published similar values for the α-helix ratio in different protein fractions of quinoa: 20% globulins and 4–10% albumins. On the other hand FT-IR spectra indicated a predominance of α-helices and a low share of β-sheets due to low intensities of amide-III-bands. However, data about steric conformation is contradictory and incomplete; further research has to be conducted in this respect. As the Chenopodium genus and Amaranthus belong to the Caryophyllales order, strong similarities between amaranth and quinoa were observed (Drezewieki *et al.*, 2003).

5.3.2 Amino Acids

An overview of recently published data about amino acid profiles of quinoa is presented in Table 5.3. Tryptophan and other sulfur-containing amino acids are sensible to acidic conditions and were totally or partially destroyed during sample preparation. Most abundant amino acids were aspartic and glutamic acid, and arginine. The extraordinary high concentration of lysine is typical for legumes like soy. This overview shows a high variation between the cited sources, especially for the amino acids isoleucine, valine and arginine. A study by Gonzalez *et al.* (2011), which analysed ten quinoa varieties, showed variations of 1.7–3.4 g/100 g protein for isoleucine, 2.2–4.1 g/100 g protein for valine and 4.6–10.9 g/100 g protein for arginine. Similar ranges were also reported by Lindeboom *et al.* (2005) and Rosero *et al.* (2013). Consequently, variety was identified as the main factor responsible for variations, but the development stage of seeds, conditions of cultivation and climate also affected the profile of amino acids to a minor degree (Prakash and Pal, 1998; Gonzalez *et al.*, 2011; Mickowska *et al.*, 2013; Miranda *et al.*, 2013). According to WHO (2002) quinoa complied with the requirements. Only isoleucine and valine were not available in sufficient amounts in all cases. Ruales *et al.* (2002) reported a chemical score of 86; the primarily limiting amino acids were tyrosine and phenylalanine, followed by lysine and threonine. The amount of sulfur-containing amino acids (methionine and cystine) was relatively high. The data presented by Abugoch (2009) also showed a deficiency in aromatic amino acids, which caused a low chemical score of 80. But Vega-Galvez *et al.* (2010) showed abundant tyrosine and phenylalanine as well, which ranged between 6.2–7.5 g/100 g protein. Generally, the content of essential amino acids in quinoa is higher than in common cereals like wheat, barley, rye, rice and maize (Vega-Galvez *et al.*, 2010) and thus the amino acid composition of quinoa is nutritionally superior to common cereals.

5.3.3 Nutritional Quality

The nutritional value of a food is influenced by its protein quality, which depends mainly on its amino acid composition, digestibility and antinutritional factors, for example

Table 5.3 Overview of amino acid composition in quinoa (g/100 g protein).

	Repo-Carrasco *et al.* (1992)	Lindeboom *et al.* (2005)[a]	Gonzalez *et al.* (2011)[b]	Stikic *et al.* (2012)	Palombini *et al.* (2013)	Rosero *et al.* (2013)[c]	Gallego-Villa *et al.* (2014)	Estimates WHO (2002)
Essential AAS								
Histidine	2.7	2.9	2.4	2.6	2.2	2.4	2.0	1.5
Isoleucine	3.4	4.3	2.3	5.0	2.9	3.1	7.4	3.0
Leucine	6.1	7.4	5.2	8.3	5.1	5.5	7.5	5.9
Lysine	5.6	6.5	4.1	3.9	4.3	4.4	4.6	4.5
Cystine	1.7	1.8	n.d.	3.9	0.9*	1.2*	2.2	0.6
Methionine	3.1	2.4	1.2*	2.2	1.9*	0.9*	2.3	1.6
Phenylalanine	3.7	4.5	3.1	4.7	3.0	4.5	4.3	3.8***
Tyrosine	2.5	3.3	2.5	3.6	2.5	3.7	3.1	3.8***
Threonine	3.4	4.7	3.0	3.0	2.3	3.1	3.5	2.3
Tryptophane	1.1	1.3	0.7*	n.d.	n.d.	n.d.	n.d.	0.6
Valine	4.2	5.3	2.9	5.3	3.5	3.9	6.0	3.9
Nonessential AAS								
Alanine	4.1	5.3	3.5	13.3**	3.2	4.1	5.7	-
Arginine	8.1	10.2	6.9	13.6	7.3	9.2	8.4	-
Aspartic and glutamatic acid[d]	21.0	24.5	19.4	22.8	18.0	17.2	23.4	-
Glycine	5.0	6.0	4.9	2.2	5.4	4.1	6.1	-
Proline	3.4	4.6	3.1	13.3**	3.4	2.8	2.3	-
Serine	3.9	5.7	3.9	3.6	3.5	3.4	3.8	-

n.d.: not detected;
a) average of three quinoa varieties;
b) average of ten quinoa varieties;
c) average of four quinoa varieties;
d) asparagine was converted to aspartic acid due to acid conditions of sample preparation;
* partially destroyed due to conditions of sample preparation;
** sum of alanine and proline;
*** sum of the aromatic amino acids tyrosine and phenylalanine.

protease inhibitors. *In vitro* digestibility in raw quinoa ranged between 76.3–80.5% (Ruales and Nair, 1994; Repo-Carrasco-Valencia and Serna, 2011). Dehulling or washing increased the digestibility to 83–84% (Ranhotra *et al.*, 1993; Ruales and Nair, 1994); cooking caused even higher digestibility of up to 95% (Ruales *et al.*, 2002). *In vivo* tests accomplished by feeding experiments showed better digestibility of 92% (Ruales and Nair, 1994). Some studies showed that it is necessary to decrease the amount of saponins to increase digestibility (Gross *et al.*, 1989; Ruales and Nair, 1994). That is also a reason why commercial quinoa seeds are washed and lightly dehulled.

Ruales *et al.* (2002) reported a PDCAAS of 0.67 based on requirements for infants, which are much higher in respect to some essential amino acids compared to adults.

Net protein utilization in quinoa was 67.7–75.7 and BV 71.1–82.6. These values were significantly better than cereals but still lower than animal protein sources like casein (Ruales and Nair, 1992; Ruales *et al*., 2002). Ranhotra *et al*. (1993) reported PER-values of 3.8 and cPER values of 2.7, which were even superior to the casein values (PER 3.5, cPER 2.5). Gross *et al*. (1989) confirmed the high quality of quinoa polypeptides and similar PER values to casein were found for cooked quinoa seeds. Utilization of proteins can be reduced by trypsin inhibitors but in quinoa the activity of trypsin inhibitors is low (Chauhan *et al*., 1992). Activities of 1.36–5.04 TIU/ml sample were found, which is lower than in legumes. By heat treatment, washing or dehulling the inhibition can be diminished (Ruales and Nair, 1992; Chauhan *et al*., 1992; Ranhotra *et al*., 1993). However, due to the excellent amino acid pattern and BV, quinoa belongs to the top single plant foods (Woolf *et al*., 2011).

5.3.4 Allergy and Coeliac Disease

Quinoa's dicotyledonous origin and low prolamin content indicate little or no toxicity for coeliac disease patients. In contrast to wheat, rye and barley, quinoa prolamins lack proline (Comino *et al*., 2013). Several studies examined the potential of quinoa in respect to coeliac disease by either applying immunological tests or *in vitro* systems of cell cultures. One of the first studies of toxicity of quinoa proteins was performed by De Vincenzi *et al*. (1999). The extracted prolamins were digested by tryptic enzymes to simulate in vivo digestion, which were separated into two fractions by affinity chromatography. Afterwards cells from human myelogenous leukaemia origin were used for an agglutination test. The first fraction showed no agglutination, whereas a second fraction, accounting for only 1% of the whole digest, gained agglutination. However, the whole peptic digest showed no agglutination, which indicated the safety of quinoa prolamins for coeliac disease patients. An interference of these fractions of peptides might be responsible for inhibition of cell agglutination. Berti *et al*. (2004) applied ELISA and immune blotting methods to evaluate the gluten-free status of quinoa. Both methods showed no relevant or only marginal immune response. Bergamo *et al*. (2011) used intestinal T-cell lines to evaluate the *in vitro* response of seven patients. These results also showed no immune cross reactivity toward wheat gliadin, which was used as reference. Mickowska *et al*. (2013) extracted alcohol soluble proteins from different grains to evaluate toxicity for coeliac disease patients by Western blot and ELISA tests, based on polyclonal and monoclonal antibodies, respectively. The immunodetection of prolamins revealed again the absence of toxic proteins in quinoa. A very detailed study with 11 varieties of quinoa was recently presented by Peñas *et al*. (2014). Immunoblotting was used as *in vitro* screening for the safety of different quinoa varieties. Finally, this study showed that even cultivation of quinoa in regions with incidence of wheat agriculture did not affect the gluten-free status of quinoa. Recently a medical study with 19 coeliac disease patients, who consumed 50 g of quinoa every day for 6 weeks, was published. Detailed histological assessments of ten patients were examined before and after the supplementation with quinoa. The inclusion of quinoa within the gluten-free diet of these coeliac patients was well tolerated. Even a positive trend in respect to enhanced histological and serological parameters was observed (Zevallos *et al*., 2014). Numerous studies confirmed that quinoa can safely be consumed by coeliac disease patients. No significant *in vitro* or *in vivo* effects were observed.

5.3.5 Functional Properties of Proteins

Protein solubility of quinoa flour is strongly affected by pH, with highest solubility under strong alkaline conditions. Lowest solubility was observed at a pH of 4.7–6; these conditions can be used for precipitation (Chauhan *et al*., 1999; Oshodi *et al*., 1999; Aluko and Monu, 2003; Abugoch, 2009). These results were in good accordance with isoelectric points of the main proteins, which were identified at pH 4.4, 5.4, 5.6, and 5.8 (Scanlin, 2006). Emulsification capacity and stability are higher compared to pearl millet or wheat, whereas foaming capacity seems to be lower (Oshodi *et al*., 1999). Protein isolates of quinoa have a water-holding capacity of 2.8–4.5 mL water/g sample depending on extraction conditions, which is similar to soy isolates (Abugoch, 2009). Abugoch (2009) examined the thermal properties of protein isolates by DSC, which showed two endotherm peaks between 85.6–103.1 °C. Higher pH during isolation changed the conformation and no peak of denaturation was detected. To avoid these alterations Aluko and Monu (2003) used enzymatic hydrolysis to increase solubility. This resulted in an increase of foaming capacity, whereas a decrease in the emulsifying capacity of the hydrolysed polypeptides could be observed compared to the nonhydrolysed polypeptides.

5.4 Buckwheat

Two buckwheat species have been commonly cultivated around the world for centuries: common buckwheat (*Fagopyrum esculentum* Moench) and tartary buckwheat (*Fagopyrum tataricum*). Its seeds are used in many forms in human foods for flour and groat products (Steadman *et al*., 2000; Alvarez-Jubete *et al*., 2010).

5.4.1 Protein Content

In literature, the protein content of buckwheat whole grains has been reported to be around 12%, depending on the variety, environment and fertilization, which are likely to affect the total protein concentrations (Table 5.4) (Christa and Soral-Šmietana, 2008). In bran, the protein content was above 20%, while in the flour these values were about 10% (Alvarez-Jubete *et al*., 2010).

The protein content of all buckwheat grain fractions increases in the order from the inner fraction to the outer fraction of the grain. The protein content of the inner fraction is only 1–2% whereas the outer fraction contains about 40% of the proteins. In the embryo it reaches values up to 56% (Morita *et al*., 2006) whereas the protein concentration in the hull is low, around 4% (Pomeranz and Robbins, 1972; Christa and Soral-Šmietana, 2008).

5.4.2 Amino Acid Composition

Buckwheat proteins have a higher biological value than the cereal proteins, which lies above 90%. This can be explained by a high and more balanced concentration of essential amino acids (Table 5.5). Due to the presence of exogenous antinutritiens (e.g. dietary fibre, protease inhibitor and tannin-type compounds) and the susceptibility of the protein to proteolytic action, the true protein digestibility is slightly below 80%, however

Table 5.4 Protein content of buckwheat grains in different studies.

Protein (% dry matter)	Reference
12.6–15.4	Pomeranz and Robbins (1972)
12.3	Steadman *et al.* (2000)
12.2	Li and Zhang (2001)
11.7	Bonafaccia *et al.* (2003)
13.3–15.61	Wei *et al.* (2003)
12.5	Alvarez-Jubete *et al.* (2010)
12.2	Hager *et al.* (2012)

(Pomeranz and Robbins, 1972; Bonafaccia and Kreft, 1994). Buckwheat proteins show a similar or even higher content of nearly all amino acids except for glutamine and proline compared to wheat (Aubrecht and Biacs, 2001). Buckwheat proteins are rich in lysine, which is an advantage compared to other plant proteins, and arginine. In buckwheat species, threonine and methionine are the first and the second limiting amino

Table 5.5 Amino acid composition of buckwheat (Christa and Soral-Šmietana, 2008) compared to wheat (FAO) and the WHO recommendation of essential amino acid daily intake for adults.

Amino acid	Buckwheat (g/100 g protein)	Wheat (g/100 g protein)	Recommended daily intake (mg/kg/day)
Asp	5.2–9.5	3.08	
Thr*	1.9–4.04	1.83	15
Ser	2.4–4.9	2.87	
Glu	9.7–19.38	18.6	
Pro	2.6–7.93	6.21	
Gly	4.2–6.23	2.45	
Ala	3.0–4.82	2.26	
Cys	2.06–3.27	1.59	
Val*	3.4–4.97	2.76	26
Met*	0.99–2.3	0.94	10.4
Ileu*	2.6–3.41	2.04	20
Leu*	2.8–6.12	4.17	39
Tyr*	1.5–3.03	1.87	25
Phe*	2.0–4.42	2.82	25
Lys*	4.9–6.7	1.79	30
His	1.4–2.52	1.43	
Arg	5.4–11.6	2.88	

* essential amino acids.

acids (Pomeranz and Robbins, 1972). The lysine / arginine and methionine / glycine ratios in buckwheat proteins are lower than in other plant proteins. By mixing buckwheat with other cereal grains, a balanced amino acid profile can be achieved (Krkošková *et al.*, 2001).

The amino acid composition differs in the various sections of the buckwheat seed and a nonuniform distribution of proteins within buckwheat seeds and a variation of protein properties within the different sections of buckwheat seeds can be observed (Krkošková *et al.*, 2001).

5.4.3 Protein Composition

The main difference regarding protein fractions between buckwheat flour and wheat flour is that buckwheat is rich in albumin and globulin, but very low in prolamin and glutelin content. The amino acid composition of globulins and albumins also differs significantly from that of prolamins. Globulins and albumins contain less glutamic acid and proline than prolamins, and more essential amino acids such as lysine (Gorinstein *et al.*, 2002). The quantity of the individual protein fractions varies in a large range depending on the species (Aubrecht and Biacs, 2001). Imai and Shibata (1978) reported 40–77% albumin and globulin, 0.7–2.0% prolamin, and 23–59% glutelin and residual protein for commercial buckwheat flour. Tahir and Farooq (1985) measured the proportions of albumin and globulin, prolamin, glutelin, and residual protein in four buckwheat species: they were 38–44%, 2–5%, 21–29% and 28–37%, respectively. Wei *et al.* (2003) reported that proportions of albumin, globulin, prolamin, and glutelin were 16.8–30.3%, 4.96–21.6%, 3.08–7.01%, and 11.5–16%. In the study by Guo and Yao (2006) albumin was the predominant protein fraction of about 43.8%, followed by glutelin with 14.6%, prolamin and globulin were 10.5 and 7.82% (Tahir and Farooq, 1985; Wei *et al.*, 2003; Guo and Yao, 2006).

Globulins consist of 12–13 subunits with molecular weights from 16 kDA to 66 kDA (Krkošková and Mrázová, 2005). The main storage protein of buckwheat grains is the 13S globulin, which represents approximately 43% of the total seed protein (Aubrecht and Biacs, 1999; Krkošková *et al.*, 2001). The 13S globulin is salt soluble and resembles the legumin-like seed storage protein of other species, such as rice glutelin and soybean glycinin (members of the 11S globulin family) in terms of its sedimentation factor, amino-acid homology and similarities in biosynthetic and accumulation processes. The protein exists as an oligomeric complex with a molecular mass of 280 kD. Like other legumin-like seed storage proteins, the buckwheat 13S globulin is composed of multiple subunits, each of which contains α- (acidic) and β- (basic) polypeptides covalently linked by a disulphide bond (Sano *et al.*, 2014). Buckwheat globulins are also composed of 8S vicilin-like proteins (Radović *et al.*, 1999).

Thiamin-binding proteins (TBP) serve as B1 vitamin transporters in the plant and stabilize it during technological processing. They can also improve thiamin stability during storage as well as its bioavailability. Mistunaga *et al.* (1986) were the first who isolated TBPs from buckwheat grains. Thiamin-binding proteins in buckwheat represent an oligomer (140 kDA); during SDS-PAGE they migrate as a single band corresponding to the molecular weight of 42 kDA to 45 kDA. They have a 1 : 1 binding stoichiometry with thiamin (Krkošková *et al.*, 2001). Thiamin-binding proteins may be used in cases of thiamin deficiency and difficulties in its storage (Wanatabe *et al.*, 1997; Krkošková and Mrázová, 2005).

5.4.4 Allergy

Since the prolamin content in buckwheat is low, and immunological assays revealed that buckwheat contains no toxic prolamins, its flour is suitable for use in gluten-free diets or food products (Wieslander and Norbäck, 2001; Ličen and Kreft, 2005). On the other hand, buckwheat contains proteins, which can cause a hypersensitive reaction (allergy). This immunoglobulin (IgE)-mediated hypersensitive response can cause serious symptoms including anaphylactic shock.

Buckwheat allergies are not common; however, it is considered to be a very potent allergen, particularly in children. Allergy to buckwheat was first reported in the early 1900s. Since then, an increasing incidence of allergy manifestations has been observed in people who consume buckwheat-containing food products frequently and in high quantities, mainly in Europe, North America and Japan as well as some other Asian countries (Wang *et al*., 2004; Hirao *et al*., 2005; Morita *et al*., 2006). The allergens in buckwheat have been identified and characterized by several research groups (Table 5.6). The allergens varied among the patients' sera and electrophoretic immunoblotting measurements confirmed that IgE-antibody binding to the seed storage proteins of buckwheat showed varying patterns between the patients. It was revealed that the low molecular-weight proteins, particularly those with molecular weights of 9, 16, 19, and 24 kDA proteins, were strong candidates to be major allergens and that the 30, 43, and 67 kDA proteins were less responsible for such immunological disorders. Also, in the lower molecular weight range (<9 kDA) some studies described IgE-binding effects (Park *et al*., 2000; Matsumoto *et al*., 2004; Christa and Soral-Šmietana, 2008).

The 9 kDA protein is a trypsin inhibitor and the 16 kDA protein shares 38% homology with the α-amylase / trypsin inhibitor of finger millet. The 16 to 18 kDA protein is referred to as Fag e 2 and shows similarities to peanut and castor-bean allergens (Yoshioka *et al*., 2004). The 19 kDA protein has a 50% homology with the 19 kDA α-globulin of rice (Park *et al*., 2000). Furthermore, the 22 kDA protein displayed binding activity with almost all sera from different patients, and the protein is considered to be an important allergenic protein (Urisu *et al*., 1994). The 24 kDA protein is named Fag e 1, which is also recognized as one of the most significant allergens by researchers. It is a β polypeptide of the 13S globulin (Park *et al*., 2000; Morita *et al*., 2006).

Sensitization to specific buckwheat allergens is related to specific symptoms, leading to three different clinical patterns. The first are predominant gastrointestinal symptoms, which are more commonly observed in patients sensitized to a 16 kDA protein, who also show grass and wheat-flour cosensitization. The second are predominant cutaneous symptoms that are usually observed in patients sensitized to a 25 kDA protein. Anaphylaxis occurs in patients who are sensitized to a 40 kDA protein, and also

Table 5.6 Main buckwheat allergens (Heffler *et al*., 2014).

Name of the allergen	Family	Molecular weight	Biological function
Fag e 1	13S Globulin	24 kDa	Legumin-like protein
Fag e 2	2S Albumin	16 kDa	2S Albumin
Fag e 3	7S Vicin	19 kDa	7S Vicilin-like globulin
Fag e TI	Trypsin inhibitor	9 kDa	Trypsin inhibitor

cosensitized to other allergens (Heffler *et al*., 2011). Clinically relevant cross-reactivity has been described between buckwheat proteins and other allergens like rice, poppy seeds and hazelnuts (Oppel *et al*., 2006).

5.5 Conclusion

All three pseudocereals, in particular amaranth and quinoa, show an excellent protein composition with a high content of essential values. This is also expressed in a high nutritional value of the protein as determined by methods like protein digestibility, BV, NPU, PER, or the PDCAAS. The balanced amino-acid composition of pseudocereals is close to the optimum protein reference pattern in the human diet according to FAO/WHO requirements. The use of pseudocereals or their protein isolates for a wide range of food products offers a great opportunity to enhance the final quality in terms of nutrition but also physical parameters like texture and consistency.

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6

Lipids of Kernels

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6.1 Introduction

Nowadays, a diet containing around 30% of lipids is common (National Center for Health Statistics, 2014). A Mediterranean diet, where olive oil is the main source of fat (Willett *et al*., 1995), is known for its role in reducing heart disease. Trichopoulou *et al*. (2003) demonstrated that there was a significant reduction in total mortality among those who followed a Greek diet. Work by Keys *et al*. (1986) on the Seven Countries Study (Hu, 2003; Perez-Jimenez, 2005; Widmer *et al*., 2014), which involved the United States, Finland, the Netherlands, Italy, former Yugoslavia, Greece and Japan, emphasized that inhabitants of the Mediterranean region, despite ingesting a large amount of lipids in their food, have a low risk of suffering heart disease. This fact is mainly due to the ingestion of olive oil as the principal fat source (Hu, 2003). The recommended daily allowance (RDA) of the US Food and Drug Administration (FDA) is about 23 g of olive oil daily to reduce the risk of heart disease (FDA, 2004).

Mozaffarian *et al*. (2010) stated that the consumption of polyunsaturated fat instead of saturated fat in the diet could lower the risks of coronary heart disease. This study also recommended the consumption of vegetable oil due to the considerable amount of omega-3 and omega-6 polyunsaturated fatty acids present in, for example, canola and soybean oil. The Andean crops in this study show a higher concentration of polyunsaturated fats with respect to the saturated fats. Therefore, the consumption of certain grains could provide health benefits if they are consumed instead of foods containing saturated lipids.

Furthermore, some polyunsaturated fatty acids are not synthesized by the human body (Chapkin, 1992); these have to be provided via food consumption. Amaranth, buckwheat and quinoa present a profile rich in linoleic (omega-6), oleic, and linolenic (omega-3) acids, which reveals the quality of their lipid content.

6.2 Oil Content

Lipids are appealing to consumers due to their appreciable organoleptic (flavors, texture, aroma, etc.) and chemical (water insolubility) characteristics. Edible animal and vegetable foods are sources of lipids (Vaclavik and Christian, 2008).

Pseudocereals: Chemistry and Technology, First Edition. Edited by Claudia Monika Haros and Regine Schoenlechner.

Lipids contain highly hydrophobic units, which in turn affects theirs solubility. The latter is the property that characterizes a lipid, more than its structural features. In food cells, lipids may be part of the building blocks of the membrane (Belitz *et al*., 2009). These biomolecules contain carbon, hydrogen and oxygen, which form hydrocarbon chains that could be aliphatic or aromatic. These chains may also include nitrogen and phosphorous (Badui Dergal, 2013).

6.2.1 Oil Content of Quinoa, Amaranth and Buckwheat

The extraction of quinoa lipids yields a colourless to yellowish oil (Ahamed *et al*., 1998). In the case of amaranth, the extracted oil is yellow, comparable to corn oil in appearance and composition (Becker, 1989).

The oil content of amaranth, buckwheat and quinoa is higher than that of other cereals. It is in the range of 5.8–19.3% for amaranth (Berganza *et al*., 2003; Cai *et al*., 2004; Martirosyan *et al*., 2007), 2.4–3.2% for buckwheat (Pomeranz and Lorenz, 1983; Mazza, 1988; Ryan *et al*., 2007; Tang, 2007), and 4.0–9.7% for quinoa (Ruales and Nair, 1993; Wood *et al*., 1993; Miranda *et al*., 2012).

Table 6.1 gives an overview of the oil content of these three grains and others. Among the three seeds, quinoa exhibits the highest lipid content on average, followed by amaranth and then buckwheat. Amaranth has similar oil content to corn and cottonseed.

Table 6.1 Oil content of quinoa, amaranth, buckwheat grains and other plants.

Crop	Oil content (g/100 g)	Reference
Amaranth	5.83–7.13[a]; 5–8[t]; 6–9[c]; 19.3[n]	[a]Berganza *et al.* (2003)
Barley	1–2[r]; 1.9[b]	[b]Valencia-Chamorro (2004)
Lupin	2.6–15.8[q]; 7.0[b]	[c]Martirosyan *et al.* (2007)
Oats	6–8[r]; 5.2[m]; 8[o]	[d]Da Silva *et al.* (2006)
Ricebran	16–22[d]	[e]Becker (1994)
Sesame	40–60[s]	[f]Ruales and Nair (1993)
Soybean	18.9[b]; 20[s]	[g]Palombini *et al.* (2013)
Wheat	2–3[r];2.3[b]	[h]Tang *et al.* (2015)
Corn	4[e]; 4–10[r]; 4.7[b]	[i]Mazza (1988)
Cottonseed	7[e]; 13.3[p]; 16[s]	[j]Pomeranz and Lorenz (1983)
Rice	1–3[e]; 2.2[b]	[k]Tang (2007)
Olive	36[e]	[l]Ryan *et al.* (2007)
Peanut	41[r]; 47[e]	[m]Kent (1985)
Quinoa	9.7[f]; 9.71[g]; 6,58–7,17[h]; 6.3[b]	[n]Singhal and Kulkarni (1998)
Buckwheat	2.6–3.2[i]; 2.4[j]; 3.0[k]; 2.7[l]	[o]Arendt and Zannini (2013)
		[p]Adelola and Ndudi (2012)
		[q]Trugo *et al.* (1988)
		[r]Wrigley (2004)
		[s]Mailer (2004)
		[t]Cai *et al.* (2004)

In the case of buckwheat, the oil composition is similar to wheat and rice but higher than in oats. For quinoa, the oil content is between cottonseed and rice bran.

Wood *et al.* (1993) stated that the lipid content of 5.3% in quinoa grains makes it satisfactory for a staple food, although it does not have enough oil to be considered as an oil crop. However, other authors consider that quinoa is a potential seed for oil extraction (Kozioł, 1992; Repo-Carrasco *et al.*, 2003).

6.2.2 Lipid Analysis

Lipids have a low solubility in water, but a good one in organic solvents. Its low solubility in water is taken into account when separating these from carbohydrates and proteins (Wassef Nawar, 1996; McClements and Decker, 2007).

Usually, lipid extraction from kernels is carried out by Soxhlet (Horowitz, 1984), or by chloroform / methanol mixtures (Folch *et al.*, 1957; Bligh and Dyer, 1959; Omoti and Okyi, 1987). Lipid extraction in kernels is generally done via Soxhlet with petroleum ether, in a 30–60 proportion over 24 h (Gonzalez *et al.*, 1989). The chloroform / methanol mixtures method involves the use of three two-hour extractions with hot n-butanol saturated with water in the ratio of 17 mL of solvent per 1 g of extracted material, followed by two extractions with a solution of chloroform-methanol-water in the ratio 1 : 2 : 0.8 v/v/v. The lipids can be separated from the solvents via evaporation using a rotary evaporator. Finally, the amount of lipid is determined by weight (Przybylski *et al.*, 1994).

Fatty acid quantification can be done by analysis of their methyl esters. The latter can be obtained by first extracting the lipids with a solution of chloroform and methanol in the ratio 2 : 1 v/v. The chloroform phase then is treated with boron trifluoride 10% in methanol, which transforms fatty acids into methyl ester fatty acids. Finally, the fatty acids can be separated and quantified by gas chromatography (Vidueiros *et al.*, 2015).

A similar method for fatty acid quantification is the hydrolysis of the lipids extracted with petroleum ether with the addition of 3% concentrated sulfuric acid in methanol, from which methyl esters of the fatty acids are separated by gas chromatography (Ruales and Nair, 1993).

A study of amaranth showed that these methods give similar results for oil content (Dhellot *et al.*, 2006). Nevertheless, a study of avocado (*Persea americana* Mill.) shows different contents of *trans* fatty acids (TFA) by using different chemical solvents, such as hexane and acetone (Ortiz-Moreno *et al.*, 2003). It is therefore important to notice that different extraction methods could lead to different composition results.

6.2.3 Factors Influencing Oil Content of Quinoa, Amaranth and Buckwheat

Some studies show that species, cultivars and accessions cause a high variation in oil content in amaranth grains (Belton and Taylor, 2002; Berganza *et al.*, 2003). Varietal influence is evident in amaranth related to oil content. The literature shows variation in amaranth oil content from 4.9 to 19.3% (Table 6.2). However, Berganza *et al.* (2003) do not detect significant differences in oil content between five varieties of *Amaranthus cruentus*. One possible explanation is that other factors are at play. It would seem that the effect of location, in particular altitude above sea level at which amaranth is cultivated, is another determinant factor in oil content. Five varieties of *Amaranthus cruentus*, which were planted in three localities at different altitudes above sea level, showed significant differences in oil content.

Table 6.2 Oil content of different amaranth species.

Species	Oil content (g/100 g)	Reference
A. hypochondriacus	4.9–8.1[a]; 3.1–6.3[b]; 5.35–7.72[c]	[a]Lorenz and Hwang (1985)
A. caudatus L.	7.1[d]	[b]Sanchez-Marroquin *et al.* (1980)
A. cruentus L.	7.7[d]; 8.5[e]	[c]Becker (1994)
A. tricolor	5.1[e]; 5.08[c]	[d]Gamel *et al.* (2007)
A. spinosus	17[f]	[e]He *et al.* (2001)
A. tenuifolius	19.3[f]	[f]Singhal and Kulkarni, (1998)
A. hybridus	11–14[g]; 6.40[c]	[g]Dhellot *et al.* (2006)
A. acutilobus	5.2[h]	[h]Budin *et al.* (1996)
A. acutilobus	7.6[h]	

Accessions have also been shown to be a key factor in the oil content of amaranth (Bressani *et al.*, 1987; Budin *et al.*, 1996). A study displayed that the oil content on dry basis of seeds in 21 accessions of eight amaranth species ranged from 5.2 to 7.7% (Budin *et al.*, 1996). Another work exhibited the range of 7.7 to 12.8% of oil content for 14 selections of four amaranth species (Bressani *et al.*, 1987).

In buckwheat, fatty acid content is influenced by the species (Table 6.3), cultivar, growth location and seeding time (Tsuzuki *et al.*, 1991). Oil content variability due to variety was confirmed by some works (Dorrell, 1971; Mazza, 1988; Bonafaccia *et al.*, 2003). Tsuzuki *et al.* (1991) revealed differences in fatty acid content linked to species and growth-location effects: an important variability was detected in 36 species of buckwheat. Moreover, other studies indicated the varietal influence on unsaturated total fatty acids: *Tartary buckwheat* exhibited more content in unsaturated fatty acids (UFAs) than common buckwheat (Bonafaccia *et al.*, 2003).

Early seeding times in cultivars of buckwheat in Japan appeared to improve the lipid content (Taira *et al.*, 1986). In addition, this work presented significant differences in fatty acids, compositions – arachidic and behenic acids – related to seeding time.

Table 6.3 Oil content of different buckwheat species.

Species	Oil content (g/100 g)	Reference
Common (*Fagopyrum esculentum*)	2.88[a]	[a]Bonafaccia *et al.* (2003) [b]Dorrell (1971)
Tartary (*Fagopyrum tataricum*)	2.81[a]; 8.5[b]	[c]Mazza (1988)
Wild	16.3[b]	
Mancan	2.9–3.2[c]	
Manor	2.6[c]	
Tokyo	2.9[c]; 10.2[b]	
Silverhull	9.5[c]	

Table 6.4 Oil content of different quinoa grain genotypes in Chile.

Geographical zone	Species	Oil content (g/100 g)
North	Ancovinto	6.20[c]
	Cancosa	5.95[b]
Center	Cáhuil	7.06[f]
	Faro	6.65[e]
South	Regalona	6.37[d]
	Villarica	5.57[a]

Values extracted from Miranda *et al.* (2012). [a–f]Different superscript letters, indicate that the values are significantly different using the Fisher's least significant difference test ($p < 0.05$).

Wood *et al.* (1993) revealed that the lipid content and fatty acid composition in three different cultivars of quinoa varied little. However, another study of the comparison of nutritional components of six different quinoa ecotypes and climatic and edaphic conditions in Chile (Table 6.4) showed that geographical conditions and genotype provide statistical significant differences in terms of lipid content (Miranda *et al.*, 2012).

6.3 Fatty Acid Composition

Fatty acids are aliphatic monocarboxylic acids that can be obtained from acyl lipid hydrolysis (Wassef Nawar, 1996). These lipidic compounds can be grouped according to the chain length, number and position of double bonds. In foods, the fatty acids that are present in higher amounts are linoleic, palmitic and oleic acids, whilst myristic, stearic, and linolenic acids are present in small amounts (Belitz *et al.*, 2009). In general, these are esterified.

When these are in a free form a hydrolysis of the ester bond has taken place. In industry, fatty acids are obtained from fat hydrolysis and these are used as additives in the food industry (Badui Dergal, 2013). Linoleic acid, also known as the dietary essential fatty acid, is the precursor of the longer chain polyunsaturated fatty acids (PUFAs). The latter show the following properties: could be essential for normal brain development and maintenance and could influence the integrity of cellular membranes and the normal transport of blood lipids (Rahm and Holman, 1971).

6.3.1 Fatty Acid Composition of Quinoa, Amaranth and Buckwheat

Amaranth contains mainly linoleic (C18:2), oleic (C18:1), palmitic (C16:0) and estearic (C18:0) acids in descending order (Table 6.5; Becker, 1994; León-Camacho *et al.*, 2001; Cai *et al.*, 2004).

In buckwheat, more than 93% of the total fatty acids are composed of oleic, linoleic, palmitic, linolenic, lignoceric, stearic, behenic and arachidic acids (Dorrell, 1971). The first three (linoleic, oleic and palmitic acids) are the main fatty acids (Table 6.5; Bonafaccia *et al.*, 2003), comprising 880 mg/g of total fatty acids (Horbowicz and Obendorf, 1992). A study revealed that fatty acids were influenced by buckwheat variety

Table 6.5 Fatty acid composition of amaranth, buckwheat quinoa and others (g/100 g fat).

	Fatty acids (g/100 g)						
Crop	*Palmitic*	*Stearic*	*Oleic*	*Linoleic*	*Linolenic*	*All others*	*S/U ratio*[f]
	16:0	18:0	18:1	18:2	18:3		
Amaranth	18.5[a]; 21.4–23.8[b]; 20[d]	3.2[a]; 3,11–3,98[b]; 4[d]	22[a]; 22.8–31.5[b]; 33.3[d]	44.8[a]; 39.4–49.1[b]; 38.2[d]	0.2[a]; 0.65–0,93[b]; 1[d]	11.3[a]; 7,08[b]	0.33[a]; 0.37–0.4[b]
Barley	18.5–21[a]	0[a]	15.2–15.6[a]	24–52.4[a]	2.6–5.5[a]	5.4–6.8[a]	0.25–0.29[a]
Buckwheat	18.2[a]; 19.5[b]	0[a]; 2.18[b]	36.4[a]; 37.1[b]	34.8[a]; 35.5[b]	0[a]; 1.93[b]	10.6[a]; 3.8[b]	0.26[a]; 0.34[b]
Corn	10.3[a]; 11.6[b]	0.6[a]; 1.91[b]	21.4[a]; 27.8[b]	62.9[a]; 56.6[b]	0.5[a]; 1.93[b]	4.3[a]; 0.69[b]	0.13[a]; 0.16[b]
Cottonseed	25.7[b]	2.45[b]	17.7[b]	52.1[b]	0.22[b]	1.93[b]	0.41[b]
Lupin	9[a]	0[a]	57.5[a]	16.7[a]	10.9[a]	5.9[a]	0.11[a]
Oats	17.3[a]	0[a]	39.8[a]	38.5[a]	0[a]	4.4[a]	0.22[a]
Quinoa	11.4[b]; 9,7[c]	0.79[b]; 0,6[c]	25.6[b]; 24,8[c]	52.8[b]; 52,3[c]	7[b]; 3,9[c]	2.44[b]; 6,8[c]	0.15[b]–0.27[e]
Ricebran	18.6[b]	1.75[b]	42.4[b]	34.8[b]	1.1[b]	1.23[b]	0.27[b]
Sesame	9.51[b]	5.41[b]	40[b]	43.5[b]	0.33[b]	1.14[b]	0.19[b]
Soybean	12.7[b]	3.96[b]	21.7[b]	53.9[b]	7.23[b]	0.6[b]	0.2[b]
Wheat	15.4[a]	0[a]	22.3[a]	54.2[a]	3.5[a]	4.6[a]	0.19[a]

a) Data from Budin (1996);
b) Data from Jahaniaval *et al.* (2000);
c) Data from Ruales and Nair (1993);
d) Data from Léon-Camacho (2001);
e) Data from Vidueiros (2015);
f) S/U ratio = saturated / unsaturated = (16:0 + 18:0)/(18:1 + 18:2 + 18:3).

(Cai *et al*., 2004). Stearic, oleic and linoleic acids of *Tartary buckwheat* were higher in concentration than common buckwheat (Tsuzuki *et al*., 1991).

For quinoa, the fatty acids represent about 85% of the total lipid content (Wood *et al*., 1993). The major components are unsaturated fatty acids, linoleic and oleic acids. Linoleic acid is the main fatty acid, accounting for over 50% (Kozioł, 1992; Ruales and Nair, 1993; Repo-Carrasco *et al*., 2003), followed by oleic acid, which comprises over 20% of the all the fatty acids present (Table 6.5; Ruales and Nair, 1993; Repo-Carrasco *et al*., 2003; Palombini *et al*., 2013). Next is palmitic acid, a saturated fatty acid that constitutes over 8% (Vidueiros *et al*., 2015).

Amaranth fatty acid profile is comparable in composition to some kernels including corn and cottonseed. The fatty acid composition of buckwheat is similar to rice, wheat, rye or millet (Pomeranz and Lorenz, 1983). For quinoa, the fatty acid composition is similar to soybean oil; thus it appears to be a high-quality edible oil (Wood *et al*., 1993).

For amaranth and quinoa, the content of linoleic acid is higher than for the rest of the fatty acids, as in barley, corn, cottonseed, sesame, soybean and wheat. In the case of buckwheat, linoleic and oleic acids are present in similar amounts, comparable to oats and sesame. The content of palmitic acid in quinoa is similar to that of lupin. Amaranth and buckwheat have akin palmitic acid composition to that of barley and rice bran.

6.3.2 Saturated Fatty Acids

Saturated fatty acids (SFAs) are branchless compounds that comprise even numbers of 4–26 carbon atoms (Belitz *et al*., 2009; Badui Dergal, 2013). This affects their fusion temperature with an increase of the chain length or molecular weight. At 25 °C, saturated fatty acids containing 4–8 carbon atoms are liquid, whereas those with ten carbon atoms or more are solid (Badui Dergal, 2013).

In amaranth, SFAs are in the order of 20.9–24.2% (Dodok *et al*., 1997; Palombini *et al*. 2013). Palmitic acid is the main SFA (He and Corke, 2003; Hlinková *et al*., 2013) in seeds with 7.8 mg/g (Fernando and Bean, 1984; He and Corke, 2003; Hlinková *et al*., 2013).

SFAs present in buckwheat are around 16–25% of the total amount of fatty acids (Pomeranz and Lorenz, 1983; Bonafaccia *et al*., 2003; Ryan *et al*., 2007). Total saturated fatty acids are present around 0.46% of the edible portion (Pomeranz and Lorenz, 1983). The pericarp has higher contents of SFA, which are more often present in common buckwheat than either *Tartary* or wild buckwheat (Dorrell, 1971).

Quinoa contains SFAs in the range of 11–17% with respect to the total amount of fatty acids (Wood *et al*., 1993; Vidueiros *et al*., 2015). Palmitic acid is the major component in this category and represents about 8.5% of the fatty acids. Other SFAs present in the seed are myristic, stearic, behenic and lignoceric acids, but in minor quantities (Wood *et al*., 1993).

It can be withdrawn that amaranth and buckwheat have higher concentrations of saturated fatty acids than quinoa, with amaranth being the highest (Table 6.5).

6.3.3 Unsaturated Fatty Acids

Unsaturated fatty acids (UFAs) are composed of lineal chains of 16 or more carbons. These have several insaturation points (double bonds) in their aliphatic chain, which are the basis of their high chemical reactivity (Badui Dergal, 2013). The fusion point decreases with an increase in the number of double bonds (McClements and Decker,

2007; Badui Dergal, 2013). A double bond in *cis* configuration causes the fatty acid to bend; thus the compound is not linear. Meanwhile double bonds in the *trans* configuration provide more linear fatty acids (McClements and Decker, 2007).

Amaranth oil contains mainly UFAs, which comprise about 77.1% of the total amount of fatty acids (Dodok *et al*., 1997). The degree of unsaturation in amaranth grain is around 74–77% (Jahaniaval *et al*., 2000; Belton and Taylor, 2002; Martirosyan *et al*., 2007). The main UFAs in amaranth are oleic and linoleic acids, 19–35 and 25–62% from total fatty acids, respectively. The range of the ratio of unsaturated to saturated fatty acids is 2.5–3.7 (Dodok *et al*., 1997; Jahaniaval *et al*., 2000). A study of amaranth accessions shows similar unsaturated to saturated ratios in mono and polyunsaturated fatty acids (Jahaniaval *et al*., 2000).

Oleic, linoleic, linolenic and eicosenoic acids are the main UFAs in the common buckwheat (Bonafaccia *et al*., 2003). Polyunsaturated fatty acids, i.e. linoleic and linolenic acids, are present in higher amounts than other acids. Linoleic being the main acid in buckwheat seeds (Arendt and Zannini, 2013).

The saturated / unsaturated acids ratio (S/U) is an indicator for nutritional and functional value analysis (He and Corke, 2003). The S/U is similar between amaranth and buckwheat. Quinoa has a wider ratio than the other ones (Table 6.5).

Different heat treatments could influence the saturated and unsaturated fatty acids. In buckwheat grains, with respect to unsaturated fatty acids, hydrothermal treatment decreased these in free and bound lipids (Pomeranz and Lorenz, 1983). Similar results were found by Taira *et al*. (1986) who state that buckwheat is a pseudocereal sensitive to temperature related to fatty acid level and oil content.

Steaming decreases the content of saturated fatty acids of buckwheat from 22.2 to 18.2% and increases the content of unsaturated fatty acids from 77.8 to 81.8%, as well. Likewise, triacylglycerides content increases whereas free fatty acids decreases (Pomeranz and Lorenz, 1983).

In the case of quinoa, the unsaturated fatty acids account for 82.7–85.0% of the total amount of fatty acids. The main unsaturated fatty acids present are linoleic, oleic and α-linolenic acids; the existence of linoleic acid and α-linolenic acids shows that quinoa is a source of essential fatty acids (Vidueiros *et al*., 2015). Quinoa oil presents a high value on the polyunsaturation index: it has a PUFA/SFA (sum of saturated fatty acids / sum of polyunsaturated fatty acids) of 3.7–4.9 (Ruales and Nair, 1993; Vidueiros *et al*., 2015). However, a monounstaturated fatty acid, the erudic acid, is unwanted because it is related to cardiotoxicity (Imamura *et al*., 2013). Erucic acid falls slightly below 2% (Wood *et al*., 1993).

Other kernels as corn, soybean, sesame, and quinoa exhibit higher contents of UFAs (>82%) compared to amaranth. The content of PUFA is 323 mg/g (Palombini *et al*., 2013).

6.3.4 Properties of Fatty Acids

Fatty acids and their position within a triacylglycerol molecule largely determine the physical and chemical properties of fats and oils. Even though fats and oils are all esters of glycerine and fatty acids, the physical properties vary substantially due to the proportions of fatty acids present and the structure of the triacylglycerol (O'Brien, 2008).

Pseudocereal lipids play an important role in physiological factors and food quality (Nikolić *et al*., 2011). Fatty acids are the key of lipid metabolism with respect to health: for example – an elevated ingestion of trans configuration fatty acids (TFAs)

raises the content of low-density lipoprotein cholesterol (LDL) (Mensink and Katan, 1990). High levels of LDL are related to plaque formation in arteries, which causes obstruction and thus elevated blood pressure, which is associated with health problems (O'Brien, 2008).

Linoleic and linolenic acids, known as omega-6 and -3, respectively, originate specific lipids, which control cell signals, gene expression and anti-inflammatory processes (Rang *et al*., 2003). These acids are fundamental since are not generated by human synthesis. Oleic acid ingestion reduces the risk of cardiovascular diseases because it decreases the LDL levels in the blood (Elmadfa and Kornsteiner, 2009).

Oleic acid has shown beneficial results when substituting saturated fatty acids from whole milk in the study performed by Estévez-González *et al*. (1998) about the reduction of cholesterol and LDL levels in the juvenile population. The mean value for LDL and triacylglycerides were reduced after the substitution with oleic acid. The effect of palmitic acid intake on the level of cholesterol was assessed in the work of French *et al*. (2002). This work demonstrated that when the dietary linoleic acid content decreased in a diet that comprised a constant palmitic acid intake, an increase in the mean total cholesterol level took place.

6.4 Lipid Class Composition

Nowadays, there is no consensus for lipid classification. Nevertheless, Belitz *et al*. (2009) resumed two types of classification. On the one hand a classification according to the acyl residue, which comprises simple lipids and acyl lipids, and on the other hand, according to the 'neutral-polar' characteristics.

With regards to acyl residue classification, the simple lipids constitute free fatty acids, isoprenoid lipids and tocopherols. Acyl lipids are composed of mono-, di-, triacylglycerols, phospholipids, glycolipids, diols lipids, waxes and sterol esters (Belitz *et al*., 2009).

The classification according to 'neutral-polar' characteristics includes polar (surface-active) and neutral lipids. Neutral lipids comprise fatty acids ($>C_{12}$), mono-, di-, triacylglycerols, sterols, sterol esters, carotenoids, waxes and tocopherols. Polar lipids, by contrast, embrace glycerophospholipis, glyceroglycolipids, sphingophospholipid and sphingoglycolipid (Belitz *et al*., 2009).

6.4.1 Neutral Lipids (Glycerides) in Quinoa, Amaranth and Buckwheat

Neutral lipids in amaranth are in the order of 90% of total lipids. Polar lipids represent the remainder (Table 6.6). Triacylglycerides are the main neutral lipids in amaranth (Opute, 1979), and are in the order of 78–81% of amaranth oil (Opute, 1979; Martirosyan *et al*., 2007).

In buckwheat, around 81–85% of total lipids are neutral lipids (Ikeda, 2002) compared to wheat and rye, which contain 35% (Ahmed *et al*., 2014). Soral-Smietana *et al*. (1984) demonstrated that neutral lipids are the main portion in free and bound lipids of buckwheat grain and starch.

Quinoa grains contain about 55.9% of neutral lipids with respect to the total amount of lipids. The main constituents of the neutral lipids are triacylglycerides 73.7%, followed by diglycerides 20.5%, and monoglycerides 3.1% (Przybylski *et al*., 1994).

Table 6.6 Lipid classes of amaranth, buckwheat and quinoa.

Lipid classes	(g/100 g total lipids)		
	Amaranth	*Buckwheat*	*Quinoa*
Neutral	90[b]	81.3–84.6[f]	55.9[a]
Triglycerides	81[b]–6,4[c]	–	73.7[a]
Diglycerides	1.8[b]–5.6[c]	–	20.5[a]
Monoglycerides	4.7[c]	–	3.1[a]
Polar	10[b]	15.4–18.8[f]	25.2[a]
Phosphatidic acid	–	4.7[d]; 7.28–21.17[e]	1.1[a]
Phosphatidyl serine	–	10[d]	4.0[a]
Phosphatidyl etholamine	1.2[b]–3.2[c]	14.4[d]; 18.5–40[e]	18.5[a]
Phosphatidyl inositol	0.6[b]–1.7[c]	1.5[d]	10.5[a]
Lysophosphatidyl ethanolamine	–	14.4[d]	43.2[a]
Phosphatidyl choline	1.8[b]–2.6[c]	25.9[d]; 17.9–23.3[e]	12.3[a]
Lysophosphatidyl choline	–	4.2[d]; 10.9–27.8[e]	3.6[a]
Monogalactosyl diglyceride	1.3[b]–15.6[c]	4.14[d]	1.6[a]
Digalactosyl diglyceride	0.5[b]–7.3[c]	43.3[d]	1.1[a]

a) Data from Przybylski *et al.* (1994);
b) Data from Becker *et al.* (1981), Badami and Patil (1976), Chidambaram and RamachandraIyer (1945), Opute (1979), Saunders and Beciker (1984);
c) Data from Lakshminarayana *et al.* (1984);
d) Data from Obara and Miyata (1969) (as g/100 g of total conjugated lipids);
e) Data from Belova *et al.* (1971) (as percentage total of phospholipids);
f) Data from Mazza (1988).

Neutral lipids comprise a larger amount of the three grains than polar lipids. The percentages of neutral lipids are present in descending order for amaranth, buckwheat and quinoa.

6.4.2 Polar Lipids (Phospholipids) in Quinoa, Amaranth and Buckwheat

Neutral and polar lipid profiles are shown in Table 6.6. Some of the components for each group are displayed in the same table.

In amaranth, polar lipids contain 10% of the total lipid content (Table 6.6). The main polar lipids present in amaranth are phosphatidyl choline (PC), monogalactosyl diglyceride (MGD), phosphatidyl etholamine (PE), phosphatidyl inositol (PI) and digalactosyl diglyceride (DGD). The first two (PC and MGD) are the major polar lipids due to high lipid level, 1.8–2.6% and 1.3–15.6% of total lipids, respectively (Badami and Patil, 1976; Lakshminarayana *et al.*, 1984).

Buckwheat seeds exhibit a polar lipid content of between 15.4 and 18.8% of total lipid level (Table 6.6; Mazza 1988). Five lipids are mainly involved: DGD, PC, PE, lysophosphatidyl ethanolamine (LPE) and phosphatidyl serine (PS). Digalactosyl diglyceride and PC have the highest lipid content with, 43.3% and 17.9–25.9% of total lipids, respectively (Obara and Miyata, 1969; Lakshminarayana *et al.*, 1984).

Polar lipids in quinoa grains represent 25.2% of the total lipid content. The six major polar lipids are LPE, PE, PI, PC, PS, and LPC. Of these, LPE is the major component, comprising 43.2% of the polar lipids, followed by PE at 18.5% (Przybylski *et al*., 1994).

6.5 Distribution of Lipids in the Kernels

In general, lipids of amaranth, as with proteins, are localized mainly in the germ and seed coat (7.4% crude fat). A small fraction is distributed in the perisperm (2.3% crude fat) (Betschart *et al*., 1981; Becker, 1994). The lipids are distributed in the cytoplasm that surround the proteins but are not present in the perisperm cells (Coimbra and Salema, 1994) (Figure 6.1).

Buckwheat seed has a triangular form. The outer layer is the pericarp, which is usually black or dark-brown coloured, followed by the testa (seed coat); next is the aleurone, then the endosperm in which two cotyledons extend through and around it; and finally the embryo is located at the top of the achene (Pomeranz and Lorenz, 1983; Steadman *et al*., 2001).

For buckwheat, the lipid content was higher in the embryo than in other tissues. Buckwheat lipids are located in the form of lipid bodies (Guan and Adachi, 1994). A micrograph of a lipid body in buckwheat embryo cell cytoplasm is shown in Figure 6.2.

Buckwheat embryo is composed of 8.2% oil, followed by the testa with 2.0%, then the pericarp with 0.5%, and finally the endosperm with 0.4% The embryo contains around two-thirds of the total oil in the seed (Dorrell, 1971).

Quinoa seed structure comprises several tissues, which include the external hull, followed by pericarp-rich bran, seed coat, endosperm, dicotyledoneous embryo, and perisperm (Chauhan *et al*. 1992; Prego *et al*., 1998). The embryo and perisperm are the main lipid storages in the seed, which are also rich in proteins and minerals. The lipids in the embryo and endosperm cells are contained in the form of lipid bodies (Figure 6.3; Prego *et al*., 1998; Burrieza *et al*., 2014).

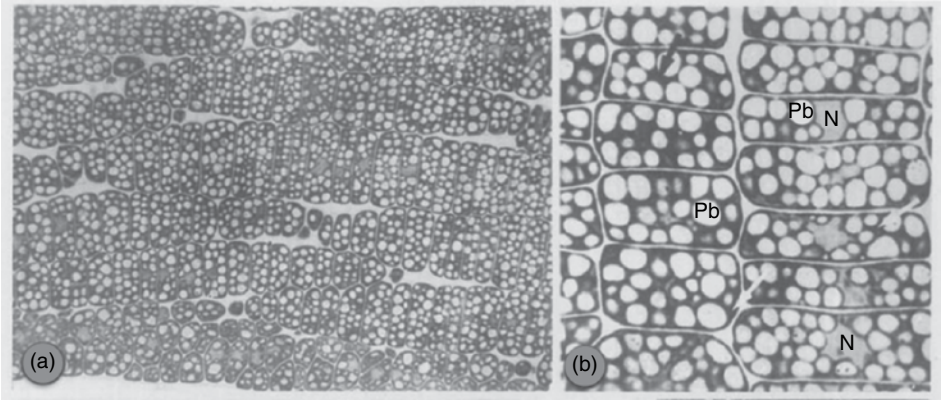

Figure 6.1 (a) Lipids in the cytoplasm surrounded the proteins (magnification × 700). (b) Higher magnification (×1700) of (a). Proteins bodies (Pb), lipids (arrows), N (nucleus). Reproduced with permission from Coimbra and Salema (1994).

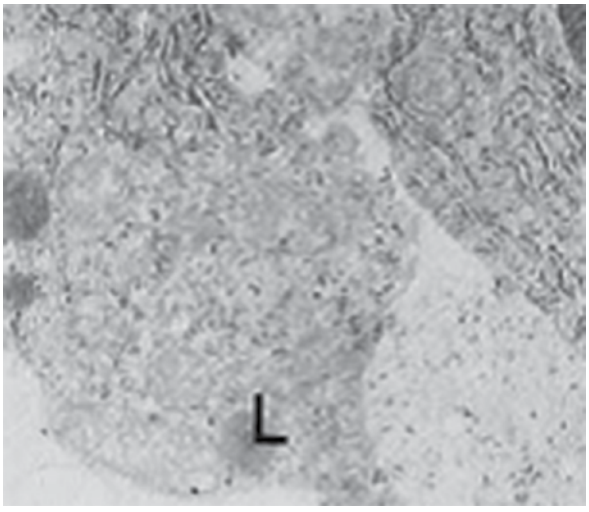

Figure 6.2 Lipid body (L) in buckwheat embryo cell cytoplasm. Reproduced with permission from Guan and Adachi (1994).

The embryo of quinoa contains around 10.2% of lipids, which represent 49% of the total lipid content. A lower amount of lipid is located in the perisperm, being 46% of the total, giving a lipid content in this fraction of 5% (Ando *et al*., 2002).

Amaranth, buckwheat and quinoa seeds have a similar distribution of lipids, in the form of lipid bodies. The greatest amounts are found in the embryo and the endosperm for amaranth and buckwheat, and in the embryo and perisperm for quinoa.

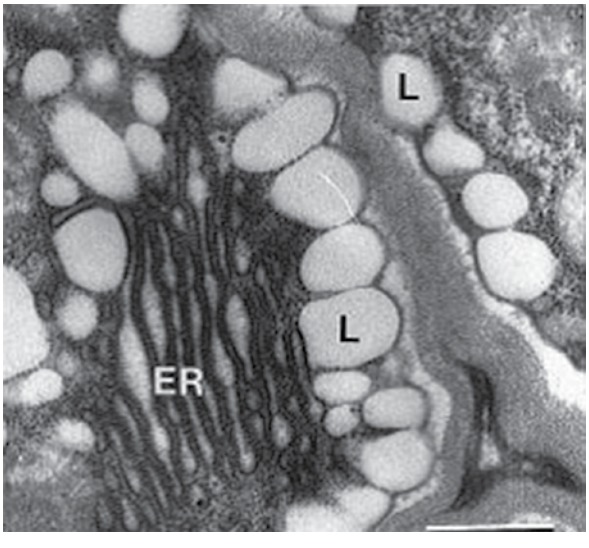

Figure 6.3 Section of an embryo cell showing lipid body (L), endoplasmic reticulum (ER). Reproduced with permission from Prego *et al*. (1998).

6.5.1 Distribution of Fatty Acids (Bran and Hull, Germ, Endosperm)

Linoleic is the major fatty acid in amaranth seeds, constituting 49%. In lower quantities linolenic acid is found in the range of 18–25% (Fernando and Bean, 1984).

Buckwheat seed is divided into four tissues: embryo, endosperm, testa and pericarp – and displays a unique fatty acid composition for every tissue. Comparison of tissues from different cultivars showed similar fatty acid profiles (Dorrell, 1971).

In buckwheat, as the lipid content is highest in the embryo (Dorrell, 1971; Steadman *et al*., 2001), this tissue controls the fatty acid composition in the seed, which comprises mainly unsaturated fatty acids in the order of 74.5 to 79.3% (Bonafaccia *et al*., 2003; Ryan *et al*., 2007). For achenes, after 20 days of pollination, the main fatty acids in embryo and endosperm are linoleic, oleic and palmitic. Other fatty acids found in the latter tissues are the unsaturated kind: eicosenoic, linoleic and saturated ones, palmitoleic, stearic, behenic arachidic and myristic acids (Horbowicz and Obendorf, 1992). In buckwheat, linoleic acid, the most important fatty acid in this pseudocereal, is present at a high level in the seed coat (Dorrell, 1971; Taira *et al*., 1986; Mazza, 1988).

The testa and the endosperm in buckwheat have a similar fatty acid composition related to the overall seed average (Dorell, 1971). The S/U ratio is the lowest, intermediate and highest, respectively, in the embryo axis, testa, and pericarp. The testa contains less oleic acid, but more linolenic acid than the endosperm or compared to the whole seed. In contrast, the endosperm has a high level of palmitic acid. The pericarp has a unique fatty acid composition compared to the other tissues, which are rich in saturated fatty acids. However, the pericarp is removed during milling; therefore it does not contribute to a milled product from groats (Dorrell, 1971).

The unsaturated fatty acids are predominant in quinoa grains, separated into bran, embryo and perisperm. The fatty acid content of these fractions in descending order are, linoleic, oleic and linolenic acids. Palmitic acid accounts for about 10% of the total fatty acids in every fraction (Ando *et al*., 2002). In another study, for quinoa grains separated into hull, bran, and flour (embryo plus perisperm), linoleic acid was found to be the main fatty acid present, accounting for over 50% of the fatty acids in every fraction. The second highest was oleic acid, followed by palmitic acid; the order remains the same in each fraction (Przybylski *et al*., 1994).

6.5.2 Distribution of Lipid Class (Bran and Hull, Germ, Endosperm)

In the literature review only a study in quinoa about the distribution of lipid classes in the kernel fractions was found. Quinoa grains separated into hull, bran and flour fractions presented variations in the amounts of neutral lipids present in each fraction. Still, neutral lipids were the main lipid components in all fractions and ranged from 40.2–76.2% with respect to their lipid content. Triacylglycerides are the main neutral lipid in all fractions: 71.7% for hulls, 82.1% for bran, and 87.2% for flour (Przybylski *et al*., 1994).

Considering polar lipids, the bran and flour contained mainly PC – 48.3 and 49.0%, respectively. However, LPE, PE, PI and PS also contributed significantly to the lipid content in these fractions. For the hull, the major component was LPE, with a value of 43.3%, with PC, PI and PE also adding significantly to the hull phospholipids (Przybylski *et al*., 1994).

6.6 Other Relevant Compounds in Pseudocereal Oils

The lipids present in amaranth, buckwheat and quinoa have several technological and stability properties. Some examples regarding antioxidative effects and nutritional benefits in lipids of these pseudocereals are presented below.

6.6.1 Tocopherols

Unsaponifiable lipids are compounds that can be isolated from a soapy solution. Tocopherols are part of this group. In terms of antioxidant capacity there are four tocopherols in decreasing order δ > ϒ > β > α (Repo-Carrasco *et al*., 2003). The order is the opposite for vitamin E activity, which is quantified in terms of α-tocopherol. This vitamin is related to slower aggregation of blood platelets and stabilization of membrane structures and other active components such as hormones, enzymes, vitamin A and ubiquinone (Belitz *et al*., 2009) and, indeed, there is an important amount of tocopherols in amaranth, buckwheat and quinoa.

In amaranth, tocopherols are essential components in the lipophilic fraction of seeds (Venskutonis and Kraujalis, 2013). Origin, accession and location could be the determinant factors for tocopherol content. Regarding the influence of origin, the *A. cruentus* grain of Mesoamerica exhibited higher content of four tocopherols than African ones. Budin *et al*. (1996) studied the contents of α, β, δ-tocopherols for different accessions, in the ranges of 0.78–2.95, 0.71–6.74 and 0.11–2.05, mg/100 g seed (in wet basis), respectively. Concerning the location effect, Ecuadorian species of *A. caudatus* showed higher tocopherol content than the Italians ones (Bruni *et al*., 2001).

In buckwheat, the total content of tocopherols is about 50 mg/kg. The existence of tocopherols in this grain is also related to a high antioxidant activity. Furthermore, there is a positive correlation between the tocopherol content and the amount of fatty acids present (Kim *et al*., 2001).

Tang (2007) explained that the presence of lipids in buckwheat affected the thermal properties of its globulins. An amount around 6.5% of lipids was positive for the maintenance of globulin conformation.

Quinoa oil comprises a high concentration of natural antioxidants: around 17.5 μg/g of α-tocopherol and 47.2 μg/kg of ϒ-tocopherol on a dry weight basis (Alvarez-Jubete *et al*., 2009). These antioxidants provide stability to quinoa oil (Kozioł, 1992). In addition, the presence of α-tocopherol in quinoa is important, because this vitamin is an antioxidant at the cell membrane (Repo-Carrasco *et al*., 2003).

The study conducted by Ng *et al*. (2007), where grounded quinoa was exposed to different temperatures (25, 35, 45 and 50 °C) for 30 days, showed that storage time and temperature had significant effects on the production of free fatty acids, conjugated diene hydroperoxides and hexanal, which are indicators of lipid oxidation. However, the overall result established that quinoa lipids were stable during the period studied due to the minor production of these indicators after the treatments. It is suggested that vitamin E provided stability of polyunsaturated fats even if the surface area was increased, and the enzyme activity promoted with higher temperatures.

With regard to antioxidative capacity, amaranth possesses a higher amount of the most active component, δ-tocopherol, followed by quinoa and then buckwheat (Table 6.7). Wheat does not register this compound in its composition. Quinoa presents

Table 6.7 Tocopherols, vitamin E and squalene content (mg/kg) in amaranth, buckwheat, quinoa, and wheat.

Crop	Tocopherols					
	α-tocopherol	*β-tocopherol*	*ϒ-tocopherol*	*δ-tocopherol*	*Vitamin E*	*Squalene*
Amaranth	nd[a]	23.9[a]	nd[a]	9.0[a]	15.4[a]	13.2–42.4[c]; 40–60[d]; 43[e]
Buckwheat	1.3[a]–7.9[b]	nd[a]	4.8[b]–49.0[a]	0.9[a]–5.64[b]	6.3[a]	0.19[c]
Quinoa	17.5[a]	4.8[a]	47.2[a]	2.3[a]	24.7[a]	5.84[c]
Wheat	6.9[a]	4.8[a]	nd[a]	nd[a]	9.8[a]	

a) Data from Alvarez-Jubete *et al.* (2009);
b) Data from Kim *et al.* (2001);
c) Data from Berganza *et al.* (2003);
d) Data from Becker *et al.* (1981) and Sun *et al.* (1997);
e) Data from Guil-Guerrero *et al.* (2000).

the highest value for vitamin E activity, which is correlated to the amount of α-tocopherols present in this seed.

6.6.2 Squalene

All edible oils contain squalene (Belitz *et al.*, 2009). Its structure, 2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-tetra-cosahexaene, corresponds to a wide unsaturated hydrocarbon (Becker, 1989). Squalene consumption has been found to possibly reduce several forms of cancer risks and cholesterol levels (Cai *et al.*, 2004). It is used in the skin cosmetic industry as well as in the lubricant industry and for computer disks (Budin *et al.*, 1996; Belton and Taylor, 2002). In amaranth grain, squalene content is above 13.2–60 mg/kg (Table 6.7; Becker *et al.*, 1981; Sun *et al.*, 1997).

Squalene is found to be higher in amaranth (Table 6.7) than in other grains. This is in accordance to some authors who view amaranth as a potential crop source of squalene (Bressani *et al.*, 1987; Becker, 1989).

On the other hand, Ariza-Ortega *et al.* (2012), pointed out that squalene content is not affected by the heat applied during the extraction of amaranth oil. However, squalene content in amaranth could be affected by environmental conditions, such as temperature and water availability (Berganza *et al.*, 2003).

6.7 Conclusions

Quinoa, amaranth and buckwheat are important sources of lipids. Interestingly, these seeds have a higher oil content than some cereals like barley, rice and wheat. Quinoa has higher oil content than amaranth and buckwheat. For the three pseudocereals, the oil is composed principally of unsaturated fatty acids; the predominant ones are linoleic and oleic acids. On the other hand, palmitic acid is the main saturated fatty acid. There are different oil content values reported for each seed, which depend on determination methods, and / or differences in species, cultivars, accessions, and growth locations.

The neutral lipids, in particular triacyglycerides, are the main lipid components in these seeds. Polar lipids constitute the rest. Digalactosyl diglyceride, phosphatidyl choline and phosphatidyl etholamine are polar lipids, which are also common in these pseudocereals. For amaranth, the lipid content is localized essentially in the germ and seed coat, while the embryo is the main lipid storage in buckwheat and quinoa. These pseudocereals have a similar distribution of lipids in the form of lipid bodies. Moreover, the lipids of these seeds contain important nutrients, like tocopherols and squalene. Amaranth, buckwheat and quinoa are therefore important seeds that provide high-quality lipids and have health-promoting components.

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7

Pseudocereal Dry and Wet Milling: Processes, Products and Applications

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7.1 Introduction

Cereals and pseudocereals are the primary sources of carbohydrates for the global population. Cereals are members of the grass family (Gramineae) and are grown for their edible starchy seeds. Pseudocereals are cultivated for the same reason but are not members of the grass family. Buckwheat belongs to *Fagopyrum* genus from the Polygonaceae family, amaranth to *Amaranthus* genus from the Amaranthaceae family and quinoa to *Chenopodium* genus from the Amaranthaceae family / Chenopodioideae subfamily. None of them has been the primary energy source for large regions but they have played significant roles in food use. The cereals and pseudocereals are essentially starchy crops; however, they may contain significant quantities of protein and oil, and these constituents frequently determine their suitability for a specific end use. Structurally, the seeds are composed of three main parts including the endosperm, embryo, and seed coat. The endosperm is the primary starch storage portion but also contains some protein. The embryo is the oil storage portion, high in protein and minerals. Finally, the seed coat, also called pericarp or bran, consists mainly of cellulose and hemicellulose with some protein and lignin. Relative proportions of the three components vary among the different cereals and pseudocereals. In general, characteristic features of cereal milling processes include separation of the endosperm from the embryo and seed coat and size reduction of the endosperm into flour or grits. Whole-grain products with pseudocereals do not have the word 'whole' in their description; however, their flours were obtained by dry milling of whole grains (Figure 7.1). For centuries, these pseudocereals have mainly been processed with traditional methods, using a hand-operated wooden or stone pestle and mortar, and this continues today. Generally, the grains are pounded further before sieving to remove coarse material to produce flour and meal. Processing has taken a huge step from grinding stones for dry milling through soaking processes to remove starch and to modern milling and extrusion processes. Milling processes today are almost entirely based on meeting end product specifications by the most efficient means possible with almost all steps controlled mechanically and electronically (Baltensperger, 2003).

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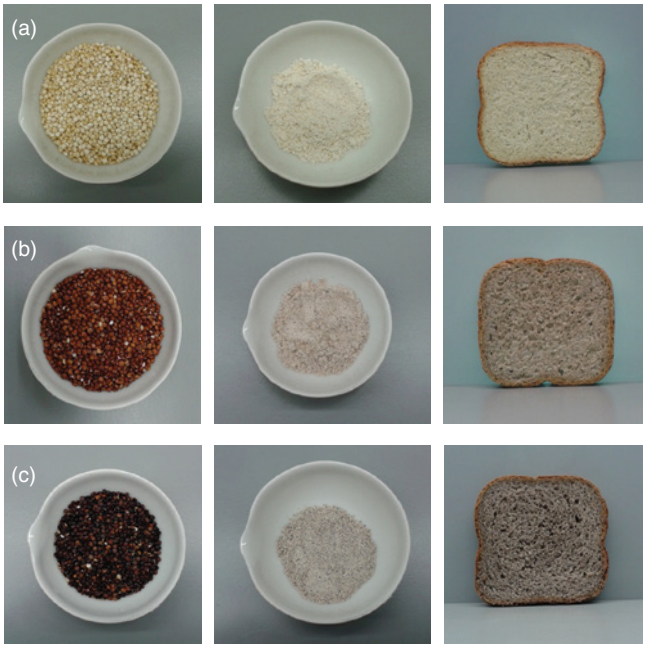

Figure 7.1 Quinoa grains, whole flour and crumb bread with 25% quinoa flour: (a) white quinoa; (b) red quinoa; (c) black quinoa. (*See color plate section for the color representation of this figure.*)

7.2 Separation of Kernel Components

Physical methods are preferred to produce flour from pseudocereal, because of their low cost and environmental concerns. Milling is a high shear process, which generates heat and thus causes an increase in temperature. By this means, it may affect the properties of the obtained byproducts. Physicochemical and functional properties of the main components of pseudocereals, starch and proteins, are widely described in literature (Koziol, 1992; Berghofer and Schoenlechner, 2002, Schoenlechner *et al.*, 2008, 2010; Oszvald *et al.*, 2009). These grains are an extremely valuable source of proteins – they have a very well balanced amino acid composition, with a particularly high content of lysine and sulfur-containing amino acids.

The objective of milling is to obtain intermediate products that can be used subsequently in the manufacture of products based on cereals or pseudocereals. In general, milling schemes are classified as dry or wet milling. As one would expect, the difference lies in the volume of water that is used. Dry milling also uses water but the volume is smaller. Moreover, in dry milling the aim is to separate the anatomical parts of the grain, such as the endosperm, germ, and pericarp, whereas the purpose of wet milling is to separate the chemical components of the grain, such as starch, protein, fibre and oil. However, few generalizations can be made about cereal or pseudocereal milling. The objective in dry milling is to obtain the maximum quantity of flour, whereas in wet milling it is to obtain the purest possible fraction of each component. There are dry-milling processes that change the shape and size of grains. Fractions produced by this step are frequently separated in another step. An additional milling process can be completed by changing the temperature or water content. Unlike dry milling, which primarily

fractionates, wet milling starts with a maceration / steeping process in which physical and chemical changes occur in the basic constituents. The objective is complete dissociation of endosperm cell contents with the release of starch granules from the protein network.

7.2.1 Dry Milling

The process of milling can be described basically as grinding, sifting, separation and regrinding. These steps are repeated to extract a particular part of the grain, the endosperm. Before milling begins, the cereal / pseudocereals grains are cleaned. Most modern equipment uses differences in size, shape, colour, solubility, specific weight and response to magnetic force to separate foreign material from the grains. Prior to grinding, water may be added to the grains, which are allowed to rest before milling (tempering). This allows absorption of water by the grains, toughening the pericarp and germ so they do not splinter during milling. If heat is also applied during tempering (to mellow the endosperm and make it easier to grind) then the process is referred to as conditioning (McKevith, 2004).

Dry milling could be also used to separate kernel components. However, the separation of pseudocereal starches from proteins is difficult because they are closely bounded. There is a method that includes purification and milling of amaranth seeds, mixture separation in different fractions, and extraction of oil from the germ fraction. The separation of mixture is carried out by sieving through screens with mesh diameters ranging from 0.8 mm to 5 mm, which are suitable for starch fraction having particles more than 0.8 mm, coating fraction with particles more than 0.5 mm and germ fraction having particles less than 0.5 mm (Miroshnichenko *et al*., 2009). The starch and coating fractions are intended for processing for food purposes, whereas the germ fraction is used to obtain oil by pressing or extraction. The known methods of amaranth seed processing include: cleaning and grinding; separation of starch, shell and germ fractions; the mixture of particles of crushed seeds and extracting oil, for example by pressing a mixture of fractions of membranes and nuclei at a temperature not exceeding 40 °C (Miroshnichenko *et al*., 2009).

The dry-milling technique for obtaining three fractions from amaranth – protein fraction (about 40% of proteins), dietary fibre fraction and starch fraction (79% of starch) – was developed by Tosi *et al*. (2000). The authors investigated various milling procedures but all involving the conditioning of the grain before milling. They optimized kernel drying conditions that give the maximum performance of flour with a high protein content taking in account drying air temperature and drying time as independent variables in a factorial design. The most suitable conditions found were 90 °C for 3 min; however, they resulted in a significant decrease in available lysine content (Tosi *et al*., 2000).

Roa *et al*. (2014) proposed a combination of abrasive milling and planetary ball milling to obtain the enriched protein and starch fractions from amaranth grains. The application of this method allows greater reduction of starch fraction with higher energy employed. The dry fractionation process applied to produce plant proteins with minimal water consumption and retention of native functionality basically involves the optimization of breakage behaviour of plant cell tissue to facilitate dry fractionation and development of that procedure using milling and air classification, which enable the functionality of protein fractions to be maintained. During milling, starch granules

should be physically disentangled from the surrounding protein matrix, which breaks into very small particles. In the air classification step, the starch granules are separated from the smaller protein particles. Finally, the enriched protein fraction is evaluated for its functionality. Previously, Wasik (1977) investigated the production of a protein-rich fraction from dehulled buckwheat by conventional roller milling. The nonflour fractions were mixed together to form a single protein-rich fraction, with more than 40% of protein, whereas the flour fraction had 6.9% of protein.

On the other hand, quinoa kernels contain a large amount of saponins, believed to be localized mostly in the outer layers of the seed. The milling process could remove these bitter compounds as an alternative to the extensive washing traditionally done before consumption (Farfan *et al*., 1978). Because of the small size of quinoa grains, they are generally milled whole, after the removal of saponins. As a result, whole quinoa flour may include pericarp if the saponins were washed out before milling, or it may include some or no pericarp if the saponins were removed by abrasion (Taylor and Parker, 2002). It is possible to produce potentially useful grain fractions by roller milling (Taylor and Parker, 2002). Chauhan *et al*. (1992) used a laboratory roller mill to reduce quinoa into bran and flour fractions. The bran fraction was very high in protein (20.4–24.3%) and lipids (11.0–13.2%), whereas the flour fraction was starch rich (73.8%) and protein poor (6.5%). One sample was manually dehulled using abrasive action in a pestle and a mortar, and the hulls were separated carefully by sieving to avoid inclusion of other seed portions (Figure 7.2). A portion of the hulled kernels was ground in a Wiley mill to obtain dehulled quinoa meal. The remaining dehulled kernels were conditioned to 15.5% moisture for 16 hours at 20 °C in an airtight contained. The conditioned kernels were milled into bran and flour using a Brabender Quadra mill (Figure 7.2). The second sample was soaked in water for 6 hours at room temperature, and the hulls were removed by abrasive action and washing with water five or six times. The dehulled kernels were dried at 45 °C, and a portion was ground in a Wiley mill to obtain a water-dehulled meal. The remaining water-dehulled kernels were conditioned and milled as described to obtain bran and flour (Figure 7.2.).

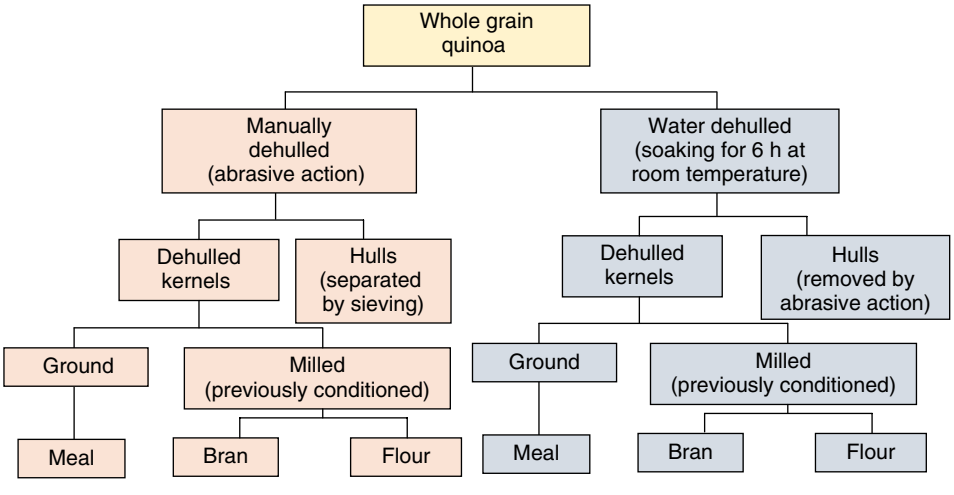

Figure 7.2 Preparation of quinoa kernel fractions by Chauhan *et al*. (1992).

Buckwheat flour is usually made from unroasted kernels and, depending on the quantity of the dark hull that remains, the flour is graded light, medium, or dark. Supreme buckwheat flour is a name sometimes given to flour milled from whole buckwheat. Flour milled from buckwheat that has been dehulled is sometimes called fancy buckwheat flour. Commercial fancy flour is mostly from central endosperm and contains 75% starch, 6% protein, 1% lipid, 1% soluble carbohydrates, 3% total dietary fibre, 1% ash and 13% other components (Steadman *et al*., 2001). Although the embryo traverses the central endosperm, parts of the embryo separate during milling with the aleurone and seed coat in the bran fraction. Bran, with little central endosperm, contains 18% starch, 36% protein, 11% lipid, 6% soluble carbohydrates, 15% total dietary fibre, and 7% other components. Buckwheat bran is also a rich source of dietary fibre, particularly bran with hull fragments (40% dietary fibre of which 25% is soluble dietary fibre), while bran without hull fragments has 16% dietary fibre of which 75% is soluble dietary fibre (Steadman *et al*., 2001).

Buckwheat dehulling could start with a traditional precooking process, where buckwheat seeds are first boiled in water and then carefully dried (Janes *et al*., 2012). During cooking, starch present in the endosperm absorbs water and stretches, and the fruit husk breaks. When the grain cools and partly dries it becomes hard and elastic and the husk becomes fragile at the edges so that the kernel can be efficiently dehulled. Buckwheat groats could be obtained after cooking seeds in water at 90–100 °C for approximately 30 min and further dehulled by throwing the seeds toward a metal surface by a rotating set of sticks (Janeš *et al*., 2012). Atalay *et al*. (2013) obtained buckwheat bran by using a pearler and milling on a hammer mill. After pearling and removing the bran fraction, the remaining naked kernels were milled into white buckwheat flour by the hammer mill. Takeuchi (2001) removed the seed coat in a short time without producing bitterness using an emery grain milling process, which has strong peeling strength, and swelling by pressure heating. Finally, the kernel was ground to flour by polish grain milling.

Traditionally, the water-driven mill, consisting of two natural stones, was used for buckwheat milling, as presented by Janeš *et al*. (2012). The first stone was 950 mm in diameter and was approximately 200 mm thick. The lower stone was stable and the upper stone rotated; the capacity was approximately 12 kg of buckwheat milled per hour. Stone milling can be employed for the production of 100% whole meal buckwheat flour, then the sieving process can be used to obtain white buckwheat flour. Adjusting the gap between the stones is just one way to control the degree of fractions fineness during the stone milling. The one-step process using millstones is in contrast with roller mills. In this process, various milling streams can be obtained. The composition and physicochemical properties of the fractions obtained are closely associated with the milling method applied (Izydorczyk *et al*., 2014). Kawakami *et al*. (2008) showed that relatively low storage temperatures are suitable for preserving flavour and taste of stone-milled buckwheat flour. The same authors found that a longer storage period significantly decreased the taste and texture indicators of stone-milled buckwheat (Kawakami *et al*., 2009). The gradual milling method, similar to that used for wheat flour, was proposed for buckwheat grain by Morita *et al*. (2006). In this method, husk is removed from whole buckwheat grain by a dehulling apparatus with disks. Then, the groats with endosperm and bran are milled to 17 fractions of buckwheat flour. The inner fractions contain mostly starch and are lighter than the outer fractions. The outer layer contains mainly phenolic compounds, proteins and dietary fibre. The protein and

ash contents of buckwheat flour fractions increased in the order from the inner to the outer fractions (Hung *et al.*, 2007). Skrabanja *et al.* (2004) milled buckwheat seeds into 23 fractions: seven fine flours, three coarse flours, four small semolina, two big semolina, six bran, and one husk fraction. They found a considerable variation in the chemical composition among the milling fractions. The protein content varied from 4.4% to 11.9% in flours and from 19.2% to 31.3% in bran fractions; whereas starch varied from 91.7% to 70.4% in flours and from 42.6% to 20.3% in bran (Skrabanja *et al.*, 2004). The percentage of soluble dietary fibre contained in total dietary fibre was higher in flours than in semolina and bran fractions. The authors propose the use of an appropriate fraction depending on technological / nutritional demands to achieve the desired product. Previously, Matsuhashi *et al.* (1984) produced buckwheat flour by a multiple stage milling system using 12 rollers in succession. Generally, most of the final flour passed through 150–250 mesh, the average apparent density was 0.5 g/cm^3 and flour colour became darker as fineness of milling increased. Starch content decreased during milling from 80% in polished grain to 40% in final flour; protein was concentrated during milling, increasing from 17 to 24% (between rollers 3 and 5) and fat content also increased during milling.

A procedure was also developed for obtaining buckwheat flour from a cold counter-jet mill (Ohisa *et al.*, 2002). This flour gave a better quality after cooking noodle with buckwheat comparing to that made from roll mill flour, which broke into smaller pieces by boiling and washing (Ohisa *et al.*, 2002). Koga (2006) also developed a system using the cold-milling method that involves generating dry ice by gushing liquefied gas in a refrigerant apparatus and showering dry ice on ground raw material in a stone-milling apparatus for cooling ground material. The ground raw material is cooled efficiently by a simple structure suppressing the heat generation of ground powder (Koga, 2006).

7.2.2 Wet Milling

The cereal that is mainly used for wet milling is corn (maize). The origins of the wet milling industry go back to the year 1842, when an American, Thomas Kingsford, started manufacturing corn starch on an industrial level (Inglett, 1970). Before that, native starch was obtained from wheat and potato. Around 1860, a substantial quantity of starch was produced by small factories distributed in the United States and northwest Europe. By 1890, corn had replaced wheat and potatoes as the main source of starch. As a result, the corn-refining industry continued to grow and also to diversify and transform into the complex processing plant that it is now. The development of this industry throughout the world has been enormous. The reason for the great demand for starch was its low price and its diversity and adaptability for many industrial processes in industries ranging from food and pharmaceuticals to paper and glue. Although the wet milling process was originally designed to produce starch for industrial use and for food, the aim nowadays is to achieve optimum efficiency in the process and maximum separation of each fraction of the grain of cereals and pseudocereals. There are constant improvements in the yield and quality of milling products in response to consumer needs, the nutritional requirements of farm animals, and the development of new technologies.

Wet milling is a more complex process than dry milling and it is a source of a great variety of products. Although the main product of wet milling is starch, other subproducts of interest for technological purposes and for the food industry are the fibre-rich

and protein-rich fractions. In the case of corn, these fractions are used for making balanced foods, but in the case of pseudocereals they may be employed for other purposes. Nowadays, starch from various sources is not only marketed as such but is also used to make dextrins, syrups, and combustible alcohol. In recent years there has also been a growth in the use of starch as raw material in the preparation of special polymers for the plastics industry. These materials, mixed with other similar products of the petrochemical industry, have the advantage of being biodegradable and renewable.

7.2.2.1 General Description of the Industrial Wet Milling Process

The process of wet milling of pseudocereals was based on the existing process for corn with variations. This process involves chemical, biochemical, and mechanical operations to separate the grain into its main components: starch, protein, fibre, and lipids. The process starts with steeping of the grain to soften it, followed by milling and separating operations. The fractions have different physical properties and can therefore be separated by methods based on differences in density and/or particle size. The basic characteristic of this industry is that it achieves the separation of the main components using large quantities of water, which differentiates it from dry milling. Unfortunately, traditional wet fractionation processes to produce plant proteins are accompanied by high water use and sometimes loss of native protein functionality.

The wet milling process starts with cleaning of the grain to remove any kind of extraneous material. Then the grain is transported to steeping tanks where it is soaked in an aqueous solution of SO_2 or alkali for a period at a predetermined temperature depending on the pseudocereal and the method used. During the steeping process, some of the solid parts of the grain dissolve. These dissolved components are the nutritive fraction of the extract of the fermented grain, which is concentrated and dehydrated. During steeping the grain absorbs a considerable amount of water and becomes so soft that it can be disintegrated by mere rubbing with the fingers. After this, the first milling step is performed. The resulting suspension is milled again to pulverize the particles of endosperm while leaving the fibrous material intact. The suspension is filtered through a series of screens with a decreasing mesh size until it affects the final screen, which allows the starch and protein fractions to pass through. The starch and protein are separated by centrifugation, and the protein, which is the lighter fraction, is concentrated and then dehydrated. The suspension or slurry of starch forms a sediment, and is concentrated and washed. This starch suspension is used in the various production channels.

One of the criteria used in the literature to evaluate the suitability of grain for wet milling is based on estimating the yield and quality of the starch fraction resulting from the process (Singh and Eckhoff, 1996). In recent decades, wet milling methods have been developed on a laboratory scale and on a pilot plant scale in order to evaluate the yield and quality of the starch obtained in the process, and the effect of the operative variables and possible modifications with respect to traditional milling. The advantage of these methods is the possibility of using small sample sizes to quantify the yield and quality of the various milling products. The efficiency of the process has not yet reached the level of development of other technological processes because of the variability of the milling characteristics of pseudocereal grains, and in some cases these aspects have not yet been explored. Growing conditions, variety and the increase in the diversity of commercial hybrids resulting from developments in biotechnology and genetic engineering, and harvesting and drying conditions can all have a considerable effect on the

quality of grain used for milling. However, the developments have been accompanied by drawbacks arising from the increase in diversity, affecting the effectiveness and efficiency of the process.

The milling characteristics of a type of grain can be estimated on a laboratory scale or on a pilot plant scale. This change of scale is more than a change of sample size, although that is the most significant factor. The laboratory-scale process uses 25 g to 2 kg of grain, whereas the pilot-plant process uses quantities exceeding 100 kg. Moreover, the laboratory-scale procedure requires small equipment, usually different from the equipment used on an industrial scale. Whichever method is used for the wet milling study, the main steps involved are: sample preparation, steeping, milling, separation of the germ containing the lipid fraction, separation of fibre, separation of starch and protein, estimation of yield and recovery.

The methods for simulating wet milling on a laboratory scale consist of steeping the grain in a batch system in the presence of SO_2 or alkali. The methods for separating starch and protein are generally based on the difference in their density or on their different granulometry. Centrifugation methods are used to separate them, because the density of the starch granules is greater than that of the protein fraction. Another separation method based on difference in density is the inclined plane or table method. In this method the starch / protein suspension is made to circulate on an inclined plane where sedimentation of the starch fraction takes place, leaving the protein in suspension. However, pseudocereals are one of the few sources of small granules, for which starch density-based separation methods are not feasible (Wilhelm *et al.*, 1998; Middlewood and Carson, 2012a). Finally, the method based on the difference in size between starch and protein is based on the fact that starch particles have a smaller diameter than protein particles. On the basis of this difference in size between the particles, methods were proposed for separation by means of a series of screens or else by microfiltration (Middlewood and Carson, 2012a, b; Wronkowska and Haros, 2014).

Yield, Recovery and Quality of the Starch Fraction Obtained by Wet Milling

One of the criteria used for quantitative evaluation of the results of wet milling is starch yield, SY, which is defined as:

$$\text{SY}\,(\%) = \frac{\text{weight of dry starch obtained}}{\text{weight of dry grain}} \times 100$$

Another criterion that is used is degree of recovery (DR), defined as:

$$\text{DR}\,(\%) = \frac{\text{weight of dry starch obtained}}{\text{weight of dry starch present in the grain}} \times 100$$

The yield values depend on the technique employed and the kind of grain that is used, whereas the recovery is independent of the starch content in the grain but is also affected by the milling method that is employed. The quality of the starch fraction is usually estimated in terms of the protein content of the fraction (Wronkowska and Haros, 2014). The protein content of the starch resulting from wet milling depends on various factors, such as the separation method that is used, whether on a laboratory scale or on an industrial scale. On a laboratory scale the protein content is generally in the range of 0.5% to 7.0% (Neryng and Reilly, 1984; Singh and Eckhoff, 1996; Haros and

Suarez, 1999; Calzetta-Resio *et al*., 2006; Wronkowska and Haros, 2014), depending on the separation method that is used. It must be noted that the degree of purity of starch on an industrial scale is less than that obtained on a laboratory scale. The reason for this difference is the process in which the starch fraction is purified by means of a series of hydrocyclones, and washed with chemicals and / or treated with enzymes (Watson, 1991; Middlewood and Carson, 2012b). The protein content of the cornstarch fraction obtained from the first hydrocyclone is between 3% and 5%, but after washing it decreases to 0.30–0.35% (Watson, 1991).

Factors that Affect Milling Characteristics

In order to determine the milling characteristics of the grain, the yield and quality of the various fractions are evaluated. As the wet milling process is relatively complex, the yield and quality of the fractions are affected by various factors, such as the effect of the variety or hybrid employed, postharvest treatment (drying and storage) and steeping conditions (temperature, time, concentration of SO_2 or alkali, pH, etc.). There are also other criteria, such as technological criteria – how the grain behaves during the process with respect to steeping time, breakage susceptibility, efficient degermination, and, above all, good separation of protein and starch. There are also quality criteria for grain, such as microbial load, mycotoxin content and fatty acids in the germ.

- *Effect of the variety.* According to Mazzoni and Robutti (1990), the quantitative analytical determination of starch is not necessarily reflected in the behaviour of a particular grain in the wet milling process. It has been shown that the grains that are richest in starch are not always those that give the greatest yield of this product (Kempf and Tegge, 1961). There are other factors to be taken into account if the yield and quality of the subproducts of wet milling are considered. These other factors include a low percentage of broken or damaged grains, low breakage susceptibility, high hectoliter weight, high oil recovery, high protein quality, and low fungus count. It is known that there are clear structural differences between the various pseudocereals in terms of shape, dimensions, covering, and structure of the endosperm, so it is likely that the grains of different pseudocereals will behave differently in response to wet milling. Moreover, there is variability between grains of the same species with regard to chemical composition and dimensions, so the same process could provide different results.
- *Postharvest treatment.* There are problems with storage, including excessive moisture content at the time of storage, excessive temperature, microbial, insect, and arachnid infestation, rodent and bird predation, mechanical damage and biochemical deterioration. The latter is especially important for cereals or pseudocereals with higher than normal oil content because the oil becomes rancid over time. During storage and transport the grain is exposed to mechanical damage as a result of handling and movement. Minimization of mechanical damage can be achieved by proper design of drying and storage plants and by optimization of the drying process it is possible to reduce and / or avoid the damage produced by this treatment. Artificial drying of cereals and pseudocereals may use excessive air temperatures and / or speeds. This can cause a considerable loss of grain quality, because the drying capacity is increased at the expense of the quality of the dry product. Excessive conditions make the grain fragile, which can subsequently be seen in the form of cracked or broken grains. It must be emphasized that, even in the case of dry grain, the presence of cracked or broken grain encourages the entry of micro-organisms whose activity can alter

humidity and temperature conditions during storage, triggering fermentation reactions. Other effects of the use of high drying temperatures are denaturation of proteins and loss of vitamins. The deterioration in the quality of the grain not only affects the grain but also has a direct influence on the quality of the products obtained from milling. For this reason it is very important to optimize the drying process. The problem caused by damage to grains that are to be processed by wet milling is that it is difficult to separate the components because of alteration of the endosperm induced by high drying temperatures. These temperatures can also alter the viscosity of the starch obtained, which affects the capacity of the starch to make homogeneous pastes. There can also be losses of pigment as a result of oxidation because of the application of high drying temperatures.

- *Steeping.* This step consists of immersion in water with control of conditions such as temperature, time, sulfur dioxide or alkali concentration, and lactic acid concentration. It is a complex process in which there are chemical and biochemical reactions and also physical changes that result in weakening of the protein matrix of the endosperm. One of the physical changes that take place during steeping is absorption of water, which helps to soften the grain and also acts as a transporter or carrier of SO_2, lactic acid, and / or alkali (Ruan *et al.*, 1992). The rate and path of diffusion affect the efficacy of the steeping operation, as dispersion of the protein matrix cannot occur without the presence of these chemicals. Sulfur dioxide causes the protein matrix to weaken by cleaving disulfide bonds and forming soluble S-sulfoproteins, providing a reducing medium that prevents reformation of disulfide bonds (Boundy *et al.*, 1967). Moreover, the presence of SO_2 in the steepwater inhibits microbial growth and provides a suitable medium for the lactic bacteria to develop. It must be borne in mind that SO_2 in aqueous solution forms sulfurous acid, which dissociates in accordance with the pH of the medium. The diffusion of this compound, and its role as a reducing agent and inhibitor of microorganisms is therefore conditioned by the pH. The SO_2 concentration employed in the steeping step ranges between 0.1% and 0.3%. Levels above 0.3% inhibit growth of *Lactobacillus*. These micro-organisms produce lactic fermentation from the soluble sugars released from the grain into the steepwater. The presence of lactic acid during this step could help to increase the starch yield. Eckhoff and Tso (1991) demonstrated that addition of lactic acid to the steeping process improved the yield and quality of the corn starch obtained. Therefore, research studies on wet milling of pseudocereals using SO_2 incorporate lactic acid (Calzetta-Resio *et al.*, 2006; Wronkowska and Haros, 2014). However, as yet the mechanism of action of this compound has not been described in the literature. Moreover, the steeping step requires time and the correct temperature for the physical, chemical, and biochemical changes that are needed to soften the grain. The temperature is generally in the range 28–55 °C because it is imperative that it should be a subgelatinization temperature. The steeping time is conditioned by the type of grain to be steeped, its dimensions, and its structure.

7.2.2.2 Amaranth

Amaranth starch is difficult to extract by wet milling due to the strong association between starch and protein (Zhao and Whistler, 1994), high protein content of the kernels, and small granule size (Calzetta Resio *et al.*, 2009; Middlewood and Carson, 2012a). Today, there is no commercial amaranth wet milling process that would allow for the separation of starch from other components. In turn, many laboratory-scale wet

milling methods have been developed to extract amaranth starch. For example, Calzetta Resio *et al.* (2003) used the wet milling procedure similar to that used in the wet milling of corn. They found an increase in moisture content with increasing soaking temperature, and that the rate of water absorption by amaranth grain during soaking was significantly related to the temperature and sulfur dioxide concentration (Calzetta Resio *et al.*, 2006). Alkaline soaking is required for the amaranth grain to leach the protein; however, it results in damage to starch granules and the loss of starch yield (Perez *et al.*, 1993; Myers and Fox, 1994; Zhao and Whistler, 1994). An alternative procedure for the isolation of amaranth starch with high recovery and purity was proposed by Radosavljevic *et al.* (1998) and involves the use of enzymes during soaking. Acid wet milling of amaranth grain is not analysed as often as alkaline starch isolation. Malinski *et al.* (2003) and Calzetta Resio *et al.* (2009) used an aqueous solution of sodium metabisulfite for steeping. Loubes *et al.* (2012) used the acid wet milling for amaranth grain and found significant correlations between temperature and acid concentration on storage and loss moduli, and temperature at which both moduli reached the highest values.

Although the Al-Hakkak process is not a wet milling process, it requires water for starch extraction. It is a dough-based starch extraction method that has been developed to extract starch from plant materials that do not contain gluten (Al-Hakkak and Al-Hakkak, 2007). The innovative step in this process is the addition of vital wheat gluten, which enables a dough to be formed as the wheat gluten proteins form a protein network with amaranth proteins. The Al-Hakkak process does not require alkaline conditions or enzymes that could denature the proteins, and the water-soluble proteins and carbohydrates remain as potential coproducts (Middlewood 2011; Middlewood and Carson, 2012a). In the pilot-scale process, the dough is mechanically agitated in water to release starch. During this stage the dough breaks into small fragments. The wash water is screened through a vibrating sieve, which produces two streams. The dough fragments retained by the sieve are returned to the mixing vessel for the next wash, while the starch suspension passes through the sieve, ready for further processing to recover the starch. Traditional starch-protein separation methods based on density, such as settling tables, hydrocyclones and centrifuges, could be used to this end. However, at pilot plants and on a commercial scale, the application of density-based processes may not be practical as the small granule size reduces separation efficiency (Middlewood 2011; Middlewood and Carson, 2012a).

Tangential flow filtration is an alternative to the density-based separation process (Middlewood and Carson, 2012a, b). It is a pressure-driven separation process that uses a semipermeable membrane to separate components in a suspension, based primarily on their size differences. Pressure is used to force the feed suspension against a semipermeable membrane. Components smaller than the membrane pores pass through it in what is termed the permeate stream, whereas components larger than the membrane pores are retained in the retentate stream (Figure 7.3).

7.2.2.3 Quinoa

As in the case of amaranth, one of the factors most unfavourable to the process of wet milling of quinoa is the very small size of starch granules. Another factor is the presence of endogenous substances that increase the viscosity of quinoa flour-in-water slurries. The composition of the pellet formed during centrifugation of the slurries also does not facilitate the wet milling process. Wet milling was used, on a laboratory scale, for starch extraction from quinoa after seed soaking in an acetate buffer by Atwell *et al.* (1983) and

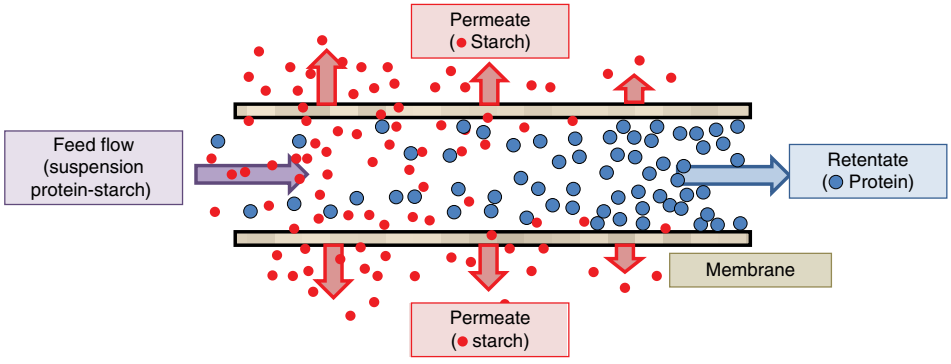

Figure 7.3 Diagram of tangential flow filtration.

Lorenz (1990). Qian and Kuhn (1999) used a similar method but with soaking in sodium hydroxide. Small-scale isolation of quinoa starch was optimized by Wilhelm *et al.* (1998). In this process, the authors used basic technology, machinery and enzymes: xylanase, cellulase and hemicellulase. Wright *et al.* (2002) used soaking in a diluted alkaline solution for the isolation and characterization of starch from sweet and bitter quinoa seeds. Ligarda Samanez *et al.* (2012) showed that neutral solvents were better for the separation of dietary fibre fractions from quinoa than the alkaline method.

Scanlin *et al.* (2010) described a process for quinoa protein isolation that consists of the following steps: (i) flaking or milling quinoa grains, (ii) extracting oil from the flaked or milled quinoa grain leaving defatted quinoa, (iii) extracting protein from the defatted quinoa in an alkaline solution, (iv) separating the fraction containing protein from the mixture, and (v) drying the solubilized protein, giving a quinoa protein concentrate containing at least about 50% protein (Figure 7.4). Quinoa oil, fibre, and starch can be obtained readily from this process by employing simple manipulations such as separation or concentration, which are well known. This process can be operated with appropriate modifications and variations to obtain these products. For example, the quinoa grain can be mechanically abraded and / or the quinoa grain can be shaped (for example, flaked) and / or the quinoa grain can be conditioned (for example, tempered) prior to the step of milling The protein fraction obtained after step (iv) can be further purified by isoelectric precipitation before step (v), if necessary. This process is designed to maximize the isolation of individual components contained in quinoa grain and thus it enables one to obtain other components such as quinoa oil, starch, and fibre at different stages of the process.

Gonzalez-Roberto *et al.* (2015) optimized the steeping conditions of quinoa kernels in SO_2 solution with lactic acid using a factorial design. They studied the effect of temperature, pH and time of steeping step on the starch recovery and quality. After steeping, quinoa was ground and the water slurry was manually sieved through a set of stainless screens: 600, 300 and 53 µm. Hulls were retained in the first screen, germen and fibre fraction in the second and protein fraction in the third. Starch slurry passing through the 53 µm sieve was finally separated by centrifugation. All the fractions were dried and their yield was calculated as a ratio of the totally dried isolated fraction to the initial amount of dried quinoa (Gonzalez-Roberto *et al.*, 2015; Figure 7.5).

Pouvreau *et al.* (2014) developed a method for processing quinoa that includes pretreatment of seeds. It starts with washing and soaking the seeds in an aqueous system

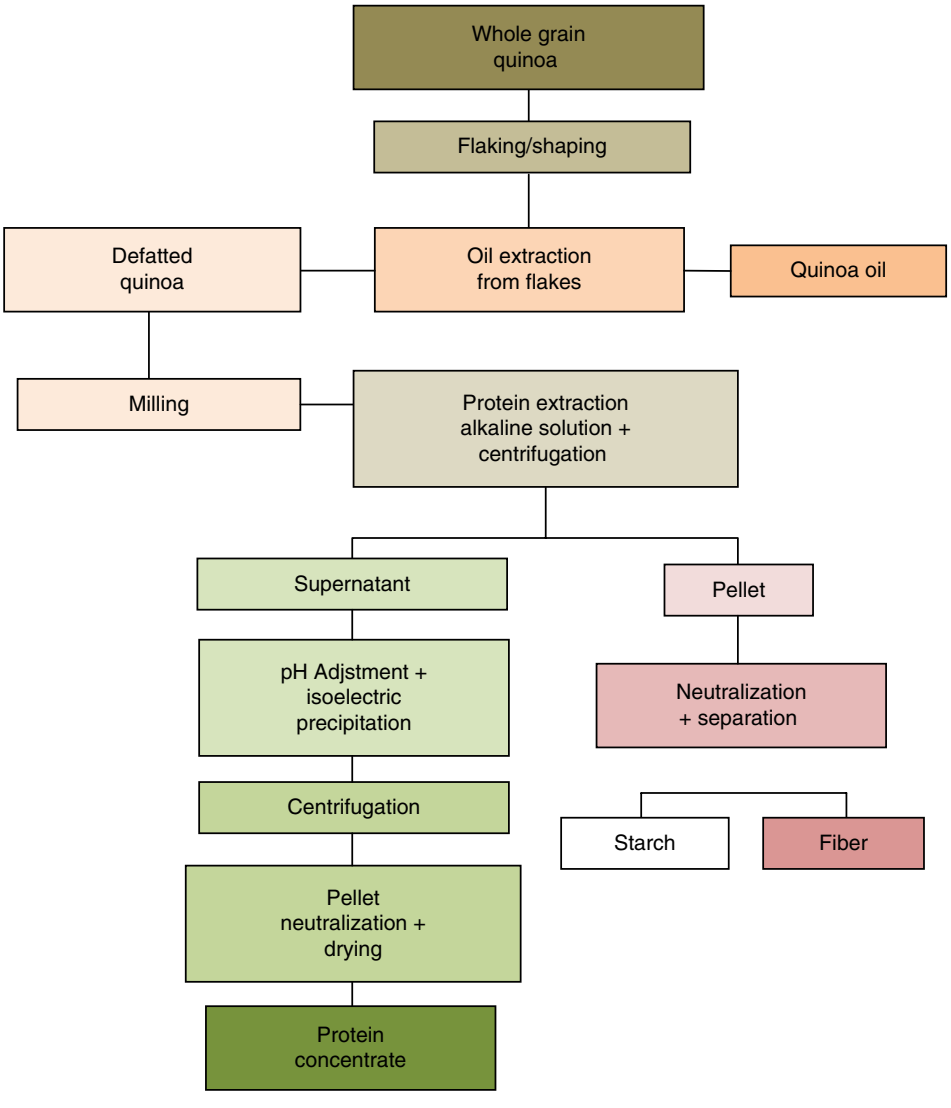

Figure 7.4 Schematic diagram of quinoa wet milling process by Scanlin *et al*. (2010).

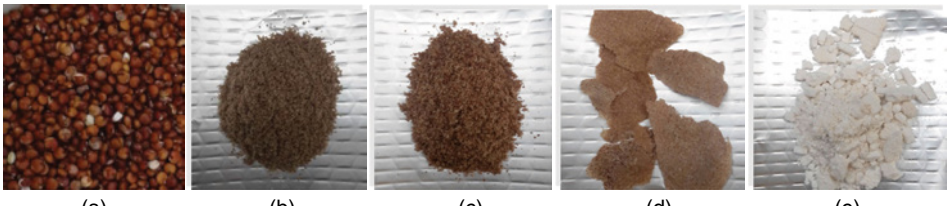

Figure 7.5 Fractions obtained by quinoa wet milling: (a) red quinoa; (b) fraction rich in Hull; (c) fraction rich in Germen and fibre; (d) fraction rich in protein; (e) fraction rich in starch (Gonzalez-Roberto *et al*., 2015). (*See color plate section for the color representation of this figure.*)

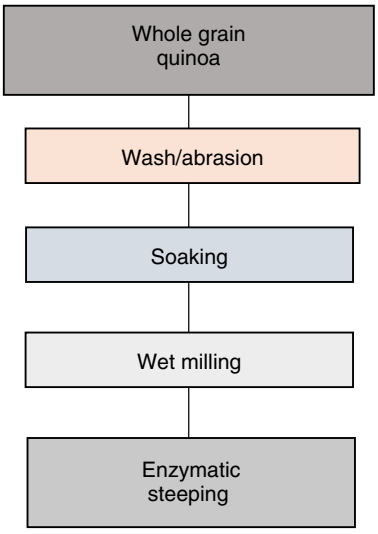

Figure 7.6 Schematic diagram of the process for preparing the quinoa seeds by Pouvreau *et al*. (2014).

with alkaline agents, and / or coating the seeds with lipases, proteases and / or esterase enzyme preparation to reduce saponin content. After the quinoa seed is ground, it may be steeped in water that is treated with enzymes or combinations of enzymes (Figure 7.6). The resulting liquid may undergo pH adjustment as well as a separation of protein from starch. The protein and starch may be concentrated to increase protein-to-carbohydrate ratios or starch may be hydrolysed prior to concentration in order to improve these ratios.

7.2.2.4 Buckwheat

Zheng *et al*. (1998) used the wet milling for dehulled buckwheat, with extraction efficiencies reaching 79 and 64% for starch and protein, respectively. These authors found about 5–10% of the total starch in protein and tailing fractions. Wronkowska and Haros (2014) applied the wet milling process for buckwheat with or without the hull to isolate the starch fraction (Figures 7.7–7.9).

The authors showed starch extraction efficiency to be higher for the total starch isolated from buckwheat with hull than for dehulled buckwheat. Several changes in pasting and thermal properties were observed in starch from buckwheat with hull steeped for longer time than dehulled buckwheat. Generally, the wet milling method used in that study did not significantly change the properties of isolated starch compared to raw material. Hull of buckwheat and steeping time did not provoke any significant changes in starch properties (Wronkowska and Haros, 2014).

7.3 Industrial Applications and General Food Uses

Today, the pseudocereals could be alternative crops to some cereals. Their proteins are highly soluble and could be used as an ingredient of functional foods. Amaranth protein concentrates have much better solubility, foaming and emulsifying properties

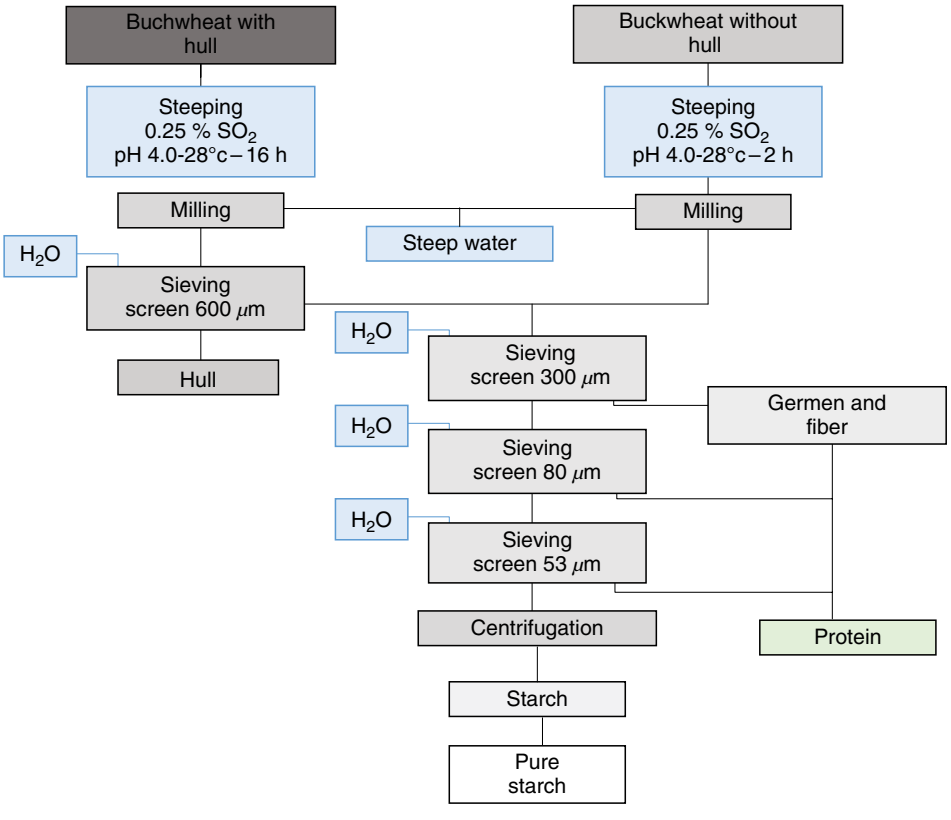

Figure 7.7 Schematic diagram of buckwheat wet milling process by Wronkowska and Haros (2014).

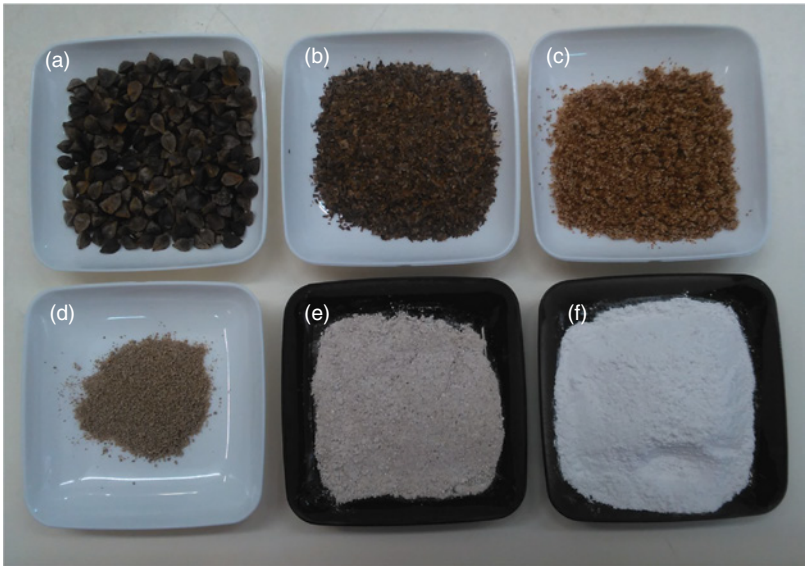

Figure 7.8 Fractions obtained by wet milling: (a) Buckwheat grain with hull; (b) hull; (c) fraction rich in germen and fibre; (d) fraction rich in protein; (e) fraction of starch; and (f) starch after purification.

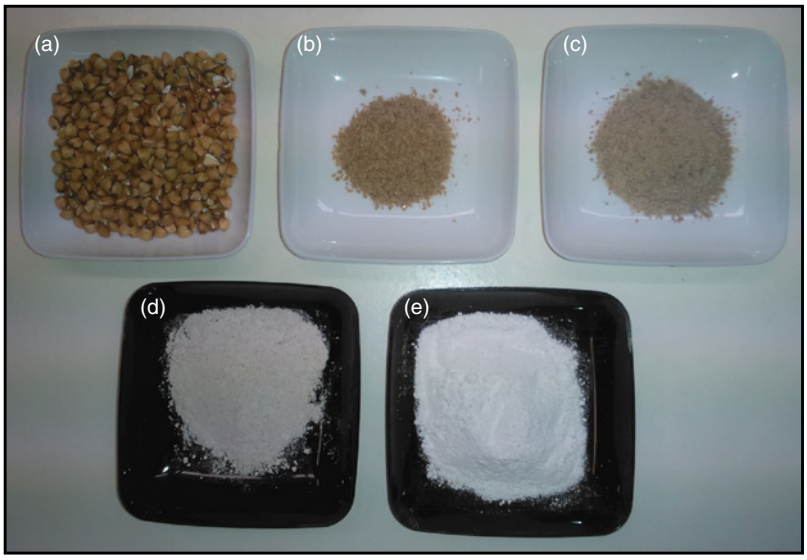

Figure 7.9 Fractions obtained by wet milling: (a) buckwheat without hull; (b) fraction rich in germen and fibre; (c) fraction rich in protein; (d) fraction of starch; and (e) starch after purification.

than two commercial soy proteins, as presented by Bejosano and Corke (1999). In turn, Fidantsi and Doxastakis (2001) showed that amaranth protein isolates acted as effective stabilizing agents for emulsions and also as effective foaming agents. The acid wet milling procedure of amaranth grain affects the yield and purity of the obtained fractions. Amaranth is an alternative and complementary source of protein compared to conventional protein sources. It could be potentially used as an ingredient in food products where gel formation is desirable. Bejarano-Luján and Netto (2010) found that the modification of the standard wet milling process of amaranth by the addition of acid washing step or heating during the alkaline extraction step changed the composition and functionality of the isolated protein fraction. These authors also observed that the protein isolation procedure of wet milling of amaranth modifies the structure and rheological properties of gels obtained from this protein (Bejarano-Luján *et al*., 2010).

It is not necessary to remove the seed coat of amaranth, in contrast with the other two pseudocereals, quinoa and buckwheat (Berghofer and Schoenlechner, 2002). Amaranth greens and grain have been used in a wide variety of foods. Vegetable types (also leaves of grain one) are usually picked fresh, used as greens in salads, or blanched, steamed, boiled, stir fried, or baked to taste. Cooked greens can be used as a side dish, in soups, as an ingredient in baby food, lasagne, pasta, pie, soufflé, and so forth. Amaranth grain, mostly rolled or popped, can be used in muesli and in granola bars. Grain can also be germinated for sprouts, malted for beer production, can be fermented or can serve as a starchy material in spirit production (Grobelnik Mlakar *et al*., 2010). The most common use is to grind the grain into flour that may then be used in breads, noodles, pancakes, cereals, granola, cookies, or other flour-based products. The grain can be popped like popcorn or flaked like oatmeal (Ogrodowska *et al*., 2014). More than 40 products containing amaranth are currently on the market in the United States (Tosi *et al*., 2002; Guerra-Matias and Arêas, 2005; Sindhuja *et al*., 2005).

Amaranth starch is characterized by the small size of granules, furthermore it has a low gelatinization temperature, good freeze-thaw stability and resistance to mechanical shear (Myers and Fox, 1994; Zhao and Whistler, 1994). Breene (1991) described the potential uses of amaranth starch as a food and nonfood ingredient, used, for example, in biodegradable plastics, dusting powders, cosmetics and food stabilizers, thickeners and gelling agents for products such as sauces and soups. The methodology applied for wet milling significantly affects the purity and functionality of the fractions obtained.

Depending on the saponin content, quinoa may be divided into sweet and bitter varieties (Koziol, 1992). It has been suggested that the presence of saponins, which can impart a bitter taste to quinoa foods, is one of the reasons that quinoa has not attained the worldwide status of several other South American food crops, such as phaseolus beans, maize and potatoes. A high content of proteins with very equilibrated composition determines the nutritional value of quinoa grain (Gross *et al*., 1989; Ranhotra *et al*., 1993), which meets the FAO/WHO/UNU ideal protein reference pattern for children (World Health Organization, 1985). Quinoa grain also contains a number of potentially useful components such as starch and oil. In fact, quinoa has been proposed as a new oil crop (Koziol, 1993). Traditionally, quinoa has been used in a wide variety of foods: in broths, soups and stews, and as a rice-like product. Flour is used in porridge and for the preparation of bread called krispina. Quinoa can also be fermented to make a beer called *chicha*. Like buckwheat and amaranth, quinoa does not contain gluten and thus is used as a component of gluten-free products.

In Central and East Europe, buckwheat is traditionally used as roasted or unroasted groats, while in East Asia it is used as a primary ingredient or an additive in the production of pasta. Buckwheat has a very low content of α-gliadin (Kreft *et al*., 1996) and that is why it is used in gluten-free products (Wronkowska *et al*., 2013).

One of the fractions obtained during the wet milling of buckwheat is hull (Wronkowska and Haros, 2014). Nowadays, the hull is used in the production of therapeutic mattresses / pillows and cushions, which adapt to the position of the body, quickly absorb moisture, do not heat up and are always cool (Pomeranz, 1983). An extremely important feature of the hulls, due to the presence of tannins, is inhibiting the development of harmful micro-organisms: mites, mould, bacteria and fungi. These byproducts of buckwheat processing are characterized by a high carbon and hydrogen content, and hence are used as a raw material for the production of granular biofuels (Borkowska and Robaszewska, 2012). However, buckwheat hull may also be used in the food industry. Oomah and Mazza (1996) have reported that buckwheat hull contains four times more phenolic compounds compared to groats. Zielińska *et al*. (2013) found that the buckwheat hull tea showed a lower content of total phenolic compounds and lower antioxidant capacity in comparison to green tea.

The buckwheat groats can be ground into several fractions with varying levels of the aleurone layer remaining (Zondag, 2003). Coarsely ground groats are called grits and can be used for porridges or in breads. Roasted groats (kasha) are used in Eastern European ethnic dishes (Vinning, 2001; Zondag, 2003). Buckwheat flour made from the aleurone layer of the groats is called Farinetta and can be used in breads, bakery products, and pancakes (Zondag, 2003). Flour made from the entire buckwheat groats (Supreme flour) can be used in breads, bakery products, extruded snacks, pancakes, and pasta (Zondag, 2003).

Buckwheat flour is applied as a food additive or in the production of such foodstuffs as pancakes, pastas and noodles (Handoyo *et al*. 2006). Buckwheat grains and buckwheat

flour may be applied for the preparation of multicomponent mixtures and for the extension of the food assortment with an assumed dietetic and nutritional value – for example, ready-to-eat foods. Buckwheat-enhanced wheat bread was better in terms of flavour and mouthfeel sensory attributes as compared to wheat bread, also that kind of bread showed the highest inhibitory activity against AGEs (advanced glycation end products) formation (Lin *et al*., 2013; Szawara-Nowak *et al*., 2014). Wronkowska *et al*. (2015a, b) demonstrated that the solid-state fermentation with *Rhizopus oligosporus* could be a useful tool for obtaining a new buckwheat product. The fermentation process used improved protein digestibility, increased contents of proteins, some minerals, water-soluble vitamins as well as tocopherols. In addition, fermented buckwheat products were quite well accepted by the evaluators in the sensory analysis. Buckwheat could be a useful and valuable raw material for extruded corn snacks as well (Wójtowicz *et al*., 2013).

Both cereals and pseudocereals have a long history of use as forage crops for livestock. The small grains have been used extensively for hay, grazing, green-chop (fresh fodder harvested and used as cattle feed) and silage.

7.4 Conclusion

Intensive research is still necessary regarding the possibilities of applying the dry- and wet milling processes to pseudocereals. Today, they seem to be a fine alternative to increase the range of plants used globally because of their nutritional / functional value and interesting technological properties. Renewed interest in pseudocereals that can be used for obtaining special flours or fractions of their components mainly arises from the finding of relevant attributes. Their innovation is related to the ways in which old and new uses and technologies are being addressed and have extraordinary potential in food science and technology.

Acknowledgements

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8

Food Uses of Whole Pseudocereals

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8.1 Introduction

It is widely accepted that by 2050 the world will host 9 billion people (van Huis *et al*., 2013). To accommodate this number, current food production will need to almost double. To meet the food and nutrition challenges of today – there are nearly 1 billion chronically hungry people worldwide – and tomorrow, what we eat and how we produce it needs to be re-evaluated. Inefficiencies need to be rectified and food waste reduced. It is necessary to find new ways of growing food (van Huis *et al*., 2013). The advent of biofuels has the potential to change the situation, causing world demand to be higher, depending on energy prices and government policies. Without biofuels, much of the increase in cereal demand will be for animal feed to support the growing consumption of livestock products (FAO, 2009). Therefore, new sources of plant ingredients, which will be important from a nutritional point of view, are still being sought.

In recent years, pseudocereals have been the subject of renewed interest. They have gained importance as alternative crops instead of typical and more utilized cereal grains such as wheat, corn and rice, and they have emerged as appropriate alternatives available for human nutrition. The International AACC in the list of recognized grains includes them, and they are stimulating increasing interest in many parts of the world (Gordon, 2006). Indeed there is considerable interest in the use of pseudocereals for the production of health foods and for special dietary purposes. The nutritional quality of pseudocereals is higher than that of most cereal grains, owing to their high protein (characterized by a balanced essential amino acid composition), mineral (minerals such as calcium, magnesium, iron, potassium, and zinc) and lipid content (characterized by a high content of unsaturated fatty acids) (Berghofer and Schoenlechner, 2007; Bodroza-Solarov *et al*., 2008; Oszvald *et al*., 2009; Alvarez-Jubete *et al*., 2010; Schoenlechner *et al*., 2010b). Lipid content in pseudocereals is two to three times that of cereals, they contain more than 75% unsaturated fatty acids and are particularly rich in oleic and linolenic acids (Bodroza-Solarov *et al*., 2008). Their unsaturated fat can be used to replace saturated and *trans* fat involved in atherogenic risk, which is very important from a nutritional point of view.

Plant proteins processed from cereal grains and legumes are valuable ingredients in a wide variety of commercial food products, pet foods, and animal feed. Examples of the

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plant proteins that are currently available are soy protein concentrate, isolated soy protein, wheat gluten, rice, and corn proteins. However, plant proteins are often deficient in essential amino acids. In the case of proteins of wheat, rice, and corn, they are deficient in lysine. Well processed, isolated soy proteins and soy protein concentrates have been found to be equivalent to animal protein with regard to the needs of human nutrition (Young, 1991), but they could be deficient in methionine and cysteine (Haard and Chism, 1996). As world food demand steadily grows, the production of protein has to be maximized. Plant proteins from cereals and legumes are the main source of proteins and energy for both human and animal nutrition. This is partly due to the fact that much more energy is required to produce animal proteins, and therefore they are more expensive to produce than plant proteins (Cheftel *et al*., 1985). Consequently, plant-derived proteins have excellent potential to replace animal-derived proteins in foods because they are much more sustainable. For the production of 1 kg of animal protein, 5 to 6 kg of plant proteins is needed. Soy, wheat, eggs, milk, peanut, tree nut, fish, and shellfish are good sources of animal or plant protein but they are involved in more than 90% of all food allergic reactions (Hefle *et al*., 1996).

Furthermore, pseudocereals are gluten free, making them suitable for people with coeliac disease, which has provided new opportunities for the production of high-quality, healthy, gluten-free products (Alvarez-Jubete *et al*., 2010; Schoenlechner *et al*., 2010b). Thus there are several ways of using pseudocereals, either as grain or as whole flour: consumption in the regions where they have traditionally been cultivated, the nutritional / functional product market, and development of gluten-free products.

Amaranth

Nowadays amaranth is recognized all over the world for its nutritional benefits and it can be used in the preparation of various types of products. Amaranth grain can be toasted, popped, extruded, or milled into flour, and therefore it can be consumed as it is, or included in other cereal products such as bread, rolls, cakes, muffins, pancakes, cookies, dumplings, crêpes, noodles, crackers, sweet and salted snacks, bars, or breakfast cereals (Léder, 2009; Sanz-Penella *et al*., 2013). Amaranth flour has traditionally been used in soups, porridges, and breads, whereas popped or toasted seeds have been used for producing snacks or bars. Amaranth milk is another product that can be made from this pseudocereal (Repo-Carrasco-Valencia, 2011). One of the most commercial uses of amaranth is for breakfast purposes.

Quinoa

Quinoa has a significant worldwide potential as a new cultivated crop species and as an imported commodity from South America (Jacobsen, 2003). In developing countries in Africa and Asia, quinoa can provide highly nutritious food under dry conditions (Jacobsen, 2003). Traditionally, quinoa has been used in a wide variety of foods. Whole seed is used in broths, soups, stews, and ricelike products. Flour is made into porridge and coarse bread. Quinoa can also be fermented to make beer called *chichi* (Taylor and Parker, 2002). The main uses of quinoa at present are for cooking, baking, animal feed, and processed food products such as bread, breakfast cereals, pasta, noodles, beverages, and cookies (Figure 8.1). In these products, quinoa is largely employed as a supplement to wheat, corn, and rice flours because of its high protein quality and nonallergenicity (Chauhan *et al*., 1992; Jacobsen, 2003). However, saponins in the seed coating give the bitter taste that is characteristic of quinoa, and it needs to be washed or

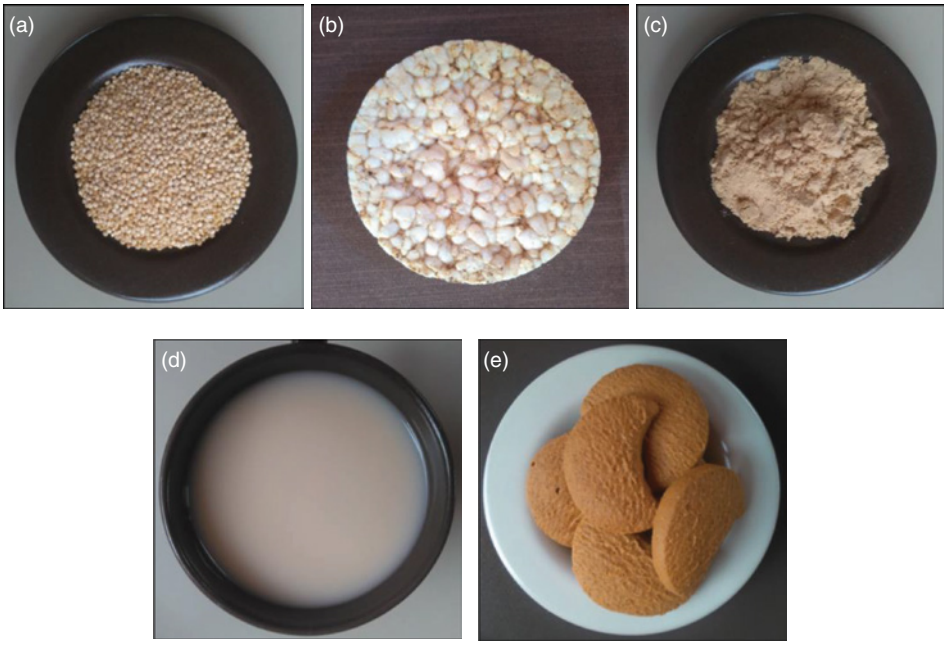

Figure 8.1 Commercial quinoa products (Spain): (a) quinoa seeds; (b) rice cakes with quinoa; (c) gelatinized quinoa powder for instant solubility; (d) rice and quinoa beverage; (e) gluten-free organic quinoa biscuits with cinnamon.

dehulled before consumption. Traditional uses of quinoa are as whole seeds in soups, salads, and casseroles, and it can also be used in several kinds of dessert. In addition, quinoa can be eaten as a rice substitute or used as an ingredient in the preparation of breakfast or infant cereals (Valencia-Chamorro, 2003).

Buckwheat

Buckwheat has regained its past importance owing to the gluten-free foods market, because of the potential that its healthy properties have for improving the nutritional and technological quality of products (Wronkowska *et al*., 2013).

Nowadays, the market offers various products, such as unpeeled buckwheat, peeled buckwheat, semolina, dark and light flour, pastas / noodles, mixtures for omelettes, pancakes, instant mash with rice, potato pancakes with buckwheat, puffed buckwheat, flakes, drinks, and tea. There is an assortment of bakery products such as bread, crispbread, and toast, confectionery products such as biscuits, cookies, and cakes, and special products for patients with coeliac disease (Dutta, 2004; Petr *et al*., 2004). The advantage of buckwheat is that it can be processed very similarly to wheat. Nowadays, buckwheat is also used in composite flour with wheat, rice, or maize flour, in various proportions, in the development of bakery products (Dutta, 2004; Petr *et al*., 2004). Common buckwheat is often used as an important functional food and is ground to make buckwheat noodles (Lin *et al*., 2009a). Husked kernels are cooked directly like rice. It is common to find various types of commercial buckwheat groats used to prepare a kind of porridge (*kasha*) in Central and Eastern Europe, and various commercial buckwheat flours, used to prepare bread and pasta (Figure 8.2).

Figure 8.2 (a) Three types of commercial buckwheat groats, raw and after hydrothermal processes used to prepare *kasha*; (b) three types of commercial buckwheat flours, raw and after hydrothermal processes used to prepare bread and pasta (Poland).

In general, pseudocereals can be added to food as supplements to provide beneficial health effects and prevent oxidation of food during processing. Bread is consumed all over the world, and many food ingredients have been included in bread formulations to increase the diversity, nutritional value, and product appeal of bakeries. In this regard, pseudocereals are an excellent alternative from a nutritional and functional point of view.

8.2 Bakery Products

Current cereal processing methods have been optimized to deliver products made from refined grains, but dietary recommendations emphasize the need to eat healthier, tastier, more suitable foods. Some researchers suggest including bran, whole cereal or pseudocereal flours, or mixtures of different grains to increase the nutritional value of products made from refined wheat flour (Marquart *et al.*, 2004; Sanz-Penella *et al.*, 2008; Miller Jones, 2009).

8.2.1 Bread

Bread is the most common cereal food. Bakery products made from refined flour are considered to be poor from a nutritional point of view. In general, white bread has a low dietary fibre and mineral content and should be supplemented to meet the daily requirements for various elements (Dyner *et al.*, 2007; Skrbic and Filipčev, 2008). The addition of other superior nutritional quality flours to wheat flour has therefore been common practice. The addition of pseudocereal whole flours, particularly in high amounts, results in technological challenges such as increases in dough yield, resulting in a moist

and shorter dough, decreased fermentation tolerance, lower volume, tense and nonelastic crumb, and various flavour changes, depending on pseudocereal and bread type, because of the fibre and the dilution of gluten (Sanz-Penella *et al.*, 2013; Poutanen *et al.*, 2014). A growing number of studies have investigated the use of pseudocereals in the production of nutrient-rich bakery products. It would be necessary to make modifications in traditional technological breadmaking procedures in order to allow the inclusion of high levels of pseudocereal seed in bread, which could enable the development of a range of new baking products with enhanced nutritive and sensory value (Demin *et al.*, 2013).

In particular, amaranth is the pseudocereal that has been most studied for breadmaking. Tosi *et al.* (2002) studied the feasibility of whole and defatted hyperproteic amaranth flours (maximum 12% replacement) as an alternative ingredient to supplement mould breads. The protein content of the bread increased significantly by 4.6 g/100 g at the maximum level of supplementation. Breads replaced at an 8% amaranth flour level did not show severe modifications in quality parameters, whereas defatted bread only allowed a replacement of 4%. In a later study (Bodroza-Solarov *et al.*, 2008), popped amaranth supplemented breads at 10, 15, and 20% levels were evaluated to test the effects on nutritional and sensory characteristics. The breads had significantly higher levels of minerals, proteins, dietary fibre, and squalene; however, loaf-specific volume decreased by up to 33%, negatively affecting crumb hardness and elasticity of the bread. The supplementation contributed to denser crumb structure, more uniform porosity, and greyish crumb colour, without adversely affecting the flavour and appearance of the breads studied (Bodroza-Solarov *et al.*, 2008). Amaranth has also been used in the preparation of traditional Brazilian bread made with cheese. This kind of bread has inherent low fibre and mineral content, but the addition of up to 20% of amaranth flour resulted in a product with higher dietary fibre and iron contents compared with the control bread (Lemos *et al.*, 2012).

The addition of amaranth in this study reduced the specific volume of the bread up to 1.5-fold, increased compression strength (from 34 N in the control to 240–265 N), leading to harder and darker breads than the controls, with significant differences in L and b colour parameters, which led to a significant difference in the total colour (ΔE_{ab}). Recently, Sanz-Penella *et al.* (2013) incorporated whole *Amaranthus cruentus* flour in wheat flour to a maximum of 40%. The use of amaranth in the formulation gradually and significantly increased protein, lipid, ash, and dietary fibre contents with regard to white bread. The substitution with amaranth flour in a proportion of 40 g/100 g increased the amount of Cu from 2.25 to 4.21 mg/g, Mn from 6.39 to 19.41 mg/g, Zn from 11.65 to 24.91 mg/g, Fe from 18.85 to 43.74 mg/g, Ca from 0.31 to 0.99 mg/g, Mg from 0.29 to 1.32 mg/g, and K from 1.88 to 3.21 mg/g, respectively. The contributions of mineral intake from bread to the dietary reference intakes (DRIs) given by the Food and Nutrition Board of the Institute of Medicine, National Academy of Sciences (NAS, 2014), were calculated taking into account the World Health Organization's recommendation of a daily intake of 250 g of bread per person. In terms of DRIs the control bread formulated with wheat flour contributed 38/38% (Cu), 43/54% (Mn), 16/22% (Zn), 36/16% (Fe), 4.7/4.7% (Ca), 11/14% (Mg), 28/28% (P) and 6.1/6.1% (K) of the amounts recommended for adults (males / females, respectively), whereas the breads incorporating amaranth (10–40% substitution) contributed significantly increased mineral intakes ranging from 43–70 / 43–70% (Cu), 65–126 / 83–160% (Mn), 22–34 / 30–46% (Zn), 43–81 / 19–36% (Fe), 7–15 / 7–15% (Ca), 19–47 / 25–61% (Mg), 39–65 / 39–65 (P), and

7–10 / 7–10% (K) (males / females, respectively) (Sanz-Penella *et al*., 2013). However, these values are overestimates owing to the presence of phytates, which inhibit mineral availability (Sanz-Penella *et al*., 2013). In this regard, García-Mantrana *et al*. (2014) investigated the inclusion of *Bifidobacterium* phytases during breadmaking, leading to phytate levels in breads with amaranth below the threshold of mineral bioavailability inhibition for Fe and Zn in human nutrition. The inclusion of whole amaranth flour also showed a slight tendency to decrease specific volume from 2.74 to 2.51 ml/g (for control bread and 40% amaranth bread, respectively) (Sanz-Penella *et al*., 2013). Crumb hardness was only affected in the sample with 40% substitution, whereas crumb structure showed no significant changes (Figure 8.3). Sanz-Ponce *et al*. (2009) also investigated the replacement of wheat flour by whole *Amaranthus hypochondriacus* (from Mexico) and whole *Amaranthus spinosus* (from India) flours up to a level of 50% (Figure 8.4). Loaf-specific volume decreased significantly when compared with the control sample (wheat bread), so a significant increase in crumb firmness was observed. Colour tristimulus values were significantly affected when the whole amaranth flour was used in both crumb and crust (Figure 8.4). Sensory analysis indicated that the inclusion of whole amaranth flour significantly decreased the acceptability for consumers. However, the bread made with *A. hypochondriacus* flour showed higher acceptability than bread made with *A. spinosus* flour (data not shown). Whole amaranth flour could be used as a wheat flour replacement in bread formulations, increasing the product's nutrition value, allowing an increase in dietary fibre, mineral, and protein levels with a significant slight depreciation in bread quality when incorporated at 50% replacement of wheat flour (Sanz-Ponce *et al*., 2009). Sanz-Penella *et al*. (2013) also carried out a sensory evaluation of bread formulated with whole *A. cruentus* flour.

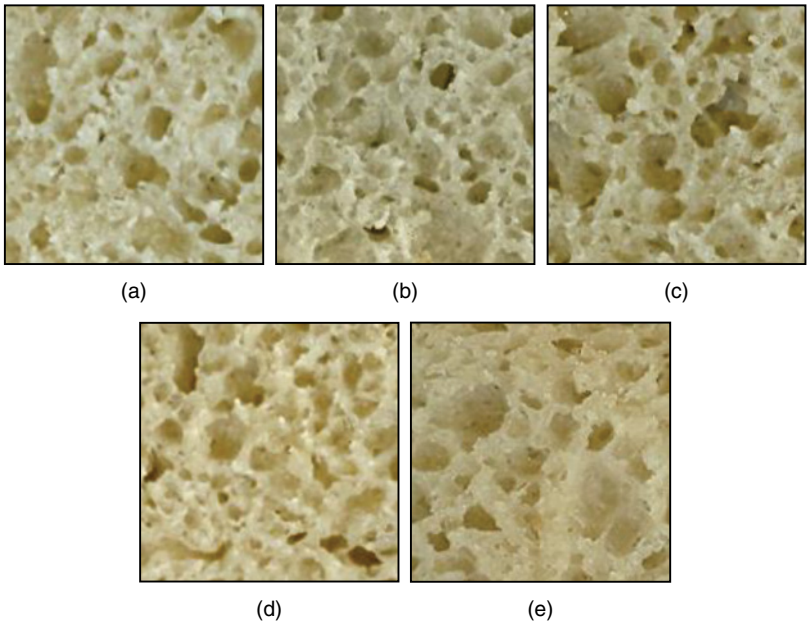

Figure 8.3 Effect of replacing wheat flour by whole amaranth flour (*A. cruentus*) on bread crumb structure: (a) 0%, (b) 10%, (c) 20%, (d) 30%, and (e) 40%.

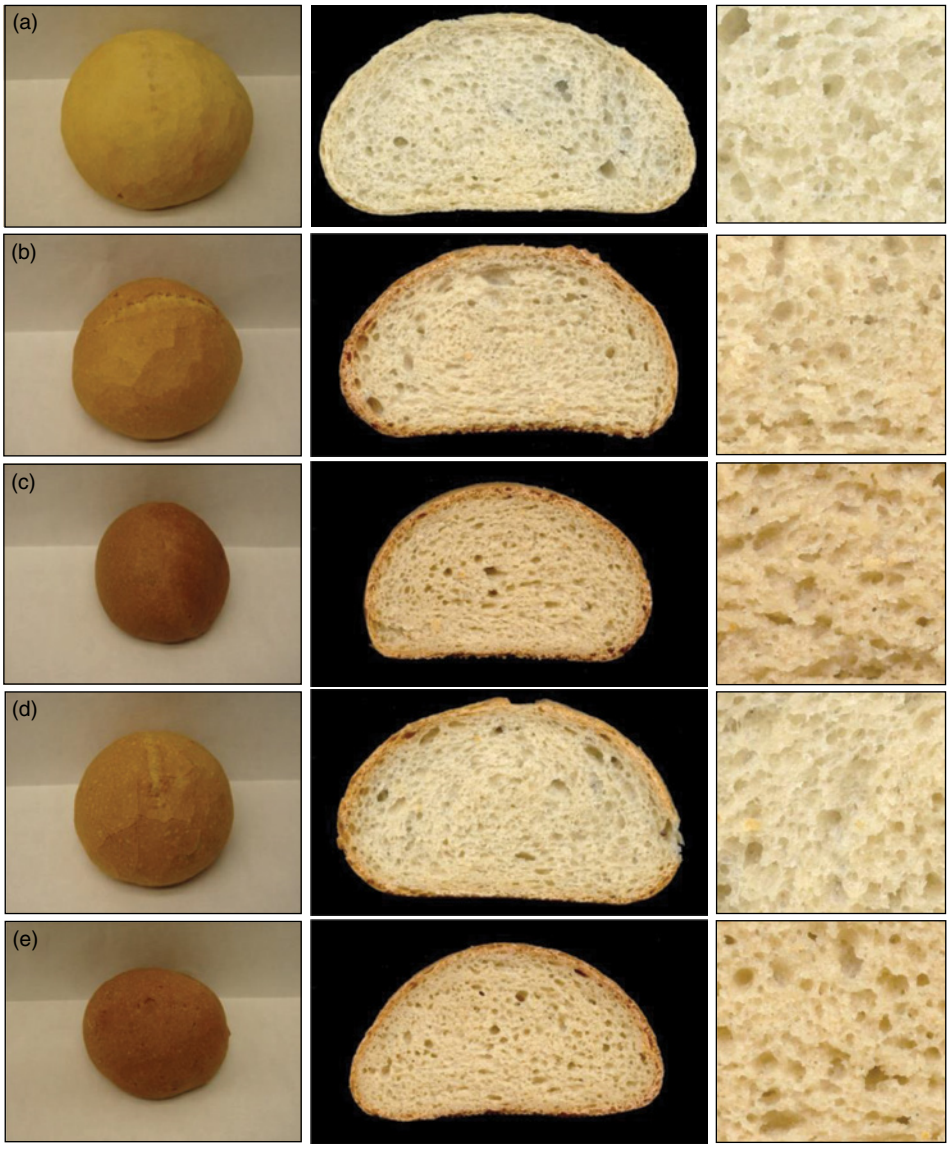

Figure 8.4 Effect of the inclusion of whole amaranth flour on loaf shape, central slice, and crumb structure. Bread formulations: (a) white bread; (b and c) Bread with 25 g and 50 g of *A. hypochondriacus* flour/100 g, respectively; (d and e) bread with 25 g and 50 g of *A. spinosus* flour/100 g.

Although bread made with amaranth did not achieve greater acceptability than wheat bread, particularly with a high percentage of substitution (40% replacement of wheat flour), the consumers concluded that preference for amaranth bread would be based on its more nutritious condition even though its taste and aroma were different from those of traditional bread. However, if the purpose of pseudocereal inclusion in breadmaking is to increase the amount and quality of protein, protein isolates could be preferred in order to avoid quality deterioration of the end product in comparison with baked goods made from wheat (Tömösközi *et al.*, 2011).

The use of amaranth as raw material for sourdough fermentation has also been investigated (Houben *et al.*, 2010; Jekle *et al.*, 2010). Amaranth is a suitable ingredient for fermentation of various species of *Lactobacillus*, and sourdough fermentation was able to produce doughs with viscosity and elasticity similar to those found in pure wheat flours (Houben *et al.*, 2010), although more balanced fermentation quotient values should be encouraged to improve the flavour of the bread (Jekle *et al.*, 2010). The impact of sourdough fermentation on the breadmaking performance of buckwheat flour was investigated by Moroni *et al.* (2011, 2012). Extensive hydrolysis of the globulin fraction and release of small polypeptides occurred upon fermentation and the buckwheat sourdough-induced inhibition of CO_2 production by baker's yeast during proofing (Moroni *et al.*, 2011). However, the properties of wheat bread were enhanced by the addition of 10% buckwheat sourdough, which led to higher specific volume and softer crumb. Fermentation positively influenced the nutritional properties in terms of polyphenols and phytate content (Moroni *et al.*, 2012). Quinoa was also investigated for the development of lactic ferment as an alternative biopreservative for packed bread because it is an optimal substrate for growth and production of improved amounts of antifungal compounds by *Lactobacillus plantarum* isolated from sourdough (phenyllactic and hydroxyphenyllactic acids), allowing a reduction in the quantity of the chemical preservative calcium propionate commonly added to bread (Dallagnol *et al.*, 2015). In another study, strains of *Lactobacillus plantarum* and *Lactococcus lactis* subsp. *lactis*, previously selected for biosynthesis of γ-aminobutyric acid (GABA), were used for sourdough fermentation of cereal, pseudocereal, and leguminous flours. In this study, chickpea, amaranth, quinoa, and buckwheat were the flours most suitable for enrichment with GABA, according to Coda *et al.* (2010).

Lorenz and Coulter (1991) studied the use of quinoa flour in baked products as an additive to wheat flour and concluded that addition of 5% to 10% was acceptable in breads, cakes, and cookies. Later, Morita *et al.* (2001) and Park *et al.* (2005) studied the characteristics of dough and bread containing quinoa flour and they concluded that a combination of quinoa flour and lipase addition to formulations improved bread quality. In another study, quinoa flour was blended into wheat flour at different weight ratios (85:15, 70:30, 55:45, 40:60, 25:75, and 10:90) to formulate composite flour for the production of cookies, bread, and Chinese steamed bread (Wang *et al.*, 2015). Compared with wheat products, the products resulting from quinoa wheat composite flour had reduced specific volume and increased density, hardness, and chewiness of the texture, darkness, redness, and yellowness. However, quinoa bread was well accepted, with an overall linking score of 5.8 (in an hedonic scale of 7 points), and showed a good commercial potential among consumers, with 85% of those interviewed stating that they would buy the product because they liked the bread taste and the benefits to their health (Calderelli *et al.*, 2010). In another study, sensory evaluation in a hedonic scale of breads made with whole quinoa flour at a 25% level of substitution (7.6) was not significantly different from the control sample (7.9). The consumers found the crumb denser and more compact in breads with 50% of quinoa (5.9) compared with the control sample, but they were still accepted by the consumers (Iglesias-Puig *et al.*, 2015, Figure 8.5). Whole quinoa flour could be a good replacement for wheat flour in bread formulations, increasing the product's nutritional value in terms of dietary fibre, minerals, proteins, and healthy fats, with only a small reduction in bread quality (Stikic *et al.*, 2012; Iglesias-Puig *et al.*, 2015). Bread containing 10% of quinoa or buckwheat flour gave similar sensory scores compared with the control (Bilgiçli and İbanoğlu, 2015).

Carreres-Rey *et al*. (2015) developed bakery products with 25% replacement of wheat by white, red, or black Real quinoa from Bolivia in order to evaluate its functionality as a breadmaking ingredient, with excellent results in the sensory evaluation (Figure 8.6). Similarly, bread produced with quinoa flour:buckwheat flour (50:50 w/w) replacing wheat flour at a 20% level gave good sensory quality values except for pore structure. It was reported that replacement of wheat flour by 25% kañiwa, *Chenopodium pallidicaule*, and 50% kiwicha, *Amaranthus caudatus*, still produced breads with good sensory acceptability but variable colour (Rosell *et al*., 2009).

The pseudocereals improved Fe, K, Mg, Mn, and Zn content of breads but all levels of quinoa or buckwheat flour significantly increased bread phytate contents (Bilgiçli and İbanoğlu, 2015; Iglesias-Puig *et al*., 2015). High phytate contents were easily avoided by

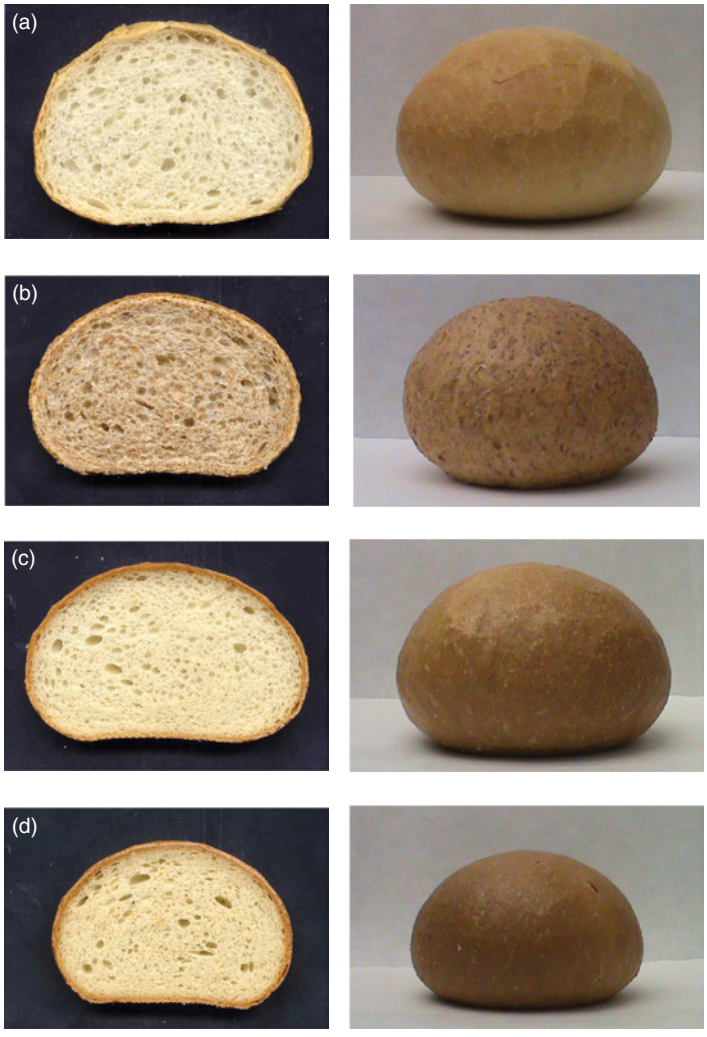

Figure 8.5 Effect of the inclusion of quinoa on loaf shape, central slice, and crumb structure. Bread formulations: (a) white bread; (b) whole wheat bread; (c) bread with 25 g of whole quinoa flour/100 g; (d) bread with 50 g of whole quinoa flour/100 g.

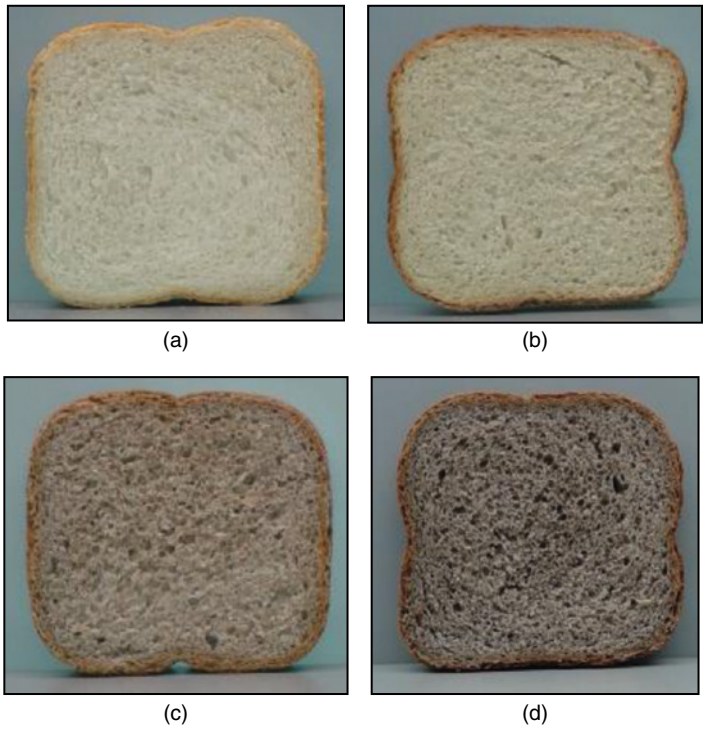

Figure 8.6 Effect of the inclusion of quinoa on crumb structure and color. Bread formulations: (a) white bread; (b) bread with 25 g of white quinoa flour/100 g; (c) bread with 25 g of red quinoa flour/100 g; (d) bread with 25 g of black quinoa flour/100 g.

the use of exogenous phytases from bifidobacteria (Iglesias-Puig *et al*., 2015). The use of flours from germinated seeds could also minimize phytate content in bakery products. Park and Morita (2005) studied the physical dough properties and baking quality of wheat flour with 10% replacement by nongerminated quinoa flour (control), or by quinoa flour germinated for 24, 48, or 72 h, and found that there were no significant differences between the sample with quinoa flour germinated for 24 h and the control. On the other hand, *Lactobacillus* strains could be used in the formulation of pseudocereal sourdough to obtain baked goods with improved nutritional quality and shelf life (Dallagnol *et al*., 2013). The use of sourdough or acidified sponges increases phytate hydrolysis (Reale *et al*., 2004; Sanz-Penella *et al*., 2012b).

According to Demin *et al*. (2013), who developed moulded breads with a mixture of quinoa and buckwheat seeds, their whole flours are valuable ingredients in the production of moulded bread, with improved nutritional characteristics and excellent sensory acceptance. The nutritional value of the supplemented breads was enhanced with regard to the amounts of minerals, proteins, fats, and fibre, and had excellent sensory characteristics, even at a 40% supplementation level (Demin *et al*., 2013). Milovanović *et al*. (2014) blended quinoa, buckwheat, and pumpkin seed kernels at a 40% level. The chemical composition of supplemented bread had increased quantities of protein, oil, and crude fibre in comparison with control wheat bread and sensory properties were similar to or higher than the control sample (Milovanović *et al*., 2014). The inclusion of buckwheat and quinoa in bread formulations could also be

exploited for their potential impact on eating behaviour / appetite control (Berti *et al*., 2005).

The use of buckwheat as a component of wheat bread is known and documented (Fujarczuk and Żmijewski, 2009; Lin *et al*., 2009b). There are many combinations / proportions of different flours / ingredients and also different traditional recipes and methods of preparation of bread with buckwheat. Some of them have been described above. Consequently, there is a wide spectrum of varieties, types, shapes, sizes and textures of breads. The flour is mixed with wheat or barley flour to make chapattis (Dutta, 2004). It is also used as sweet puddings to make *chillare*, an unleavened bread fried with butter or ghee and mixed with potatoes to prepare stuffed *parathas* (Dutta, 2004). Figure 8.7 shows two examples – the first one is a sourdough wholemeal bread supplemented with roasted buckwheat flour at a 13% level of substitution formulated on the basis of wheat and rye flour; the second one is a roll with milled hull from raw buckwheat at a 3% level of substitution. In general, buckwheat could be incorporated into bread to provide bread with more sugars, more total free amino acids, a stronger umami taste and a more characteristic aroma than white breads (Lin *et al*., 2009a). Yildiz and Bilgiçli (2012) studied the addition of whole buckwheat flour in Turkish flat bread (*lavas*) up to 30% without gluten and up to 40% with gluten. Its utilization improved the nutritional quality with the exception of an increase in phytates. Moreover, the darker colour and slightly bitter taste affected the sensory score of *lavas* bread negatively at a 40% substitution level; however, the overall acceptability values did not change significantly compared with the control sample (Yildiz and Bilgiçli, 2012). Whole buckwheat flour was used in leavened flat bread (*bazlama*) and unleavened flat bread (*yufka*) formulations to improve the nutritional status of flat breads (Yildiz and Bilgiçli, 2015). Taste and odour scores decreased above the 20% buckwheat level for *bazlama* and 30% level for *yufka* compared with control samples. It was also reported that buckwheat has potential for use in the design of foods with a lower glycaemic index (Skrabanja *et al*., 2001). The resistant starch level in bread products based on different proportions of buckwheat flour (30–70%) varied from 0.9% to 4.4%, and the rate of *in vitro* amylolysis was significantly lower ($p < 0.05$) in comparison with the reference white wheat bread (Skrabanja *et al*., 2001). The calculated glycaemic and insulinemic indices for the buckwheat bread were 66 and 74, respectively. Zhou *et al*. (2006) developed bread with tartary buckwheat flour with wheat flour in a weight proportion of 3 : 7. The authors found that the result of a test with diabetic mice indicated that buckwheat bread could help to restrain diabetes

Figure 8.7 (a) Sourdough wholemeal bread supplemented with roasted buckwheat flour (13%) formulated with wheat and rye flour; (b) roll with milled hull from raw buckwheat (3%).

to a certain degree and could reduce blood sugar level. Angioloni and Collar (2011) reported that the quality profiles of associated mixtures of oat, rye, buckwheat, and common wheat flours (20:20:20:40 w/w/w/w) were suitable for making highly nutritious baked goods meeting functional and sensory standards with lower digestible starch, and improved dietary fibre fractions, minerals, and antioxidant activity.

Whole pseudocereal grains are known to be rich in some bioactive compounds, such as flavonoids, phenolic acids, trace elements, fatty acids, and vitamins with known effects on human health (Dini *et al*., 2012). Some of them are almost unaltered after cooking and baking, as in the case of quinoa total phenolic content, total flavonoid content, and ferric-reducing ability of plasma antioxidant activity in the final product (Brend *et al*., 2012). However, the impact of the baking procedure on rutin, quercetin, and polyphenol concentrations was studied in bread formulations with tartary buckwheat (*Fagopyrum tataricum*). In this study the rutin concentration decreased during the bread-baking process and the concentration of quercetin remained stable, while a decrease in polyphenol concentration through baking was observed (Vogrinčič *et al*., 2010).

A blend of buckwheat, amaranth, chickpea, and quinoa flours (weight ratio 1:1:5.3:1) was selected and fermented with baker's yeast or with *Lactobacillus plantarum* sourdough and compared with wheat flour bread started with baker's yeast (Coda *et al*., 2010). The concentration of phenolic compounds and antioxidant activity was highest in the *Lactobacillus plantarum* sourdough bread, and the rate of *in vitro* starch hydrolysis was the lowest. Chlopicka *et al*. (2012) carried out a study to investigate the effect on the antioxidant properties of breads formulated with two different doses (15 and 30%) of buckwheat, amaranth and quinoa. The phenol content in the breads was highest (1.56-fold) in samples made from 30% of buckwheat, followed by the bread with the same dose of amaranth (1.54-fold), and the third highest result was for the bread with 30% addition of quinoa flour (1.49-fold). Breads formulated with 15% pseudocereals remained with a low total phenolic content similar to that found in the control bread, which ranged between 1.70 and 1.88 mg/g, except for the bread made with buckwheat flour (2.1 mg/g). The content of total flavonoids in quinoa and buckwheat flours was 1.31–2.19-fold higher than wheat flour, respectively. The flavonoids in amaranth flour did not show significant differences compared with wheat flour. So the results concerning total flavonoids in breads made with buckwheat, amaranth and quinoa (33.4 and 32.9 μg/g, 20.6 and 34.9 μg/g, 27.5 and 28.7 μg/g, for each pseudocereal flour at 15% and 30%, respectively) were always above the amount found for the control bread formulated with wheat flour (20.3 μg/g). The most effective in enhancing antioxidant activity was the addition of buckwheat flour at the higher dose, although the other pseudocereals (quinoa and amaranth) also showed a significant increase in this parameter in comparison with the control bread.

Pseudocereals have also been investigated as potential sources of folate (Schoenlechner *et al*., 2010a; Hager *et al*., 2012). Amaranth, quinoa, and buckwheat were compared with 14 varieties of different cereals (wheat, barley, oat, and rye). Pseudocereals showed higher total folate content, except for buckwheat, which was below the range for cereals. The total folate content in breads formulated with pseudocereals ranged between 26.1 and 41.1 μg/100 g. With these results the authors concluded that pseudocereals could be considered as substantial folate sources, contributing up to 14% of the daily folate intake requirement when a portion of 300 g of product was consumed (Schoenlechner *et al*., 2010a). Amaranth, quinoa, and buckwheat grains proved to be good sources of vitamin

E and could also be used as ingredients in breadmaking products for improving this vitamin (Alvarez-Jubete *et al.*, 2009).

8.2.2 Biscuits, Cookies and Cakes

Cookies / biscuits are other cereal products in the bakery industry in which efforts have been made to improve the composition of the product by the inclusion of pseudocereals. They are typically low in fibre, high in fat and sugar, with low levels of water and with air cells varying in size embedded within the protein–starch–lipid matrix (Brennan and Samyue, 2004; Poutanen *et al.*, 2014).

In order to develop functional biscuits with improved mineral content, bioavailability, and uptake, *in vitro* bioavailability in a Caco-2 cell culture system was used to assess Ca, Mg, and Fe bioavailability from different types of biscuits enriched with mixtures of pseudocereals and legumes with inulin (Vitali *et al.*, 2011). Polyphenols and dietary fibre were determined as the principal components impairing uptake of Fe and Ca. Enrichment of the reference recipe with a mixture of inulin with soy or amaranth flour positively influenced bioavailability / uptake of Ca, Mg, and Fe (Vitali *et al.*, 2011). Biscuits with a lower glycaemic index were developed by Vujic *et al.* (2014) as functional cereal-based products. Replacement of 30% white wheat flour with selected pseudocereals (buckwheat or amaranth flour) and legumes (soya or carob flour) resulted in a decrease of *in vitro* starch digestibility (significant decrease of rapidly available glucose and rapidly digestible starch), whereas a significant increase in the resistant starch content was achieved by the implementation of pseudocereals (Vujic *et al.*, 2014).

Microbiological stability, lysine evolution, and sensory evaluation of amaranth-based biscuits and crackers were investigated during storage under controlled conditions (Hozová *et al.*, 1997, 2000).

Amaranth-based products produced from grain irradiated by ionizing radiation provided maximum hygienic, nutritional and sensory quality, maintained up to the end of 1 year storage (Hozová *et al.*, 2000). Sensory evaluation of biscuits prepared with whole meal barley or wheat flour supplemented with amaranth showed that addition at 20% and 30% levels to barley and wheat flour, respectively, gave the best colour, and at levels of 10–20% gave the best biscuit taste (Sandak and El-Hofi, 2000).

Cakes and biscuits supplemented with linseed meal, amaranth and / or buckwheat flours enhanced their final nutritional quality in terms of protein content and dietary fibre, macroelements and microelements (K, P, Mg, Ca, Fe, Mn, Zn, and Cu), as compared with the controls. In addition, taking into account the amino acid composition, it was reported that amaranth proved a more beneficial supplement for gluten-free products than linseed (Gambús *et al.*, 2009). Dias-Capriles *et al.* (2008) found that the sum of wheat flour and corn starch could be successfully replaced by up to 20% amaranth flour in conventional and up to 30% in reduced fat (around 33% reduction) pound cakes without negatively affecting sensory quality in fresh cakes.

Sindhuja *et al.* (2005) produced sugar snap cookies with amaranth–wheat flour blends to study their technological quality. Blends were prepared by replacing wheat at different levels of substitution by amaranth (5–35%). The incorporation of amaranth flour improved cookie surface cracking as a consequence of the reduction of cookie breaking strength. As a result of increasing the percentage of amaranth in the formulation an increase in thickness was also observed (Sindhuja *et al.*, 2005). The sensory evaluation revealed that cookies containing 25% of amaranth scored the best marks

owing to their golden brown colour, larger size and island uniformity, malty-sweet flavour, and tenderness.

Yamsaengsung *et al.* (2012) compared the addition of chickpea to amaranth and buckwheat cookies with counterparts made with whole wheat flour. The addition of chickpea revealed an improvement in the acceptability of the cookies, particularly for the recipes in which amaranth and buckwheat were included. Nidhi and Indira (2012) developed chapatti, biscuits, and puttu with amaranth. This study highlighted the significance of value-added products made from grain amaranth as a solution to problems related to malnutrition in India. Biscuits have also been developed with amaranth, bhagar and sago, prepared in a proportion of 80:12:8, respectively, proving highly acceptable (Zanwar and Pawar, 2015).

Quinoa flour was also blended into wheat flour at different weight ratios to formulate composite flour for the production of cookies, providing products with various technological and sensory characteristics (Wang *et al.*, 2015). However, cookie antioxidant activity was increased by the addition of quinoa flour and the peroxide value was lower after storage at room temperature (Watanabe *et al.*, 2014). So cookies containing quinoa flour had greater oxidative stability and nutritional quality and were rich in dietary fibre, essential amino acids, linolenic acid, and minerals, with good sensory acceptability (Pagamunici *et al.*, 2014; Watanabe *et al.*, 2014; Brito *et al.*, 2015). The performance of quinoa–wheat flour blends was also evaluated in cakes and cookies (Lorenz and Coulter, 1991). Cake quality was acceptable with 5–10% of quinoa flour, taste improved and cake grain became more open and the texture less silky as the level of quinoa substitution increased. On the other hand, cookie spread and top grain scores decreased with increasing levels of quinoa flour blended with high-spread cookie flour. Flavour improved with incorporation of up to 20% quinoa flour in the blend, whereas cookie spread and appearance were improved with a quinoa / low-spread flour blend by using 2% lecithin (Lorenz and Coulter, 1991). It has also been reported that quinoa flour is an acceptable replacement for flour in the preparation of peanut-butter cookies (Harra *et al.*, 2011). Unroasted quinoa seems to obtain higher sensory scores for appearance, colour, and texture than roasted quinoa in the preparation of cakes (Rothschild *et al.*, 2015). The overall performance of quinoa starch in baked goods was similar to that of other noncereal starches, such as amaranth and potato starch, and cakes baked with quinoa starches were of poor quality (Lorenz *et al.*, 1995).

The possibility of using quinoa fermented with *Rhizopus oligosporus*, known as quinoa-tempeh or Q-tempeh, as an ingredient for preparing soft and hard biscuits (Matsuo, 2006) was examined. The absorption of iron from Q-tempeh powder was found to be higher than that of quinoa powder in rats because of partial hydrolysis of phytates. Therefore Q-tempeh powder is more suitable than quinoa powder as an ingredient of biscuits and it may be added to flour in amounts of up to 20% according to the biscuit quality and sensory analysis.

In order to improve the nutritive profile and functionality of ginger nut biscuits (popular traditional biscuits with honey), a standard formulation based on wheat flour was replaced with buckwheat flour (Filipčev *et al.*, 2011a). Doughs with buckwheat were significantly harder and less sticky. The biscuits enriched with buckwheat had increased spread, hardness and fracturability. The opposite behaviour was found by Baljeet *et al.* (2010), who reported that, as the concentration of buckwheat flour increased, the spread ratio and fracture strength of biscuits decreased. Spread ratio and hardness values were also significantly affected by flour combinations (buckwheat flour with rice

and corn flour at different levels) in gluten-free cookie formulations (Altõnda *et al*., 2015). However, addition of transglutaminase resulted in increased spread ratio and fracturability but decreased hardness values (Altõnda *et al*., 2015).

No significant differences in sensory tests were obtained among biscuits tested by Filipčev *et al*. (2011a, 2011b), whereas other studies found that with an increase in the level of buckwheat flour in the formulation the sensory scores for texture, appearance, and flavour of cookies decreased (Baljeet *et al*., 2010; Chopra *et al*., 2014). Substitution with buckwheat flour resulted in a significant increase in protein, Zn, Fe, Mn, Cu, total polyphenols and antioxidative and chelating activity (Filipčev *et al*., 2011a; Vranac *et al*., 2013; Altõnda *et al*., 2015; Bhavsar *et al*., 2015; Jan *et al*., 2015). In addition, negligible degradation of rutin to quercetin occurs during the phase of dough preparation and the baking process, so most of the rutin present in whole buckwheat flour can be recovered in biscuits (Brunori *et al*., 2009).

Crackers made from buckwheat flours (refined and wholegrain) were also significantly higher in total phenolic content than wheat crackers, with high concentrations of tocopherols (present in the following order: α->> β-> δ-tocopherols). Consequently, buckwheat crackers were superior in scavenging activity on 1,1-diphenyl-2-picrylhydrazyl radicals in comparison with wheat crackers (Sedej *et al*., 2011). Cracker sensory quality showed that buckwheat flours may be used in gluten-free cracker formulations without adversely affecting sensory properties (Sedej *et al*., 2011). According to Pandey *et al*. (2015), biscuits developed from husked buckwheat flour were found to be more acceptable than those made with dehusked flour. In addition, hydrothermal treatment of buckwheat had a beneficial effect on nutrient composition (in terms of crude lipid, fibre, and ash) and techno-functional properties (swelling power and solubility) of flour, with dehusked flour being nutritionally richer than husked flour (Pandey *et al*., 2015). In general, the addition of low amounts of pseudocereals to wheat flour does not significantly impair rheological properties of bakery dough or overall quality of final products but provides bakery products with enhanced nutritional and functional value.

8.2.3 Others

There are many homemade products and commercial additional bakery products that use pseudocereals (with or without gluten), such as pastries, pretzels, muffins, croissants, pies, fritters, pancakes, waffles and crêpes, among others.

Muffins are prepared with various amounts of buckwheat powder (0–50%), and the specific gravity is not affected by the addition of buckwheat powder up to 30%. No significant differences were observed in muffins containing buckwheat with regard to baking loss rate, specific volume, cohesiveness, springiness, and gumminess, whereas hardness decreased. In sensory evaluation, the score for colour decreased with increasing buckwheat amounts, whereas differences in grain, flavour, taste, texture, and overall acceptances were insignificant between formulations (Bae and Jung, 2013). The incorporation of amaranth protein isolates enhanced batter viscoelasticity and resulted in muffins with higher specific volume, springiness, and cohesiveness. Amaranth protein isolates can be used successfully to prepare gluten-free muffins with characteristics comparable to those made from wheat gluten (Shevkani and Singh, 2014).

Buckwheat was also included in recipes for pancakes. A coarse cereal leavened pancake comprising wheat flour, maize meal, soybean meal, millet flour, rice flour and pulverized vegetable, fruit, melon, dried fruit, and / or flower was developed by Wang (2009).

Leng and Shi (2006) also developed pancakes using buckwheat and various grains (millet, soybean, wheat, mung bean) with several flavouring materials, such as fennel fruit, star anise, xanthoxylum and coriander seed, with good taste and high nutritive value. Kwon (2003) developed a buckwheat pancake method that starts by soaking buckwheat in water, maturing, pulverizing with water, extracting buckwheat syrup, filtering the extract, and mixing with *kimchi* (traditional Korean food made from vegetables) and Welsh onion in boiling water. The final composition of the buckwheat pancake comprises 80% of buckwheat suspension, 17% of *kimchi*, and 3% of Welsh onion. Recipes and methods for making waffles with roasted amaranth flour or whole amaranth flour and desiccated milk, melted cocoa oil, milk butter, sweetener and wafer crumb were developed (Shmalko *et al*., 2006). A method that uses buckwheat flour, high gluten flour, glutelin powder and full egg liquid as ingredients to make candied fritters that are healthy and tasty, and that are moderately crisp and soft and have a long shelf life was described by Deng (2005).

8.3 Snacks and Breakfast Cereals

The extrusion cooking process is based on starch gelatinization and protein denaturation, combining high pressure and high temperature. This methodology is ideal for manufacturing snacks and breakfast cereals. The use of pseudocereals in products of this type is focused on obtaining healthier and more nutritious food, particularly for patients with coeliac disease. In this regard, Guerra-Matías and Areas (2005) investigated starch digestibility in an extruded product formulated with amaranth. The glycaemic index and insulinemic response were determined in healthy women. The results indicated high glycaemic response with fast digestibility in the amaranth snack and white bread (as control), whereas the snack showed a greater capacity for stimulating insulin release than the control. According to Chavez-Jauregui *et al*. (2009) it is possible to produce acceptable snack food made with pure amaranth flour or amaranth blended with corn or chickpeas. Under conditions that induced the maximum snack expansion ratio, extrusion produced a highly acceptable product based on amaranth flour. Dogan and Karwe (2003) optimized the extrusion of quinoa flour. They demonstrated that quinoa can be used in novel, healthy, snack-type food products. Because of its high lipid and low amylose contents, extrusion cooking requires very high shear to disrupt the quinoa starch granules. Quinoa was also blended with corn grits at different levels (10%, 20%, and 30%) and extruded at 15% and 25% moisture (Lorenz *et al*., 1995). Its addition produced a darker, less yellow product than corn grits alone. The density and expansion ratio were lower for products containing greater levels of quinoa and the most favourable products were produced at 15% initial moisture content and a 3:1 compression ratio of the extruder screws. On the other hand, Ramos-Diaz *et al*. (2013) proved that it was possible to increase the expansion index by adding amaranth, quinoa and kañiwa to pure corn flour in extruded snacks, which showed remarkable stability after exposure to high relative humidity. The use of amaranth or buckwheat flours in the preparation of extruded breakfast cereals altered some of the physical quality characteristics, such as product density and bulk density, without reducing the degree of expansion (Brennan *et al*., 2012). In addition, the products resulted in a reduction in readily digestible carbohydrates released from the extruded breakfast cereals compared with control samples (Brennan *et al*., 2012). The use of buckwheat flour in extruded snacks and

ready-to-eat breakfast cereal products (with wheat flour or corn meal and with nonfat milk) offers a desirable variation in flavour and can take advantage of the nutritional quality of buckwheat. It has been suggested that expansion index is the most important indicator of overall buckwheat-containing extrudate quality (Rayas-Duarte *et al*., 1998).

8.4 Beverages / Drinks

In the literature there are recipes and methodologies for producing various types of beverages from amaranth seeds or flour, roasted or extruded, such as beer or milk. Teas made with various mixtures of leaves, flowers, or heads of amaranth are also described.

Quinoa is used to prepare gluten-free beer or milk. Dezelak *et al*. (2014) analysed the brewing attributes of quinoa in comparison with barley, reporting that it had lower malt extracts, longer saccharification times, and higher total protein and fermentable amino nitrogen contents. The quinoa beer contained some distinctive volatile substances not found in barley beer and had many unique properties. Pineli *et al*. (2015) reported that quinoa milk provides a novel alternative to current milk-substitute products that cause no known adverse effects in humans and that have increased protein content and a low glycaemic index. The effect of supplementing fermented milk with quinoa flour was also investigated and no increase in probiotic activity was found during fermented milk production and storage (Casarotti *et al*., 2014). However, its incorporation in fermented milk can be recommended because of its high nutritive and functional value, which may increase the appeal of the product to consumers.

In recent years, buckwheat has also been used as a substitute for other grains in the manufacture of gluten-free beer. It can be used in the same way as barley to produce malt. According to Dezelak *et al*. (2014), buckwheat beer appears quite similar to barley beer. The fermentable carbohydrate content in wort and the volatile compound content commonly associated with beer aroma were comparable in the barley and buckwheat beverages. Sensory analysis indicated that buckwheat beer was acceptable with regard to odour, purity of taste, mouthfeel, tingling, and bitterness, with commonly encountered levels of the esters that give beer a fruity character (Nic Phiarais *et al*., 2010). Buckwheat malt can also be used for preparing whiskey after distilling and aging in oak casks. There are other drinks made with buckwheat, such as country liquor, which is prepared from buckwheat grains by tribal people residing in remote high-altitude areas in India (Dutta, 2004), or *shōchū*, which is a distilled beverage made from buckwheat (or barley, potatoes, or rice) in Japan (stronger than wine or sake, but weaker than vodka or whiskey).

Mixes of buckwheat flour and oat bran were investigated as prebiotics in the production of probiotic fibre-enriched fermented milks (Coman *et al*., 2013). Lee and Park (2013) varied the concentrations of buckwheat saccharification solution added to milk, followed by fermentation with commercially available mixed strains of lactic acid bacteria. They observed that undesirable compounds, such as acetic acid and 2-butanone, decreased as the buckwheat solution concentration increased, so the flavour quality of plain yogurt improved by adding buckwheat (Lee and Park, 2013). Tartary buckwheat sprout was also mixed with mung beans, black rice, and skimmed milk with sweeteners to develop a yogurt with health-promoting properties (Wang *et al*., 2013). Buckwheat tea is a popular health product in Asian and European countries, made from flowers, leaves or hulls (Giménez-Bastida *et al*., 2015). In China it is common to find buckwheat

tea. It is produced by soaking, steaming, dehulling, and baking buckwheat seeds. The final buckwheat tea product is in granule form, with an attractive yellowish colour and pleasant baked flavour (Qin *et al*., 2014).

8.5 The Most Popular Traditional Foods

Amaranth and quinoa were important food crops in the Aztec, Mayan, and Incan civilizations in the past. These crops have a long history of safe use by local populations and have contributed to the nutrition and wellbeing of people for centuries (Repo-Carrasco-Valencia *et al*., 2010). Aztecs used amaranth in beverages and sauces, or for a type of tortilla. Popped or ground amaranth was often mixed with honey or other sweet, sticky plant materials and then shaped into a variety of figures and shapes that were used in celebrations and religious ceremonies. The most common commercial use of amaranth in Mexico and Peru is as a snack (*alegrias* in Mexico; *turrones* in Peru) made by mixing the popped seeds with molasses (Early, 1990). Nowadays, commercial amaranth honey poppies and amaranth bars are typical snacks in these countries (Figures 8.8 and 8.9, respectively). Amaranth flour (*pinole* in Mexico; *mash'ka* in Peru), made by grinding the popped seeds on a grinding stone, is the next most common use. Less frequently, in Mexico, tamales are also made with the flour (Early, 1990). In Bolivia, quinoa flour is used frequently to prepare coarse bread called *kispiña* (Lorenz and Coulter, 1991). Ash from the stalk is used for soaking maize and making *tokra* balls, which are gnawed on when chewing coca leaves. The fermented beverage made from amaranth, quinoa, or corn seeds is called *chicha* (Early, 1990). The boiled red flowers of amaranth are also used to colour *chicha*. In Ecuador, they boil the flowers and add the coloured water to *aquardiente* rum to 'purify the blood'. It is also used by women, who claim it helps to regulate irregular menstrual cycles (Early, 1990).

On the other hand, buckwheat was domesticated and cultivated in inland southeast Asia around 6000 years before the Christian era and spread from there to central Asia and Tibet and then to the Middle East and Europe. In Japan, Korea, and China, buckwheat flour is used for making soba noodles from 100% buckwheat or a mixture with wheat flour. Today buckwheat is used commonly as an important functional food and the traditional Asiatic dish of buckwheat noodles is very popular and well known

Figure 8.8 Commercial amaranth honey poppies (Mexico).

Figure 8.9 Commercial amaranth bars (Mexico).

throughout the world (Figure 8.10). In Central and Eastern Europe, especially Poland, Russia, and Ukraine, *kasha* is one of the oldest known dishes, made with any kind of grains (buckwheat, wheat, barley, oats, millet, or rye) boiled in water or milk as a type of porridge but generally with roasted whole-grain buckwheat or buckwheat groats (Figure 8.2) (Marshall and Pomeranz, 1982). In Italy there are *pizzoccheri*, short, flat ribbon noodles made with buckwheat and wheat flour, and France is known for its traditional buckwheat pancakes (crêpes). In India, buckwheat pancakes called *kuttu ki puri* and *kuttu pakoras* (potato slices dipped in buckwheat flour and deep-fried in oil) are also famous.

8.6 Pasta Products

Pasta products of various types are becoming increasingly popular worldwide because of their convenience, nutritional quality, and palatability. Traditional Italian pasta is made with semolina flour, which is milled from durum wheat. Pseudocereals have also been proposed as an alternative source to increase the nutritional and functional quality of pasta, as in the case of bakery products. The production of pasta by blending various cereals / beans with pseudocereals has been studied and there are countless recipes of gluten-free or non-gluten-free products such as noodles, macaroni and spaghetti, among others. One example is the work of Rayas-Duarte *et al*. (1996), who used light and dark buckwheat, amaranth and lupin flours as substitutes for durum wheat flours at 5, 15, 25, and 30% levels to produce multigrain pasta. Their results showed that multigrain spaghetti can be produced with higher levels of lysine than commercial pasta made of 100% durum wheat flour, and also with acceptable cooking quality and sensory attributes. Choi (2011) reported that sensory evaluation of cooked noodles with amaranth scored higher values than those of the control (wheat flour), and amaranth added at a concentration of up to 30% increased the brown colour and the peculiar amaranth odour. A texture profile analysis of raw noodles showed significantly higher levels of hardness, cohesiveness,

Figure 8.10 Commercial buckwheat noodles (Spain).

gumminess, chewiness and springiness in amaranth noodles compared with those in the control sample. Lorenz *et al.* (1993) added quinoa to pasta products, using various ratios of durum semolina and quinoa flour. However, the noodles made with quinoa were inferior in colour, flavour, texture and overall acceptability compared with noodles prepared only from durum semolina. Schoenlechner *et al.* (2010b) investigated the possibility of producing amaranth, quinoa, and buckwheat pasta with good textural quality. The inclusion of amaranth in the formulation of pasta reduced the texture firmness and cooking time. However, the use of quinoa showed the opposite trend with respect to cooking time. Minor adverse effects on the functional properties of pasta were obtained with samples formulated with buckwheat. With the help of an experimental design the authors succeeded in combining amaranth, quinoa, and buckwheat (20 : 20 : 60) in an advantageous formulation in which negative effects were minimized.

8.7 Infant Food

Quinoa is the pseudocereal most used for infant food. An infant food product was manufactured by drum-drying quinoa flour slurry by Ruales *et al.* (2002). It was shown that the product was a potential source of valuable nutrients such as protein, vitamin E, thiamine, iron, zinc and magnesium for preschool children. Cerezal-Mezquita *et al.* (2012) also developed a beverage with a high protein content for the diet of preschoolers by using a mix of Chilean mesquite, lupin and quinoa. Repo-Carrasco *et al.* (2003) reported that quinoa and kañiwa can be used in weaning food mixtures. They formulated two dietary mixtures, quinoa–kañiwa–beans and quinoa–kiwicha–beans, both with high nutritional value. The mixtures had protein efficiency ratio (PER) values close to that of casein (2.5): 2.36 and 2.59, respectively. Cook *et al.* (1997) evaluated the absorption of iron contained in, or added to, dry cereals used for infant feeding (wheat, corn, rice, millet, oat, and quinoa). They concluded that the type of cereal grain has little influence on iron bioavailability of infant cereals with the exception of high

absorption in corn and modestly low absorption in quinoa, probably because of its high levels of phytates.

8.8 Others

Quinoa has been considered as a potential crop for NASA's Controlled Ecological Life Support System (CELSS). The CELSS concept will use plants to remove carbon dioxide from the atmosphere, thereby generating food, oxygen and water for crews on long-term human space missions. Quinoa was selected for its high productivity and desirable nutritional characteristics. Generally, CELSS has had to combine the nutritional values of several crops to obtain the right amino acid balance but quinoa seems to supply it on its own (Schlick and Bubenheim, 1996). NASA feeds quinoa to crews on long space missions because it is a nutritious, healthy, easily grown food (TWB, 2014).

Another curious use of pseudocereals is the manufacture of biopolymers for the development of edible and / or biodegradable films. This could be an alternative way of increasing their applications and creating new markets as well as substituting nondegradable synthetic plastic in pharmaceutical and food applications (Tapia-Blácido *et al*., 2007). Polysaccharides, proteins, and lipids, or combinations of them, have been used to prepare edible films. In this connection, amaranth protein–lipid and protein films were made and compared with amaranth flour films in order to determine the contribution of the interactions between the biopolymer (starch and protein) and lipids to the film properties (Tapia-Blácido *et al*., 2007). The nonseparation of the lipid phase of the flour film matrix contributed to good plasticization and to the excellent barrier properties of the amaranth flour films.

8.9 Conclusion

Pseudocereals are recognized as potential nutritious food sources with functional properties because of their high content and quality of proteins, minerals, vitamins, and bioactive compounds such as dietary fibre, polyunsaturated fatty acids and antioxidants such as phenolic compounds. They can be included to develop new functional food and health products, one of the most attractive trends for the modern food industry. In addition, their versatility allows them to be applied in a wide spectrum of foods similar to cereals, such as bread, biscuits / cookies, cakes, pancakes, snacks, breakfast cereal, infant food, pasta, beverages / drinks, teas, and yogurts, among others. Lastly, because they are gluten-free, pseudocereals are particularly suitable for incorporation in the diet of coeliac disease patients. Moreover, as pseudocereals do not have special agronomic requirements and can be grown by simple methods, they are potential nutritional sources for the fight against world hunger.

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9

Pseudocereals in Gluten-Free Products

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9.1 Introduction

The demand for gluten-free products has increased worldwide due to the increased prevalence of gluten-related disorders like coeliac disease or gluten sensitivity. Gluten-free foods are also consumed by many who are not affected by any of these disorders but still consider gluten-free food to be healthier. The supply of gluten-free products has increased immensely in the last few years. Today a huge variety of new gluten-free products is available on the market. Due to much ongoing research, and links with science and innovation, the quality and nutritional value of these products are gradually improving (Gallagher, 2013).

All pseudocereals contain a low amount of prolamins (Aubrecht *et al*., 1998) and do not contain protein fractions that are toxic to coeliac disease patients, although studies were only recently undertaken to prove this fact. Bergamo *et al*. carried out an immunological evaluation of the alcohol-soluble protein fraction from amaranth and quinoa. They examined the grains in intestinal T-cell lines from CD patients and transgenic mice and did not detect any immune crossreactivity toward wheat gliadin. Peñas *et al*. (2014) provided biochemical and immunochemical evidence supporting the inclusion of quinoa in the gluten-free diet. They characterized several quinoa varieties by electrophoresis and immunoblotting techniques and found no protein bands that were comparable to wheat gliadins, the toxic protein for coeliac disease persons. Ballabio *et al*. (2011) performed a similar study on 40 amaranth varieties. By application of electrophoresis, immunoblotting methods and enzyme-linked immunosorbent assay (ELISA) it was proven that the content of glutenlike proteins was blow 20 ppm. Thus it was suggested that the pseudocereals are safe for coeliac disease patients and they are suitable to be consumed within the gluten-free diet. Another advantage is their high nutritional value, which allows the quality of gluten-free products to be increased.

In recent years research on gluten-free processing has increased immensely, and efforts have also been undertaken on the use of amaranth, quinoa or buckwheat for diverse gluten-free products. These research studies will be described in this chapter, after a short introduction to the gluten-related disorders, the gluten-free diet and gluten-free processing in general.

Pseudocereals: Chemistry and Technology, First Edition. Edited by Claudia Monika Haros and Regine Schoenlechner.

9.1.1 Gluten-Related Disorders – Coeliac Disease and Gluten Sensitivity

Coeliac disease has reached special attention in recent years. Until the mid-1990s coeliac disease was considered extremely rare and therefore was almost completely ignored by healthcare professionals. In only 10 years coeliac disease has moved from obscurity into the popular spotlight worldwide (Sapone *et al*., 2012). Figures for the prevalence of coeliac disease (in particular in northern countries) are steadily increasing. Its mean prevalence is estimated to be 1–2% of the world population (Reilly and Green, 2012). One of the countries with the highest stated prevalence for coeliac disease is the United States, where 1% of the population, or about 3 million people, suffer from coeliac disease (Broz and Horne, 2007). In Europe the figures are not much different. Based on serological diagnosis the prevalence for coeliac disease ranges from 1 : 50 to 1 : 100 in Sweden (Carlsson *et al*., 2001) or 1 : 180 in Italy (Volta *et al*., 2001). Along with coeliac disease, other conditions related to the digestion of gluten have emerged as healthcare concerns. There are three main forms of gluten reactions: allergic (wheat allergy), autoimmune (coeliac disease, *dermatitis herpetiformis* and gluten ataxia) and possibly immune-mediated (gluten sensitivity) (Sapone *et al*., 2012).

Wheat allergy is defined as an adverse immunologic reaction to wheat proteins and is triggered by repeat sequences in gluten peptides, which cause an immune reaction. Ig E antibodies play a central role in the pathogenesis of wheat allergy diseases. Its prevalence worldwide is considered to be below 1% (Sapone *et al*., 2012). Persons suffering from wheat allergy have to exclude wheat from their diet but can include all other cereals.

Coeliac disease is a multisystemic autoimmune disease marked by a dysregulated immune response to tissue transglutaminase (tTG). Coeliac disease is strongly associated with specific human leukocyte antigen (HLA) class II genes, HLQ-DQ2 and HLQ-D8. Only people who are HLQ-DQ2 and / or HLQ-D8 positive can develop coeliac disease. Coeliac disease causes small intestinal mucosal injury classified into different stages of severity. These symptoms of coeliac disease are triggered by gluten, a protein complex in wheat with equivalent toxic proteins found in other cereals, in particular rye and barley. The only effective treatment of these symptoms is a strict exclusion of gluten from the diet. Achieving mucosal healing is essential, because persistent villous atrophy appears to increase the risk of long-term complications including osteoporosis, autoimmune disease and malignancy (Catassi and Yachha, 2009; Sapone *et al*., 2012).

Another gluten disorder has recently been recognized, where neither allergic nor autoimmune mechanisms are involved. These are generally defined as gluten sensitivity (Nejad *et al*., 2012). People affected by gluten sensitivity suffer from gastroenterological symptoms similar to coeliac disease but, unlike in coeliac disease, mucosal damage in the small intestine does not occur and it is not accompanied by the occurrence of tTG antibodies. Diagnosis of this disorder is not easy, because currently there are no specific biomarkers for gluten sensitivity. Prevalence of gluten sensitivity is estimated to be up to 7% of total population (Nejad *et al*., 2012). To treat this disorder, again gluten has to be removed from the diet but it is yet not fully clear if and to what level traces of gluten can be tolerated.

Gluten-related disorders can only be treated by a lifelong gluten-free diet. The term 'gluten' comprises endosperm storage protein fractions, namely prolamin and glutelin, of specific cereal species (wheat, rye, barley, and eventually oats). Their toxic effect is not even minimized by denaturation or enzymatic hydrolysis to peptides (Urban, 2007).

Therefore, people suffering from coeliac disease cannot consume any of the above cereals or products made from them. Theoretically, an alternative exists, which is, however, much more difficult to realize – this involves removing these fractions from the raw materials or enzymatically hydrolysing them to their amino acids, thus enabling consumption by coeliacs.

9.2 The Gluten-Free Diet and General Aspects of Gluten-Free Processing

As mentioned above, people suffering from coeliac disease or gluten sensitivity have to eliminate gluten strictly from their diet. Gluten or the epitopes triggering these disorders are found in all *Triticum* species (wheat and all related species like spelt wheat, einkorn wheat, emmer, khorrassan wheat, durum wheat), rye, barley, triticale and oat. A gluten-free diet has to exclude all these species. Remaining cereal species that are currently considered to be safe for coeliac disease patients are rice, maize, millet and sorghum. Pseudocereals (amaranth, quinoa, buckwheat) as well as legumes and tubers can also be used within a gluten-free diet (see Table 9.1).

9.2.1 Definition of 'Gluten Free'

In the *Codex Standard for Foods for Special Dietary Use for Persons Intolerant to Gluten* (2008) two possibilities for 'gluten-free products' are discussed:

- Gluten-free foods:
  - consisting of, or made only from, at least one ingredient that does not contain wheat (i.e., all *Triticum* species, such as durum wheat, spelt and kamut), rye, barley, oats or their crossbred varieties, and the gluten level does not exceed 20 mg/kg in total, based on the food as sold or distributed to the consumer; and / or
  - consisting of one or more ingredients from wheat (i.e., all *Triticum* species, such as durum wheat, spelt and kamut), rye, barley, oats or their crossbred varieties, which have been specially processed to remove gluten, and the gluten level does not exceed 20 mg/kg in total, based on the food as sold or distributed to the consumer.

Table 9.1 Gluten-free raw materials.

Cereals		Pseudocereals	Others
Not allowed	*Allowed*		
Wheat (and all its related species like: emmer, einkorn wheat, spelt wheat, Khorasan wheat, durum wheat triticale) Rye Barley	Rice Maize Millet Sorghum (oat)*	Amaranth Quinoa Buckwheat	Legumes (beans, peas, lupines) Tubers and roots Chestnut Banana and plantain

* Oats can be tolerated by most but not all people with coeliac disease. Therefore the use of oats, which are not contaminated with gluten, in gluten-free foods for the dietary management of coeliac disease may be determined at national level.

- Foods specially processed to reduce gluten content to levels above 20 up to 100 mg/kg. These foods consist of one or more ingredients from wheat (i.e., all *Triticum* species, such as durum wheat, spelt and kamut), rye, barley, oats or their crossbred varieties, which have been specially processed to reduce the gluten content to levels above 20 up to 100 mg/kg in total, based on the food as sold or distributed to the consumer.

European Union Regulation 41/2009 (in effect since 1 January 2012) regulates the composition and labelling of 'gluten free' in Europe. According to this regulation, a food may be labelled 'gluten free' when gluten in the food as sold does not exceed 20 mg/kg; and may be labelled as containing very low gluten if the content of gluten does not exceed 100 mg/kg.

According to the medical requirements of coeliac patients, an adequate gluten-free diet has to consider the following aspects:

- no gluten-containing foods;
- gluten-contaminated foods have to be avoided;
- compensation for malnutrition (micronutrients), in particular when intestinal absorption is still impaired.

It is important to ensure nutritional adequacy as well as excluding gluten (Kennedy, 2013).

9.2.2 Gluten-Free Processing – General Aspects

About 87% of all gluten-free products are made from rice or maize flour or starch. All other raw materials mentioned in Table 9.1 can only be found in 2–4% of the gluten-free products (see Figure 9.1).

Rice flour is one of the major ingredients in many gluten-free baking mixes in Western countries due to its white colour, neutral taste, high digestibility and hypoallergenic properties (Marco and Rosell, 2008). Usually rice is used in its refined form (debranned), thus regarding nutritional quality, rice-based gluten-free formulations

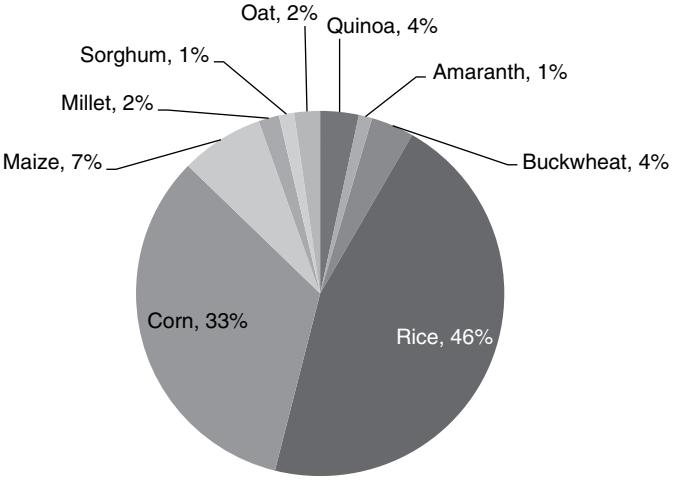

Figure 9.1 Raw materials used for gluten-free products on the market (Product Launch Analytics, Datamonitor ©).

have in particular low content of vitamins, minerals, proteins and dietary fibre (Thompson *et al*., 2005; Sciarini *et al*., 2010). Maize is the second most used raw material for gluten-free products. It is particularly suitable for pasta products due to its yellow colour.

This limited use of rice and maize flour or starch has undesired consequences for the gluten-free diet: Regarding nutritional quality of the products, they show high-energy density but low content of nutrients like vitamins, minerals, trace elements, dietary fibre or secondary plants and often they lack sensory properties (appearance, taste, smell, texture), which are still low in many products, in particular bread products (O'Shea *et al*., 2014). Thus the challenge for the production of gluten-free products is the improvement of their nutritional quality as well as the improvement of their sensory properties. This challenge can be met to some extent by the use of the remaining gluten-free raw materials mentioned in Table 9.1, but the three pseudocereals amaranth, quinoa and buckwheat offer many benefits for gluten-free products in particular (see section 9.3).

Millets, like sorghum, offer a range of health benefits to the consumer. They contain substantial levels of various phenolic compounds, which are much higher than in wheat, and they have health-promoting properties (Taylor *et al*., 2006). Although millet and sorghum thus have a huge potential for (gluten-free) food production and, in particular, for bread baking, research on its use is limited. Only few (Western) products can be found on the market.

Starch-rich legume seeds, such as peas, beans or lupines, are suitable to be added to or to replace cereal flours. By combining cereals and legumes within one product, the final protein quality is improved to a great extent, because the amino acid patterns of cereals and legumes complement each other in an ideal way. Lupine is the most used legume for gluten-free breads or cookies, which are often based on maize flour with an addition of lupine flour up to 10%. Lupine flour exhibits strong viscoelastic properties, which are similar to those of gluten (Jingyuan and Mohamed, 2003). Another good source for value-added food or gluten-free food processing is white beans (*Phaseolus vulgaris*). Its flour is of white colour, they have a good chemical composition (for example, iron content) and its flavour in the final product is only little 'beany', which allows incorporation to a higher extent (Schoenlechner *et al*., 2006). Chickpea (*Cicer arietinum*), being the second most important legume in the world, offers great possibilities for value-added or gluten-free products. It contains relatively high amounts of protein (23–27%) and lipids (5.8–6.2%) compared to other leguminous plants (Dodok *et al*., 1993). Its incorporation into cereal foods not only improves the final chemical composition (mainly regarding micronutrients) but also decreases their glycaemic index (Goñi and Valentin-Gamazo, 2003).

Tubers and roots that are used for gluten-free products are potato starch, cassava flour, sweet potato or tapioca starch. They can provide beneficial product texture. Additionally, flours from chestnuts, almonds, banana or plantains can be included in gluten-free baking mixtures. When banana or plantains are used in their unripe states they contain high amounts of starch and resistant starch (in particular unripe plantain flour) and introduce no 'banana' taste in the products. Due to their high content of resistant starch they are a good source to improve the nutritional properties of 'white' gluten-free products. A patent has been published, which describes the use of cassava, almonds and plantains for gluten-free food products (Singh-Meneghini, 2007). However, studies on the use of these raw materials for gluten-free bakery

products have only rarely been reported in recent decades. Zandonadi *et al.* (2012) undertook a study to develop and analyse gluten-free pasta made with green banana flour. The modified sample presented greater acceptance (84.5% for coeliac individuals and 61.2% for noncoeliacs) than standard samples (53.6% for noncoeliac individuals). Sarawong *et al.* (2014) used green plantain flour (GPF) as a functional ingredient to produce gluten-free (GF) bread based on a flour blend of rice flour and GF wheat starch (50 : 50) to improve their functional properties and to increase their resistant starch content. A satisfying gluten-free bread quality and highest resistant starch content were achieved by an addition of 30% plantain flour addition and 160% of water.

9.3 Potential of Pseudocereals for Gluten-Free Processing

The three pseudocereals – amaranth, quinoa and buckwheat – are destined to substitute cereals in many respects but in particular due to their favourable nutritional composition (see other chapters in this book). However, as amaranth and quinoa have long been neglected within food production and nutrition, mainly on account of wheat, current knowledge is still very limited. This is one reason why only few food products based on or including pseudocereals are available, in particular Western-type foods like bakery products and pasta. And, so far, gluten-free products are not commonly found on the market – this is described in more detail in section 9.7. As mentioned before, coeliac disease often manifests itself by malabsorption and subsequent vitamin or mineral deficiencies, which make high-quality nutrition even more important. As amaranth, quinoa and buckwheat are highly nutritious, their integration into the gluten-free diet could be a valuable contribution and they have been proven to be safe for coeliac disease patients (see section 9.1).

Pseudocereals can be used for many processes like cooking, popping, extrusion cooking, fermentation, baking or pasta making but all three pseudocereals lack dough-forming and thus baking properties due to the absence of gluten (which thus makes them suitable for the production of gluten-free alternatives). The production of (gluten-free) bread and bakery products or pasta using pseudocereals flour alone is therefore a great challenge and cannot be carried out without addition of further ingredients or without the specific adaptation of relevant processing steps.

Up to a certain amount of pseudocereal can be added to wheat-based products, which improves the nutritional properties of the resulting product. Sanz-Penella *et al.* (2012), for example, supplemented wheat bread with amaranth (20% and 40%) and found an increased iron concentration in the resulting bread but the levels of soluble phytates increased. However, the authors concluded that the use of up to 20% amaranth in bread formulation appears as a promising strategy to improve the nutritional value of bread, as indicated by the ferritin concentrations quantified in cell cultures. A higher proportion of amaranth flour increased iron concentration, although no increased iron uptake was detected.

According to Omary *et al.* (2012) germinating pseudocereals may improve the nutrient, vitamin, mineral, and total polyphenol content and antioxidant activity, while decreasing antinutrients. Thus germinated gluten-free cereals and pseudocereals have the potential to be used as a natural means of fortification and enrichment in

gluten-free foods. Their substitution may affect texture and taste (Mäkinen *et al*., 2013), which needs further investigation.

Another alternative to using amaranth in particular is to take advantage of its unique ability for popping, which otherwise is only possible for maize. Amaranth can be popped simply through applying intense, short and dry heat (without addition of fat). This was already practised by the South Americans before Columbus and therefore presents one of the oldest food processes for amaranth. Popped amaranth grains are quite soft in texture and are ready to be eaten or to be incorporated (eventually after milling) into existing or new food formulations. During popping a partial gelatinization of the starch granules occurs and due to the short processing time, of only seconds, the nutritional profile of the grain is more or less maintained. Another advantage is that popped amaranth presents a nice, nutty flavour and may thus enhance the palatability of food products, in particular sweet products like cakes, cookies or granolas. Some studies described in the following sections have considered popped amaranth flour for various gluten-free foods.

Besides their nutritional advantages, pseudocereals and isolated fractions or components thereof offer unique properties and technological functionality that have not yet really been exploited to a large extent in research and food development. Protein or starch fractions can be obtained by wet extraction methods or by dry milling methods. Due to the small seed size and the botanical differences of amaranth and quinoa, the production of defined milling fractions presents a great challenge and up to now no explicit milling protocol exists in this respect. Wet extraction of protein and starch fractions from pseudocereals, on the other hand, can be performed without demanding efforts, although specific adaptations have to be considered in this respect. Details on this topic are described in Chapter 8.

9.4 Gluten-Free Bread Baking with Pseudocereals

For all food products that include dough preparation, like bread (fermented or unfermented), breadlike products as well as bakery and pasta products, the dough-forming properties of the raw material is indispensable. Traditionally, these products are made mainly from wheat and they cannot be produced from gluten-free raw materials without specific adaptation of the recipe or the processing method. The challenging task for gluten-free processing is to replace the functionality of gluten (formation of a three-dimensional network in bread, agglutination and elasticity in pasta, etc.) by other means like using specific ingredients or adapting processing conditions. Gliadins, the prolamin of wheat, form a viscous fluid together with water and act as a plastifying aid within the dough. Glutenins, on the other hand, are responsible for the elastic, film-forming structure within the dough. During dough making the starch kernels are covered by a gluten film and the dough thus becomes extensible. Additionally the carbon dioxide bubbles formed by yeast or other leavening agents are enclosed, which gives a porous foam structure in the final bread product.

The simulation of these unique properties of gluten is a great technological challenge that makes the production of sensory appealing, gluten-free bakery products very difficult. In most cases it is not the use of one single gluten-free raw material that meets this aim but the use of a mixture of components in combination with additional chemical or physical methods and treatments.

Numerous studies have been published in which the use of various ingredients and their effects are described (Gallagher, 2006, 2009). Briefly, they can be classified into groups:

- water-binding and film-forming ingredients – hydrocolloids or thickening agents (e.g. locust bean gum, guar gum, pentosans, xanthan, pregelatinized native or modified starches, cellulose derivates);
- structure-forming, volume-filling, taste-giving ingredients – proteins (e.g. soy protein, milk protein, fish protein, modified proteins, fats, low molecular weight carbohydrates);
- surface-active substances (emulsifiers);
- use of enzymes (e.g. transglutaminase) for the formation of a protein network.

For gluten-free bread baking, the addition of a system hydrocolloid-emulsifier-protein (e.g. egg, soybean or milk protein) has emerged to be the most suitable for acceptable gluten-free bread quality within the research in the last decade. Of the hydrocolloids, hydroxyl-propyl-methyl-cellulose (HPMC) has been demonstrated to be somewhat superior to others. The modified cellulose derivative HPMC (linear and neutral polymer) has a high water-binding capacity because of its hydrophilic character. Due to the presence of hydrophobic methyl as well as hydrophilic hydroxypropyl groups, HPMC shows interface activity within the dough system during the resting period, which promotes dispersion and prevents coalescence of the gas bubbles (Haque *et al*., 1993). In recent research the use of enzymes for gluten-free food processing has been increasingly exploited. Some of those enzymes that are often used in gluten-free bread production are the starch-modifying amylase, cyclodextrin glycosyltransferases, or the protein-connecting transglutaminase. Glucose oxidase, laccase and proteases can also be found in the recipes (Goessart *et al*., 2008; Gallagher, 2009).

Most of the gluten-free breads available on the market are still based on refined flour (e.g. rice) or pure starch, which are characterized by a low nutritional quality (low content of dietary fibre, minerals or vitamins) (Thompson, 2009; O'Shea *et al*., 2014). Major efforts are therefore now undertaken to investigate and develop gluten-free bread products based on wholemeal flour or by addition of different dietary fibres. The use of specialty cereals or pseudocereals has a very good potential in this respect, as they are highly nutritious and up to now they have been used mainly as wholemeal flour (Hager *et al*., 2012).

In recent years, research on including pseudocereals (in particular amaranth and quinoa) in gluten-free baking has increased immensely. Several researchers investigated gluten-free baking by using pseudocereals within differing flour blends (e.g. combined with rice flour, potato starch, maize flour and other gluten-free starches) other researchers used them as the sole flour component.

Alvarez-Jubete *et al*. (2010) compared the baking properties of all three pseudocereals (amaranth, quinoa and buckwheat), each blended with rice flour (50:50), with a control bread (rice flour and potato starch 50:50). Additives and additional ingredients were 0.5% xanthan gum and 6% sunflower oil. Water content was 87%. Bread volumes were found to increase significantly for the buckwheat and quinoa breads in comparison to the control. For the addition of amaranth flour, no significant differences were measured in volume. All three pseudocereal-containing breads were characterized by a significantly softer crumb texture. Sensory analyses detected no significant differences in the acceptability of the baked breads, showing that pseudocereal flour

may be introduced into a gluten-free bread formulation to enhance crumb softness and cohesiveness and without adversely affecting sensory properties of the loaves.

A blend of a gluten-free bread flour mix (containing maize starch, potato starch, rice flour, locust bean gum) and 40% amaranth flour was optimized regarding water, protein (albumen) and fat addition by Schoenlechner *et al*. (2010). Water was the most critical parameter to influence final bread quality like specific volume, crumb texture and pore density. In this study the best results were achieved by an addition of 80% water (percentage based on flour). A combined addition of albumen and fat increased texture and pore structure and, in particular, sensory properties of the bread. In Figure 9.2 the differences between the bread slices containing varying amounts of water, albumen and fat are shown.

Leray *et al*. (2010) found that the addition of amaranth flour to gluten-free dough increased its resistance to freezing but decreased its resistance to storage conditions.

The use of quinoa flour and specific flour fractions produced from it was investigated in detail by Elgeti *et al*. (2014). Quinoa flour addition in general improved bread quality parameters but the addition of quinoa white flour, a flour fraction of quinoa where the bran components were removed, to a flour blend of corn flour and / or starch and / or rice flour enhanced the specific volume of gluten-free bread even further. This was related to the absence of bran components and the increased α-glucosidase activity. Although this improvement in the physical bread properties is advantageous, the lack of nutrients remains unaffected. Föste *et al*. (2014) incorporated quinoa whole grain and quinoa bran fractions into gluten-free bread based on a blend of rice and corn flour in order to improve the nutrient profile. Quinoa fractions significantly increased carbon dioxide formation due to a higher substrate availability, but gas retention was reduced by increased bran levels. An addition of 10% bran improved the bread volume by 7.4%

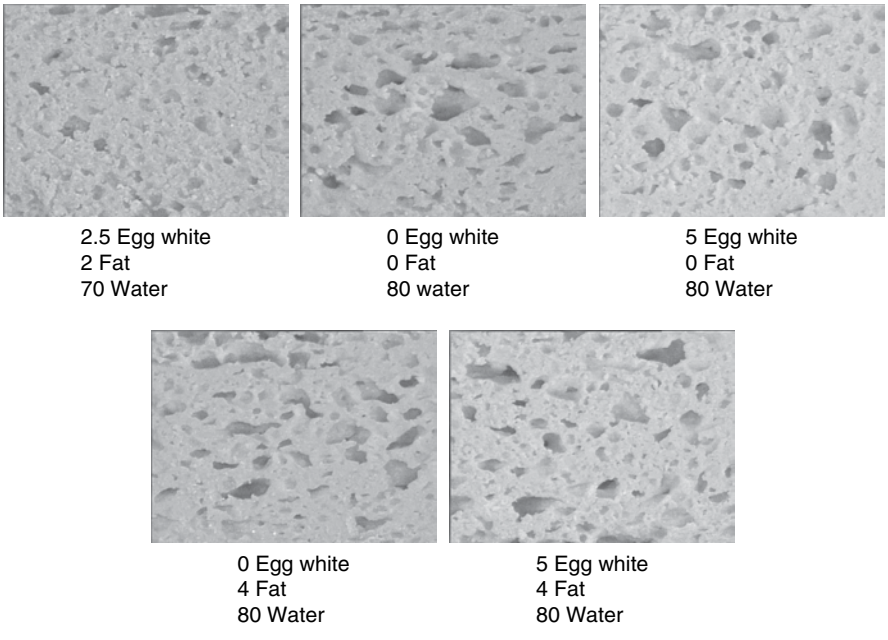

Figure 9.2 Gluten-free amaranth bread containing varied amounts of egg white, fat and water.

and enhanced the appearance without compromising the taste. Higher bran addition affected specific bread volume adversely.

Gluten-free bread from quinoa flour gave a higher glycaemic index reading compared to gluten-free breads produced from buckwheat or other gluten-free cereals (teff, sorghum, oat), which is most likely the result of the small starch granules present in quinoa (Wolter *et al*., 2013). Sour dough fermentation even increased the glycaemic index in quinoa and buckwheat breads further (Wolter *et al*., 2014).

Calderon de la Barca (2010) investigated the production of gluten-free bread by mixing raw amaranth flour (30–40%) with popped amaranth flour (60–70%), which produced loaves with homogeneous crumb and acceptable bread volume. Inclusion of popped amaranth flour improved dough consistency due to its higher water adsorption capacity and it allowed the production of gluten-free bread without addition of hydrocolloids. Another advantage of using popped amaranth flour might be an improvement of taste of the resulting end products. Popped amaranth flour has a nutty, roasted flavour, which can mask to some extend the 'musty' flavour, which is sometimes mentioned by (Western) consumers.

Another possibility to improve the sensory and nutritional properties of cereals and pseudocereals is germination. Quinoa malts were produced by Mäkinen *et al*. (2013) and incorporated into a rice- and potato-based gluten-free formulation. In quinoa malt only little change was observed except for a decrease in proteolytic activity, which had no negative impact on gluten-free bread quality. Thus, it might be used to increase palatability and nutritional properties of gluten-free breads.

The addition of buckwheat flour to gluten-free bread was studied as a potential healthy ingredient for improving the nutritional and technological quality of gluten-free bread by Wronkowska *et al*. (2013). An increase in loaf specific volume and a decrease in crumb hardness during storage with rising buckwheat flour addition were observed. Also Mariotti *et al*. (2013) investigated the effect of buckwheat in gluten-free bread. A dehulled (DBF) and a puffed (PBF) buckwheat flour were used, and high substitution levels (40%) were tested, with the aim of improving the nutritional value of the final gluten-free breads without decreasing their technological quality. The inclusion of 40% DBF was demonstrated not to reduce but actually improve the baking performances of the commercial gluten-free flour mixtures. Moreover, the presence of a small amount of PBF turned out to be useful in limiting both the diffusion and the loss of water from the bread crumb and the interactions between starch and protein macromolecules, resulting in a softer GF bread crumb and reduced staling kinetics during storage.

Apart from recipe parameters, emphasis has also been placed on the modification and adaptation of the baking process. Sourdough fermentation has come into interest in this respect as it offers textural and sensory advantages. According to Houben *et al*. (2010) sourdough fermentation was able to produce gluten-free doughs with viscosity and elasticity similar to that found in pure wheat flours. As an additional benefit, sourdough fermentation was found to be beneficial for coeliac disease patients in a study performed by Calasso *et al*. (2012), where they investigated the effect of corn, rice and amaranth gluten-free sourdoughs on duodenal inflammation parameters in eight coeliac disease patients. The consumption of sourdough fermented products could enhance the recovery from intestinal inflammation of coeliac patients at the early stage of the gluten-free diet.

As amaranth in particular, among the three pseudocereals, is very challenging for gluten-free baking, acidification of amaranth flour by adding lactic acid directly or by

fermentation via lactic acid bacteria is a possible method of changing the rheological behaviour in the desired direction. It is important to select the appropriate starter culture for pseudocereals, as the effects of different lactic acid bacteria on sourdoughs produced from pseudocereals are not the same (Jekle *et al.*, 2010). Sterr *et al.* (2009) investigated spontaneous fermented sourdoughs from five amaranth flours for the presence of lactic acid bacteria predominating the autochthones microbiota. Several strains of *Lactobacillus* and *Pediococcus* were revealed by DNA-PCR. Two selected strains (*L. plantarum* RTa12 and *P. pentosaceus* RTa11) were applied in growth experiments. They allowed stable fermentation characteristics and might thus be considered as suitable candidates for amaranth sourdough starter cultures. In the study of Wolter *et al.* (2014) sourdoughs of buckwheat, quinoa and other gluten-free cereals were produced using *Lactobacillus plantarum* and added to a basic bread formulation of flour from the same grain type. Sourdough fermentation changed the protein profiles in all sourdoughs, and its addition led to decreased dough strength. No influences on specific volume and hardness were found, while crumb porosity was increased after sourdough addition. Staling rate was reduced in the buckwheat sourdough bread.

Some lactic acid bacteria might additionally act as biopreservatives as they exhibit fungal activity. Axel *et al.* (2015) fermented quinoa flour with the antifungal *Lactobacillus amylovorus* and used this as an ingredient in gluten-free quinoa bread, which not only enhanced the nutritional properties of the gluten-free bread, but also introduced higher safety and thus extended shelf life.

9.5 Use of Pseudocereals in Pasta

Compared to gluten-free baking, gluten-free pasta was much underresearched. Until 2013, only about 20 research papers could be found for the previous three decades. Between 2013 and 2016 about the same number of studies on this topic have been published in relevant journals. This reflects the increased attention that gluten-free processing and research has been receiving in recent years.

Gluten-free pasta represents a challenge for food technologists because the available gluten-free raw materials have low functional qualities to provide pasta with good structure. In pasta, the network formation properties of gluten are not responsible for volume, it is significantly responsible for the typical pasta texture. Without specific adaption of recipe or processing method, pasta produced from gluten-free raw material have low cooking quality, they disintegrate upon cooking, have a very soft texture, high cooking loss, low bite resistance and little or no elastic character. Thus, gluten properties have to be replaced by other means for pasta too.

There are several possibilities to replace gluten in pasta (Marti and Pagani, 2013).

- replacing gluten by adding various ingredients, like proteins (egg-white protein, whey protein, soy protein), hydrocolloids, emulsifiers, and enzymes;
- modification of macromolecular starch organization;
- use of heat-treated flours (e.g. extrusion cooked flours);
- adopting nonconventional pasta-making processes.

The first possibility, the effect of various ingredients on gluten-free pasta quality and its potential to ensure pasta structure, while the three latter approaches have only been taken up in research more recently.

The replacement of gluten by proteins (egg-white protein seems to be most suitable), emulsifier or enzymes allows producing gluten-free pasta that does not disintegrate during cooking and cooking loss remains more or less in an acceptable range. But none of these ingredients is able to give the resulting gluten-free pasta the same textural properties as its wheat counterpart. In particular, the missing elasticity, perceived as the typical pasta texture, is missing.

Research has revealed that for gluten-free pasta production the role of starch and its properties are important (Marti *et al*., 2011). Phenomena related to starch retrogradation were found to play a central role for the final texture of the products (Mariotti *et al*., 2011). Thus recently, more attention has been paid to the technology of pasta making, utilizing pregelatinized flours or doughs, or applying different temperature regimes (Mastromatteo *et al*. 2011; Marti *et al*., 2013). Both approaches seem to be promising for improving gluten-free pasta quality.

Gluten-free pasta are only available on the market to a limited extent. They are usually based on maize flour, refined rice flour or pure starch (e.g. Asian-type mung bean noodles). Their nutritional properties are therefore not optimal. Compared to bread, the low nutritional quality in particular in terms of dietary fibre or micronutrients, is even more predominantly for pasta. Thus also, for gluten-free pasta the use or incorporation of pseudocereals is a valuable option. But, up to now, research has presented only a limited number of studies on this subject.

The use of amaranth, quinoa and buckwheat for the production of gluten-free pasta was studied by Schoenlechner *et al*. (2010). Several recipe and processing parameters were investigated, like dough moisture, flour blend, addition of isolated proteins (casein, soy protein, albumen), the addition of emulsifiers (distilled monoglycerides, DATEM), the addition of transglutaminase, the addition of xanthan and others. The results showed that pasta produced from amaranth had reduced texture firmness and cooking time, while pasta from quinoa mainly showed increased cooking loss. The fewest negative effects were observed in buckwheat pasta. By combination of all three raw materials to one flour blend in the ratio of 60% buckwheat, 20% amaranth and 20% quinoa, the dough matrix was improved. Dough moisture had to be lowered (30% versus 34.5% in wheat pasta). The addition of isolated protein (the most suitable was albumen) had the highest effect on improving pasta firmness, but while with increasing amount of addition firmness is increased, elasticity is reduced. The addition of emulsifier and enzymes could counteract this loss of elasticity to some extent. Also Marti *et al*. (2014) demonstrated the greater suitability of albumen compared to whey proteins. The application of high temperature drying (up to 80 °C) on this gluten-free pasta could improve the pasta properties even further (D'Amico *et al*., 2015). High-temperature drying is commonly used for the production of durum wheat pasta because it induces superior product quality and reduces process costs. Texture properties of the gluten-free pasta dried at elevated temperatures reached values comparable to the wheat reference. Although elasticity was improved partially, it still did not reach the values achieved by wheat pasta, and thus still needs further improvement. Figure 9.3 shows the determination of the elasticity of gluten-free pasta.

Popped amaranth flour can be incorporated into gluten-free pasta as well. According to Islas-Rubio *et al*. (2014),10% addition of popped amaranth flour to untreated amaranth flour was feasible to produce acceptable gluten-free pasta.

Verardo *et al*. (2011) produced gluten-free spaghetti form buckwheat and determined their free and bound phenolic compounds. Thirty-two free and 24 bound phenolic

Figure 9.3 Determination of elasticity in gluten-free pasta.

compounds in buckwheat flour and spaghetti have been characterized and quantified. A reduction in free phenolic compounds from flour to cooked spaghetti of about 74.5%, with a range between 55.3 and 100%, for individual compounds was measured. The decrease in bound phenols was 80.9%, with a range between 46.2 and 100%. The spaghetti-making process and the cooking caused losses of 46.1 and 49.4% of total phenolic compounds, respectively. Of the total phenolic compounds present in dried spaghetti, 11.6% were dissolved in water after cooking.

Cabrera-Chavez *et al.* (2012) applied a novel extrusion process of the production of amaranth-enriched, gluten-free pasta (based on rice flour). They subjected the flours to extrusion cooking at 120 °C for 2 min (single screw extruder) and used these (pregelatinized) flours to replace in part or fully the flour component in the pasta recipe. A blend of 75/25 rice / amaranth flour that was fully extruded prior to pasta making, gave the best results for pasta texture and nutritional properties. Mineral and fibre content, as well as protein digestibility were improved by amaranth enrichment. The results suggested that starch in rice flour interacted best with amaranth proteins when starch gelatinization occurred simultaneously to protein denaturation in the extrusion cooking process. A blend of amaranth and cassava flour was used for pasta production by Fiorda *et al.* (2013). These researchers also pregelatinized part of the flour prior to pasta processing. A blend of 10/60/30 pregelatinized flour / cassava starch / amaranth flour gave the best pasta quality, which was highly accepted during sensory evaluation tests.

Alamprese *et al.* (2007) developed fresh gluten-free egg pasta based on buckwheat and rice flours (raw, precooked or pregelatinized). Samples containing the precooked rice flour gave the best results, in terms of workability, break strain and weight increase during cooking. The formulation of gluten-free fresh and dry pasta based on quinoa,

maize and defatted soy was optimized by Mastromatteo *et al.* (2011). Results showed that the addition of pregelatinized maize flour increased dough firmness and sensory properties. Quinoa flour addition adversely affected sensory properties of the pasta.

9.6 Other Products

9.6.1 Cookies and Biscuits

Cookies (biscuits) are a convenience product. They are ready to eat, have a relatively long shelf life, good eating quality and are thus widely consumed. In order to introduce or increase the consumption of new or rarely used raw materials they are an appropriate food product. For the production of cookies, gluten (quality) plays only a minor role as other ingredients like eggs, fat and sugar are also responsible for the texture quality of the end product. Thus the absence of gluten often does not require so much attention as for bread baking or pasta production.

Gluten-free cookies using raw and popped amaranth were formulated by Calderon de la Barca *et al.* (2010). The best cookie recipe had 20% of popped amaranth flour and 13% of whole grain popped amaranth. Additional ingredients were egg, sugar, sodium bicarbonate, butter and water. The expansion factor was similar to maize starch-based controls and the hardness was similar to other gluten-free cookies. The final products had a high nutritional value as determined by the authors.

In an earlier study the production of biscuits (short dough biscuits) from the three pseudocereals, amaranth, quinoa and buckwheat blended with common bean, was investigated by Schoenlechner *et al.* (2006). Each pseudocereal was blended with 25%, 50% and 75% bean flour. For comparison, biscuits of 100% of the respective pseudocereal and 100% bean flour were produced. The results of the physical measurements (texture, colour and spread factor) showed that buckwheat biscuits were crispier than quinoa biscuits and even more than amaranth biscuits. Addition of bean flour increased the crispness of all biscuits. During the sensory evaluation, quinoa biscuits were least preferred due to their strong taste. In order to increase the textural properties of the amaranth biscuits, part of the amaranth flour was successfully replaced by popped amaranth flour. The biscuits had a good nutritional composition – addition of bean flour gave a significant enrichment with dietary fibre and proteins. As an alternative to white bean addition, chickpea had great potential to increase the quality of gluten-free cookies based on amaranth or buckwheat, as determined for spread factor and hardness (Yamsaengsung *et al.*, 2012). Sensory evaluation demonstrated that the addition of chickpea could increase the acceptability of the gluten-free cookies. A ratio of 60/40 chickpea / amaranth or buckwheat flour was preferred by the consumer test panel.

Gambus *et al.* (2009) supplemented gluten-free cakes (sponge cake, carrot cake and coconut cake) and biscuits with amaranth and / or buckwheat flour in order to increase their nutritional value. The final products received high consumer scores, exceeding in some cases those of the control samples (based on corn flour and potato starch). Both amaranth and buckwheat increased the nutritional value in terms of protein and dietary fibre content, as well as micronutrients (in particular minerals). Amaranth proved to be a beneficial supplement to gluten-free products by enhancing the amino acid composition.

A study on the addition of protein isolates from selected legumes and amaranth to a starch-based gluten-free muffin batter was undertaken by Shevkani and Singh (2014). The protein isolates enhanced batter viscoelasticity and resulted in muffins with higher specific volume, springiness and cohesiveness of the final products (Shevkani and Singh, 2014).

9.6.2 Snack Products – Granolas and Breakfast Cereals

Several snack products like granolas and breakfast cereals are produced by extrusion cooking. Extrusion cooking is a continuous process by which food biopolymers and ingredients are mixed, plasticized, cooked and formed by combination of moisture, temperature, pressure and mechanical shear. Extrusion cooking as a versatile and very efficient technology is widely used in the processing of grains, particularly in the production of convenience products such as puffed snack foods and breakfast cereals. It is difficult to produce expanded products by extrusion cooking of amaranth or quinoa alone because of their high fat content. Fat provides a powerful lubricating effect in extrusion cooking and reduces product expansion. Additional starch must be used in extrusion cooking of amaranth to improve extrudability and product properties. Therefore extrusion cooking of amaranth or quinoa in combination with nutritionally complementary cereal grains such as rice is of even more interest to produce nutritionally balanced products in the well accepted form of expanded extrudates.

Several authors described the use of pseudocereals for gluten-free breakfast cereals or granolas in the past. Morales *et al.* (1988) investigated the nutritional value of grain amaranth and maize-amaranth mixtures for young children and found high protein digestibility for popped and flaked amaranth. Wesche-Ebeling *et al.* (1996) developed a high-quality granola containing popped amaranth grain. Ramos Diaz *et al.* (2013) used amaranth, quinoa and kañiwa in extruded corn-based snacks. The addition of these pseudocereal flours increased the expansion index of the extrudates. The evaluation of lipid oxidation suggested a remarkable stability of these extrudates even after exposure to high relative humidity.

Amaranth, buckwheat and millet were used in the manufacture of extruded breakfast-cereal products as a replacement for wheat and maize flour by Brennan *et al.* (2012). The use of these flours altered the physical and nutritional quality of extruded breakfast cereals. All of the extruded products made with the inclusion of pseudocereals showed a significant reduction in readily digestible carbohydrates and slowly digestible carbohydrates compared to the control product during predictive *in vitro* glycaemic profiling. The results illustrate the potential use of these nontraditional cereal flours in lowering the glycemic response to the ingestion of extruded breakfast cereals. Gluten-free granolas containing quinoa or amaranth were produced by de Souza *et al.* (2014). The gluten-free granola formulations had good physicochemical and nutritional properties and achieved good sensory ratings. Capriles and Gomez Areas (2010) enriched amaranth bars with inulin and oligofructose, which were accepted during sensory tests. In an older study a crunchy muesli was developed at the Department of Food Science and Technology, BOKU, which contained 29.5% amaranth and 3.8% of quinoa. This recipe was best rated in sensory evaluations. Higher amounts of quinoa were not acceptable by Austrian consumers. Pagamunici *et al.* (2014) developed a gluten-free granola from quinoa, amaranth and linseed and evaluated it during storage for the physicochemical sensory, and nutritional characteristics.

The granolas had high nutritional properties, acceptable sensory properties and excellent shelf life, probably due to the low water activity of the formulation, which contributed to inhibiting microbial growth.

9.6.3 Beverages and Beer

Cereal-based beverages have a huge potential as functional food. They can serve as carriers for a range of nutrients. Principally they can be produced from pseudocereals in a similar way to cereals.

El-Deeb *et al*. (2014) investigated the use of water extract of quinoa seeds water extract (QSWE) in the manufacturing of a milk-based fermented beverage using 2% of yogurt starter. The data showed that total solids and carbohydrates contents decreased with increasing ratio of added QSWE but there were no significant differences in the protein, fat and ash contents. Iron content increased by the addition of QSWE and sensory properties of fermented beverages with 75 or 100% QSWE were acceptable. Extruded or roasted amaranth was used for the production of a high antioxidant capacity beverage by Milán-Carrillo *et al*. (2012). The beverages were evaluated with an average acceptability of 8.1–8.4 (level of satisfaction between 'I like it' and 'I like it extremely') and had a high nutritional, antioxidant value, which can be attributed at least partially to the use of the optimum roasting and extrusion processing conditions.

Beer is one product that is usually produced from barley and is toxic to coeliac disease patients. Thus alternatives have to be found for this product. Attempts to malt, mash and brew using buckwheat, amaranth and quinoa have been undertaken by several authors (Zarnkow *et al*., 2005; Wijngaard and Arendt, 2006; De Meo *et al*., 2011). Based on these studies, gluten-free beerlike beverages from malt pseudocereals are close to commercial production, but rather high costs are expected during their production mainly because of the low intrinsic activity of hydrolytic enzymes and the need for external enzymes supplementation during mashing. In particular the suitability of quinoa for malting is limited by its very small grain size and the significantly lower enzyme activities compared to wheat or barley, according to Hager *et al*. (2014). Also radicle growth is rapid, resulting in high malting losses. Due to these grain parameters, some modifications of the process technology, the malting protocol, various brewing parameters such as temperature and pH of mashing, boiling, fermentation conditions, yeast strain used, pitching rate, temperature, pressure, aeration, agitation and stirring as well as storage and ageing conditions, are required due to the specific nature of the grain.

Beer from 100% amaranth or quinoa malt was produced by Zweytick *et al*. (2005). Amaranth beer resulted in a slightly opaque and yellow product, which was excessively bitter to taste. Additionally, beer foam stability was reported to be unsatisfactory. For quinoa beer the authors reported a slightly opaque yellow product with acceptable foam and taste. Zarnkow *et al*. (2007) investigated the influence of degree of steeping as well as germination time and temperature on the quality of quinoa malt and developed an optimized malting procedure.

Optimized malting and mashing conditions for 100% buckwheat malt have been described in a number of studies (Hager *et al*., 2014), which demonstrated that by using commercial enzymes, the production of wort from 100% buckwheat malt is feasible. These authors showed that the utilization of commercial cellulase, amyloglycosidase and α-amylase can sufficiently increase extract levels, fermentability, total fermentable extract, total soluble nitrogen and free amino nitrogen (FAN).

De Meo *et al*. (2011) performed micro-malting experiments on buckwheat, quinoa and amaranth using different malting parameters to study their brewing behaviour. Alkaline steeping has been applied, which showed an increase in total soluble nitrogen and free amino nitrogen, in particular in buckwheat. Amaranth exhibited an interesting fermentability of 56%. From this study the authors conclude that pseudocereals can successfully be employed for gluten-free beer production and the alkaline steeping seems to be a useful process, which is variable for the optimization of malt quality.

9.7 Market Today

Summing the numbers of people suffering from coeliac disease or any other form of gluten disorder, and owing to the fact that, in particular in the United States, many people consider 'gluten free' to be the healthier option, some 10% (Europe) to 18% (in the United States) of the population buys gluten-free food at present. This has caused the market to grow fast. In the United States, sales of gluten-free products reached up to 19% in the period January to September 2012. The number of new product launches featuring gluten-free claims rose from 600 in 2007 to more than 1600 in 2011. This growth is not only driven by the increase in gluten disorders. In the United States, 35% of gluten-free food buyers considered them to be 'generally healthier' (Watson, 2012). The database of Datamonitor© indicates that the gluten-free claims for new product launches reached about 3300 in 2010, declining slightly to 2700 new launches in 2013 (see Figure 9.4). According to a report by Mintel, the US market experienced a growth of 44% (Watson, 2013). It seems to have grown even faster in the years 2013–2016.

The number of new gluten-free product launches containing amaranth or quinoa or buckwheat for the period 2000–2014 is shown in Figure 9.5. The market for gluten-free products started to increase in the late 1990s. With a slight delay, gluten-free products containing amaranth or quinoa or buckwheat were launched, beginning in the year

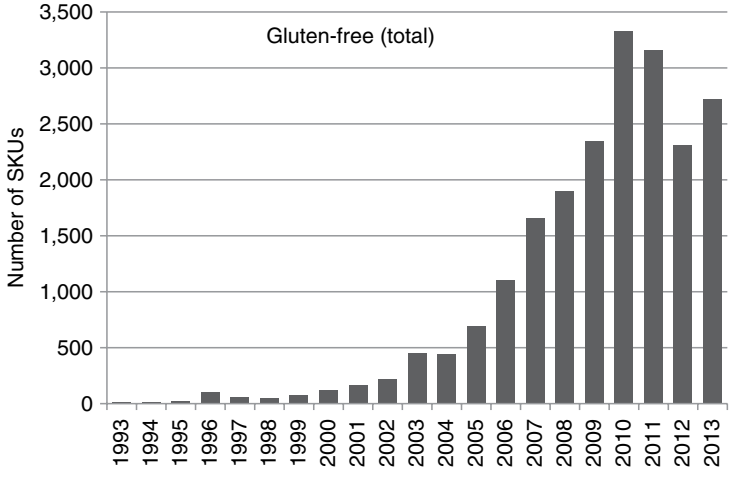

Figure 9.4 Launches of new gluten-free products (worldwide) (Product Launch Analytics, Datamonitor ©).

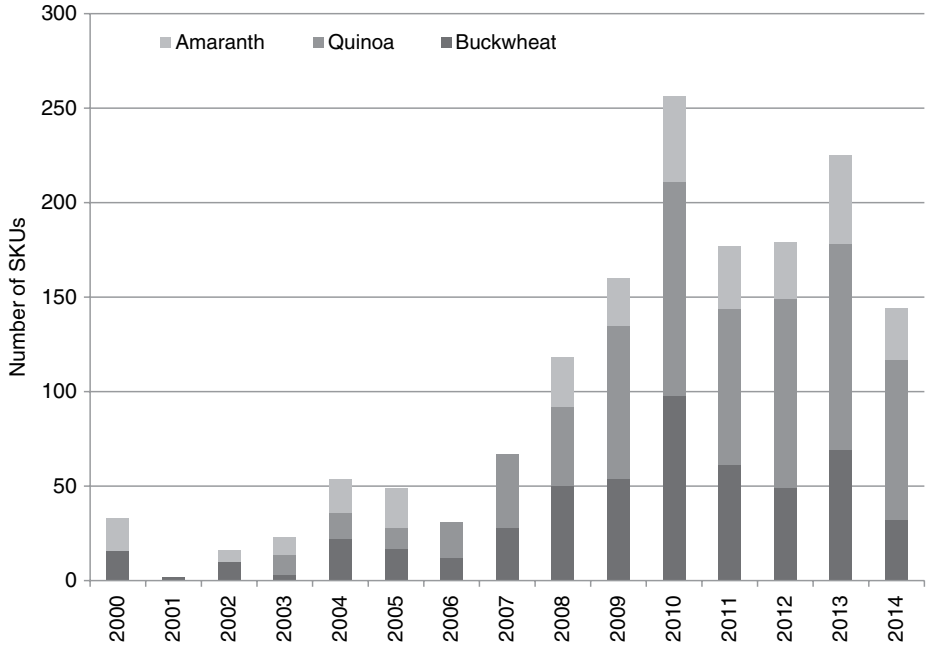

Figure 9.5 Launches of new gluten-free products containing amaranth, quinoa or buckwheat (worldwide) (Product Launch Analytics, Datamonitor ©).

2000. The development of gluten-free products from all three pseudocereals increased fast from 1999 to 2014, in particular those containing quinoa. Yet, the share of gluten-free products containing one of these pseudocereals is still very low and remains below 10% of all gluten-free products (see also Figure 9.1). Most of them are still produced from or with maize and rice. As mentioned previously, this fact is not positive – mainly for nutritional reasons. One reason for this lower use of pseudocereals might be the higher costs for the raw material. The costs of buckwheat, amaranth and in particular quinoa costs are much higher than the cost of rice or corn. The price of quinoa rose about 5–7 times between 2006 and 2016.

According to Watson (2013) the next wave of gluten-free products will be all about taste, flavour, texture and convenience. From a nutritional perspective there is definitely room for improvement. Thus, there is a high chance that more gluten-free products containing amaranth, quinoa and / or buckwheat will enter the market.

9.8 Conclusion

All three pseudocereals offer good nutritional advantages and are confirmed to be gluten free. Thus, they offer a excellent potential for enhancing the quality of the existing gluten-free products, which have been mainly based on rice and maize flour.

In general, research on food processing utilizing the three pseudocereal varieties has increased immensely in recent years, but market analyses show that gluten-free products based on or containing pseudocereals are scarce. This situation is unsatisfactory because the use of amaranth, quinoa or buckwheat in gluten-free products adds better

nutritional value to the final products, which is very much needed by the coeliac disease patients.

On the other hand, greater utilization of pseudocereals would be desirable for all consumers so that they can enjoy the benefits of these varieties and increase their diet variation again. This requires continued efforts from food technologists and industry to enable the development and production of sensory appealing, value-added, gluten-free products.

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10

Nutritional and Health Implications of Pseudocereal Intake

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10.1 Introduction

There was increased interest in pseudocereals in the 1980s, when the United States National Academy of Sciences performed research on the grains and described their high nutritional value and agronomic potential (FDA, 1999). Pseudocereals are currently emerging as healthy alternatives to gluten-containing grains in the gluten-free diet. They make modern and innovative baked goods (Bergamo *et al*., 2011; Sanz-Penella *et al*., 2012). They are naturally gluten free and high in a wide range of nutrients (Caselato-Sousa and Amaya-Farfán, 2012). Pseudocereal-based food products containing amaranth, quinoa and buckwheat as composites with wheat flour are already available commercially (pasta, noodles, breakfast cereals, biscuits, and breads) but few of these products are gluten free. Pseudocereals are considered as reasonably well balanced foods with functional properties that have been shown to provide medicinal benefits.

Most cereal products, like white bread, pasta, and biscuits, are based on flour after removal of bran and germ, the two parts of grain kernels containing most of the dietary fibre and other bioactive components (Van der Kamp *et al*., 2014). The United States was the first country to adopt a whole-grain health claim for both reduced risk of heart disease and cancer (FDA, 1999). The complete set of cereals and pseudocereals (amaranth, buckwheat and quinoa) in the AACCI/FDA whole grain definition were included; however, this claim was subsequently revised and the revised health claim only refers to the reduction in risk of heart disease. The trend towards requiring convincing / conclusive evidence culminated in the evaluation by the EFSA of health claims submitted after publication of Regulation 1924/2006 on nutrition and health claims made on foods. To date, only a number of well characterized fibres and brans from wheat, rye, barley, and oats have obtained a positive EFSA opinion and are included in the positive list of authorized claims (Van der Kamp *et al*., 2013).

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Cereal proteins are of clinical interest because they are involved in both allergic processes and intestinal disorders. Current immunological and clinical data point to wheat allergens such as the α-amylase / trypsin inhibitor (ATI) family as the main culprit in baker's asthma and recently as new players in noncoeliac gluten sensitivity (Junker *et al.*, 2012). Moreover, ingestion of wheat, barley or rye triggers small intestinal inflammation in patients with coeliac disease (CD). To date, nutrition therapy for CD has centred on food allowed / not allowed in a gluten-free diet and little emphasis has been placed on the nutritional quality of this diet. From the existing data an association can be established between nutrients with important functional activities beyond their exclusive immune and nutritional value.

Amaranth (*Amaranthus* spp.) has been consumed throughout history, including by the Inca, Maya and Aztec civilizations, where it was used as a staple food. It is a reasonably well balanced food with functional properties that have been shown to provide medicinal benefits. In the 1990s quinoa was classified by NASA as an emerging crop with excellent nutritional properties for long-term human space missions due to its high protein content and unique amino-acid composition – in particular lysine and sulfur amino acids. Meanwhile, quinoa and amaranth were introduced in several countries outside of the Andean region. Quinoa is also cultivated in England, Sweden, Denmark, the Netherlands, Italy and France. Recently France has reported an area of 200 ha with yields of 1080 kg/ha and Kenya has shown high seed yields (4 t/ha). The strongest interest in amaranth in Europe has been in Austria, the Czech Republic, the Slovak Republic, Germany, Hungary, Poland, Russia, Italy and Slovenia. In Canada, United States, Japan, Australia and European countries these Andean cereals evidence are being increasingly accepted by consumers (Hirose *et al.*, 2010; Valencia *et al.*, 2010a; Rastogi and Shukla, 2013). Production and use of buckwheat grain and flour had their most prosperous era around 1900, and have experienced renewed interest because of their beneficial effects, due in part to their rich supply of flavonoids with lipid-lowering activity and favourable conditions for sourdough fermentation.

This chapter summarizes recent research reporting several different beneficial effects of pseudocereals (Figure 10.1). Animal and human trials have led to new hypotheses, including the role of cereals as a major source of micronutrients and vitamins, dietary glycine and betaine, a possible effect on phospholipid synthesis or metabolism, the role of branched-chain amino acids and improvements in insulin sensitivity, and the possibility that whole grains may have an effect on protein metabolism. Nevertheless, it is also desirable to conduct research aimed at determining the minimum amount of pseudocereals or food based on them that should be consumed in order to produce the expected effects.

10.2 Pseudocereals in Allergy and Coeliac Disease

Allergic individuals have Th2 skewing of their immune responses and studies in animal models suggest that tolerance involves T regulatory (Tregs) cells and the secretion of specific cytokines, in particular IL-10. To date, scarce data support the allergic potential of pseudocereals; however, some case reports of anaphylaxis to quinoa in France (Astier *et al.*, 2009), Rajgira seed flour (*Amaranthus paniculatus*) in India (Kasera *et al.*, 2013) and buckwheat in Asia (Lee *et al.*, 2013) can be found in the literature. Immunoadjuvant activity of quinoa (*Chenopodium quinoa*) saponins on the humoral

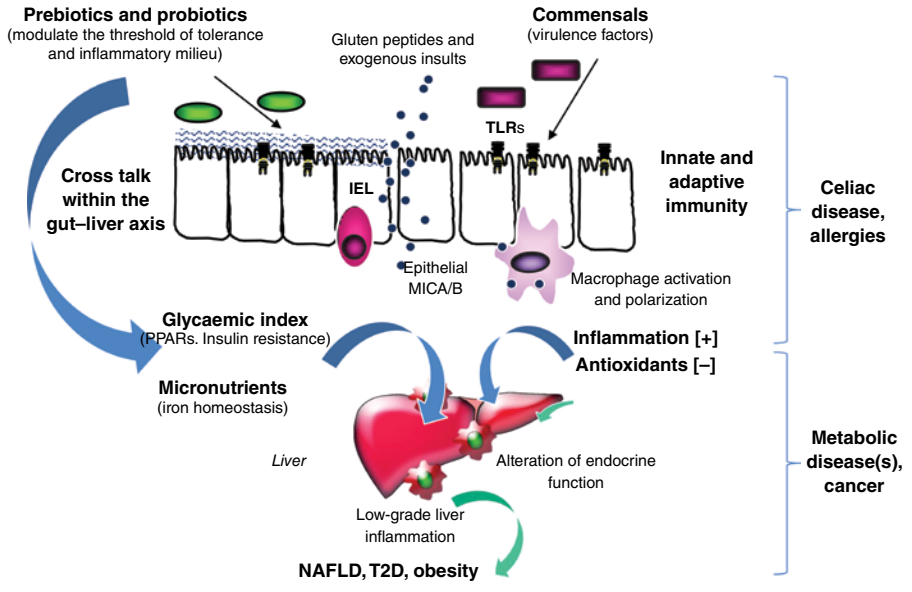

Figure 10.1 Functional interrrelationships within the gut–liver axis that can be modulated by biologically active compounds from pseudocereals. (*See color plate section for the color representation of this figure.*)

and cellular immune response(s) of mice immunized with ovalbumin have been suggested (Verza *et al.*, 2012).

Coeliac disease is an autoimmune enteropathy triggered by cereal gluten proteins (gliadins) in genetically predisposed individuals carrying HLA-DQ2 or -DQ8 molecules eliciting adaptive Th1 T cell-mediated immune response(s). In CD patients, peptides resulting from incomplete protein hydrolysis by digestive enzymes cause a deregulated immune response and inflammation. Blame for the increase of coeliac disease sometimes falls on gluten-rich, modern wheat varietals, on increased consumption of wheat and on the ubiquity of gluten in processed foods. The epidemiology of coeliac disease does not always support this idea and imbalances in environmental factors such as gut microbiota gained importance. *In vivo* human intervention trials provide evidence that the use of gluten-free flours in bread formulation from pseudocereals, for example, millet and buckwheat (Di Cagno *et al.*, 2004) and tef and quinoa (Bergamo *et al.*, 2011; Zevallos *et al.*, 2014), is well tolerated by individuals with CD and does not exacerbate the disease.

The well defined role of adaptive immunity in CD contrasts with an ill-defined component of innate immunity in the disease. Wheat gluten contains largely water-insoluble storage proteins, such as gliadins and glutenins, as well as water-soluble protein components such as salt-soluble globulins, including ATIs. The latter have recently been identified as strong activators of innate immunecompetent cells via toll-like receptor (TLR)-4, thereby inducing the release of proinflammatory cytokines / chemokines and initiating an inflammatory response (Junker *et al.*, 2012). It might well be that in patients with nonspecific gastrointestinal complaints without definite evidence of CD the symptoms could be caused by ATIs. However, no ATI activity has been found in pseudocereals such as quinoa (*Chenopodium quinoa* Willd) and kañiwa (*Chenopodium pallidicaule* Aellen) (Ranilla *et al.*, 2009). Although the presence of ATI needs further confirmatory

analysis, these preliminary data showing the lack of amylase inhibitory activity in pseudocereals support the view of pseudocereals as alternatives to wheat that can prevent 'noncoeliac gluten sensitivity'.

10.3 Prebiotic Effect of Pseudocereals

The associations between gastrointestinal disorders and the beneficial role attributed to prebiotics, promoting gut barrier function and immunity in inflammatory disorders, have led to investigations to identify environmental changes affecting host factors, to understand disease onset and to establish preventive strategies. Prebiotics are nondigestible food ingredients that affect the host beneficially by stimulating the growth and / or activity of specific intestinal bacteria. These biological effects of prebiotics depend strongly on the composition of the gut microbiota, which promote the production of short-chain fatty acid (SCFA) profiles (e.g. acetate, butyrate and propionate) able to modulate inflammatory disorders (Cavaglieri *et al*., 2003). Apart from SCFAs' trophic effects on intestinal epithelia (Sauer *et al*., 2007), they lower luminal pH, helping to control pathogen colonization. Fermentation of prebiotics may have important metabolic consequences in liver-related disorders because acetates access the portal circulation and contribute to lipid and cholesterol synthesis in the liver. Moreover, much of the beneficial effect of prebiotics on plasma lipid and hepatic triglyceride concentrations may be attributed to regulation of the expression of different transcription factors.

An overreliance on refined grain-based foods can result in diets that are low in fibre, as well as micronutrients and vitamins, as a dietary survey demonstrated in 46% of the women studied (Thompson *et al*., 2005). In addition to their favourable immune features, the pseudocereals amaranth and buckwheat emerged as healthier alternatives to wheat, providing significantly higher amounts of fibre (Alvarez-Jubete *et al*., 2009). From a technological point of view, pseudocereals have been used to investigate the adaptability of beneficial lactic acid bacteria (LAB) and yeasts to sourdoughs prepared from pseudocereals. The studies conducted have demonstrated, at the end of fermentation, different *Lactobacillus* spp. of interest (*L. fermentum*, *L. helveticus*, *L. paralimentarius*, *L. plantarum*, *L. pontis*, *L. spicheri*) as well as yeast (*Issatchenkia orientalis* and *Saccharomyces cerevisiae*) (Vogelmann *et al*., 2009). Experimental rat models fed a buckwheat-based diet have shown increases in aerobic mesophilic and lactic acid bacteria – particularly, higher proportions of *L. plantarum* and *Bifidobacterium spp*. (Préstamo *et al*., 2003). These observations were accompanied by a slight reduction in enterobacteria and other potentially harmful commensal bacteria. Similarly, methanol extracts from buckwheat enhanced the growth of lactic acid bacteria in carbon-free source media but inhibited that of *Clostridium perfringens* and *Escherichia coli* (Hoy and Moo, 2000). Recent efforts to develop a symbiotic fermented milk supplemented with buckwheat flour and probiotic strains (*L. rhamnosus* IMC 501®, *L. paracasei* IMC 502® and SYNBIO®) demonstrated a significantly faster lowering of the pH as well as an enhanced stability of the probiotics (Coman *et al*., 2013). The use of quinoa to formulate a symbiotic beverage allowed a reduction in fermentation time and survival potential of the strain *Lactobacillus casei* LC-1 (Bianchi *et al*., 2014).

10.4 Potential of Pseudocereals in Type-2 Diabetes: Glycaemic Index (GI)

A typical Western diet is characterized by a high intake of red meat, sugary desserts, high-fat food and refined grains (Capellani *et al.*, 2013). Digestion and absorption of carbohydrates is fast and usually takes place in the upper small intestine. The type and amount of dietary carbohydrate are the main determinants of postprandial glucose and insulin responses, influencing the risk of liver and biliary tract cancers, although convincing evidence is currently lacking (Fedirko *et al.*, 2013). Otherwise, when the diet contains carbohydrates not easily digestible, digestion and absorption take place mainly in the ileal portion of the intestine influenced by gut microbiota.

The GI represents the total increase in a person's blood glucose level following consumption of a food, but it might or might not reflect the rapidity of the transfer of carbohydrates to bloodstream and physiological response in relation to insulin production. An additional interest to further investigate these aspects is motivated by the higher GI values estimated in gluten-free breads than in the gluten-containing counterparts (Foster-Powell *et al.*, 2002) as well as gluten-free pasta for coeliac subjects (Bacchetti *et al.*, 2014). Elevated GI is associated to type 2 diabetes (T2D), a condition also associated with insulin resistance and eventually declining pancreatic function, which results in absolute or relative insulin deficiency. To date, a few studies support the antidiabetic potential of amaranth oil and seeds using streptozotocin-induced hyperglucemic animals (Kim *et al.*, 2006) as well as an improved aerobic metabolism in T2D patients (Yelisyeyeva *et al.*, 2012). There have been reported beneficial effects after consumption of buckwheat, reducing the postprandial response of gastrointestinal satiety hormones (GLP-1, GIP and PPY) without changes in acute insulinemia in individuals with T2D mellitus (Stringer *et al.*, 2013). However, the action of buckwheat on postprandrial plasma glucose appears controversial (Stringer *et al.*, 2013; Su-Que *et al.*, 2013). In line with these studies significant differences have been found in the starch digestibility of pseudocereals predicting a poor GI for amaranth and quinoa (Chaturverdi *et al.*, 1997; Wolter *et al.*, 2014).

The content of resistant starch is significantly reduced by fermentation (*Weissella cibaria* MG1 and *Lactobacillus plantarum* FST1.7) as demonstrated in flours from buckwheat and quinoa, thereby increasing the predicted GI values, although to a greater extent for quinoa (Wolter *et al.*, 2014). Household / industrial processing of amaranth seeds can also greatly impact their GI; pop, roast, flake or extruded amaranth seeds have been shown an increased starch digestibility rendering GI values (94.9) similar to that of white bread (Capriles *et al.*, 2008). Pressure cooking and boiling favoured more resistant starch content in waxy amaranth (Parchure and Kulkarni, 1997).

In view of the fact that the concentrations of protein, fibre and fat are strongly and positively correlated with low GI values due to their effect on digestion processes, the selection of pseudocereals as ingredients in infant formulas could contribute to the better control of postpandrial glucose responses in this sensitive group (Pina-Rodriguez and Akoh, 2009, 2010). Chemical composition analyses of amaranth-, quinoa- and buckwheat-based bread formulations revealed a particular higher fat content than gluten free and wheat bread as well as a richer proportion in unsaturated fatty acids, with the highest unsaturated / saturated ratio observed from quinoa (Alvarez-Jubete *et al.*,

2009). The content of palmitic acid and other major fatty acids in amaranth has been found suitable for the infant formula (Pina-Rodriguez and Akoh, 2009) according to the nutritional recommendations of the European Society for Pediatric Gastroenterology (ESPGHAN). Moreover, technological features of pseudocereals (size of starch granules in addition to type of carbohydrates and their molecular arrangement) can also influence GI values. In this sense, amaranth seed has been classified as a high glycaemic food, most likely because of its small starch granule size, low resistant starch content, and tendency to lose completely its crystalline and granular starch structure during processing (heat) treatments (Capriles *et al*., 2008).

10.5 Micronutrient Availability

According to the Academy of Nutrition and Dietetics Evidence Analysis Library and nutritional studies, adherence to the gluten-free dietary pattern may result in a diet that is deficient in iron, zinc, selenium, phosphorus and calcium as well as niacin, vitamin B12 and thiamine. This shows the enormous importance of educating consumers in order to improve the nutritional quality of the gluten-free diet. The nutritional profile of quinoa (*Chenopodium quinoa*), amaranth (*Amaranthus Caudatus*) and buckwheat (*Fagopyrum esculentum* M.) reveals these grains to be rich sources of micronutrients (except potassium) (Levent and Bilgiçli, 2011; Nascimento *et al*., 2014). Thus, there has been a growing tendency to use them to supplement bread formulations to improve their nutritional value.

Only a little *in vivo* data can be found concerning the impact of fortification with amaranth grain on bioavailability of essential micronutrients such as iron to prevent iron deficiency (Macharia-Muti *et al*., 2013). This study revealed that supplementation with amaranth did not improve iron status despite a large increase in iron intake (by 5.6-fold) and more favourable phytate : iron molar ratio (3 : 1 versus 5 : 1) than controls after an intervention period of 16 weeks. Most of existing data supporting beneficial effects of pseudocereals improving micronutrient bioavailablity are focused on iron and are related to experimental rodent models (Ologunde *et al*., 1991, 1994) or *in vitro* studies (Sanz-Penella *et al*., 2012; Galan *et al*., 2013). There are a number of differences concerning Fe absorption in rats compared with humans, limiting their predictive value in relation to human responses (Greger, 1992). Thus, these data need to be considered bearing this in mind. Overall, experimental rodent models showed low or negligible contribution of amaranth supplementation to iron bioavailability. Our own pilot studies revealed that iron-deficient rats administered with amaranth, quinoa or chia showed decreased plasmatic levels of the hepatic hormone hepcidin, demonstrating positive effects of pseudocereals in the reduction of inflammatory conditions within the gut–liver axis, contributing to a higher intestinal absorption of the micronutrient (Laparra and Haros, 2016). Mineral availability *in vitro* from amaranth grain has been estimated to be in the range of 2.0–7.7%, 3.3–11.1% and 1.6–11.4% for Fe, Ca and Zn, respectively (Sanz-Penella *et al*., 2012; Galan *et al*., 2013). Notably, Sanz-Penella *et al*. (2012) reported an inverse relationship between the proportion of amaranth flour used in bread formulation (0, 20 or 40%) and iron dializability (7.7, 4.9 and 1.4%, respectively). However, the use of amaranth flour was effective in increasing iron uptake to intestinal epithelial (Caco-2) cells.

Environmental and management factors have been found to exert a great effect on variation of micronutrient concentrations in wheat (Cakmak *et al*., 2000). It also appears that concentrations of protein in seeds are strongly and positively correlated with the concentrations of iron and particularly of zinc. Thus, pseudocereals might not only serve as an important source of micronutrients, but also breed genetic material for increasing micronutrient concentrations in seeds.

10.6 Hypocholesterolemic Properties

Pseudocereals have received increased attention because of their favourable hypocholesterolemia activity, in relation to which several hypotheses (unsaturated fatty acids, amino acid profile, phytochemicals and the amount of total and soluble fibre) have been proposed to explain this. It is one of pseudocereal's most frequently cited qualities. Diverse experimental attempts and intervention trials have been conducted to support the cholesterol-lowering activity of amaranth (Lucero López *et al*., 2013; Caselato-Sousa *et al*., 2014), quinoa (Paśko *et al*., 2010a; De Carvalho *et al*., 2014) and buckwheat (He *et al*., 1995; Zhang *et al*., 2007).

In a model of dyslipidemic rabbits, it was shown that concurrent intake of heat-expanded amaranth with a hypercholesterolemic diet decreased cholesterolemia and rectified endothelial dysfunction that occurs associated to an increased faecal cholesterol excretion (Caselato-Sousa *et al*., 2014). Moreover, feeding amaranth to rats showing more severe hyperlipidemic and hepatic steatosis conditions due to alcohol abuse reduced fat deposits and alterations in the lipid metabolism (Lucero López *et al*., 2013). Additional data not only from experimental models (Paśko *et al*., 2010a), but also prospective and double-blind intervention studies for 4 weeks conducted on overweight women demonstrated that consumption of 25 g of quinoa flakes significantly reduced serum triglyceride, total cholesterol and LDL-cholesterol (De Carvalho *et al*., 2014). In relation to buckwheat, it has been claimed that the cholesterol-lowering activity is mediated by its influence increasing faecal excretion of bile acid and neutral sterols probably attributable to its poor protein digestibility (Kayashita *et al*., 1997; Tomotake *et al*., 2000). Thus, several different experimental models have also revealed buckwheat's beneficial effects favouring hypocholesterolaemia (Tomotake *et al*., 2006, 2007). However, information on the cholesterol-lowering activity of buckwheat in humans is relatively scarce (He *et al*., 1995; Zhang *et al*., 2007).

Recent experimental models have associated the administration of quinoa to mice fed a high-fat diet with metabolic effects beyond the positive changes in lipid profile. Feeding quinoa increased energy expenditure and favoured the oxidative metabolism of glucose, thus impairing lipogenesis and leading to reduced fat accumulation in adipose tissue (Foucault *et al*., 2014). Taken together with the apparently positive effects, reducing intestinal inflammation might suggest a potential role of pseudocereals in liver-related disorders such as nonalcoholic fatty liver disease (NAFLD) where the participation of a second inflammatory hint appears to have an enormous influence in the onset of the disease. Moreover, obesity and obesity-related insulin resistance affect iron homeostasis in many different ways; iron deficiency and anemia are frequent findings in subjects with progressed obesity, and hyperferritinemia with normal or mildly elevated transferrin saturation appears highly prevalent in patients with metabolic syndrome or NAFLD.

10.7 Antioxidant Activity of Pseudocereals

Prospective food intake studies reveal that imbalances in cell redox status, potentially motivated by the gluten-free diet, are implied at different levels of inflammation and maturation or function of immune cells and skin and intestinal barriers (Cilla *et al*., 2015).

In vitro antioxidant activity has been reported in both extracts and byproducts obtained from pseudocereals (Paśko *et al*., 2009; Laus *et al*., 2012). In addition, this *in vitro* antioxidant capacity in both seeds and sprouts of amaranth and quinoa has been reported to take place through their radical scavenging capacity and the reduction of lipid peroxidation. Chemical composition analyses have demonstrated that buckwheat (*Fagopyrum esculentum*) possess higher of contents of ascorbic acid and total phenolic compounds than amaranth and quinoa as well as barley, wheat and oats (Gorinstein *et al*., 2008; Zielińska and Zieliński, 2009). Several components (flavones, phenolics, ascorbic acid) have been suggested as responsible for the antioxidant features of the pseudocereals. Extrusion, toasting or popping are operations that do not cause significant changes in antioxidant capacity of pseudocereals in relation to lipid oxidation; however, phenolics are affected by heat processing and reduce the antioxidant properties of food.

The pseudocereals' biological antioxidant capacity is further supported by *in vivo* experimental models fed 80% methanol extracts of *Rhizopus oligosporus*-fermented quinoa (Matsuo *et al*., 2005), a buckwheat-containing diet (310 g/kg for 9 weeks) (Zagrodzki *et al*., 2007) or a buckwheat by product-enriched diet (15% for 4 weeks) (Zduńczyk *et al*., 2006). The results showed the positive influence increasing the activity of important antioxidant enzymes as well as reducing lipid peroxidation parameters in plasma samples and red blood cells and several different organs (heart, kidney, liver and brain). Moreover, the concurrent administration of amaranth (310 and 155 g/kg of diet) and quinoa (310 g/kg fodder) has also demonstrated the antioxidant features mentioned above in animals fed a high-fructose diet to induce oxidative metabolic stress (Paśko *et al*., 2010b, 2011). Similarly, buckwheat grains exerted antioxidant effects in the livers of diet-induced obese rats (Kim *et al*., 2012).

The antioxidant features of pseudocereals also appear to be reflected in human intervention studies in relation to buckwheat. There have been reported increases in the total antioxidant capacity of plasma samples from healthy donors after the consumption of 1.5 g of buckwheat honey/kg (single dose, n = 37) (Schramm *et al*., 2003) or when buckwheat honey was added to water or black tea (160 g honey/L, n = 25) (Gheldof *et al*., 2003) as well as buckwheat-enriched wheat bread (Bojňanská *et al*., 2009). At this point it is important to indicate that according to the guidance on scientific requirements for health claims related to antioxidants, oxidative damage and cardiovascular health drafted by the Panel on Dietetic Products, Nutrition and Allergies (NDA) of the European Food Safety Authority (EFSA) (EFSA, 2011) concentrations of MDA or lipid peroxides in blood or tissue are not reliable *in vivo* markers of lipid peroxidation and can only be used as supportive evidence in addition to measurements of F_2-isoprostanes and *in vivo* LDL oxidation.

10.8 Potential of Pseudocereals against Cancer

Epidemiological studies have associated the regular consumption of whole-grain cereals or foods based on these with a reduced risk of suffer degenerative chronic diseases such as inflammation and cancer (Shen *et al*., 2008; Tantamango *et al*., 2011).

Inflammation represents a carefully orchestrated manoeuvre by the immune system to eliminate harmful environmental insults, injured cells and chemical irritants. While we might not be able to live without it, too much inflammation can cause serious damage and constitutes a powerful force in cancer development.

Plant-derived biologically active phytochemicals have been linked to antiproliferative effects on cancer cells, motility and cellular competence for gap junctional communication (Gawlik-Dziki *et al*., 2013). Flavonoids (Ren *et al*., 2001; Ren *et al*., 2003), polysaccharides (Wu and Lee, 2011) and phenylpropanoids (Zheng *et al*., 2012), extracts of buckwheat, have also shown to induce apoptotic processes against different leukemic cancer cell lines (HL-60 and THP-1) *in vitro*. Rutin and its aglycone quercetin have shown chemopreventive effect against a wide range of colorectal cancer cell lines (Araújo *et al*., 2011). These compounds are able to inhibit cell growth, by inducing cell-cycle arrest and / or apoptosis, inhibiting proliferation, angiogenesis, and / or metastasis, and exhibiting anti-inflammatory and / or antioxidant effects at concentrations as low as 0.5 µmol/L. The red clover flavone (5–10 g/L) from golden buckwheat can also inhibit the migration ability of human gastric cancer SGC7901 cells (Zhang *et al*., 2013). Ethanol extract from quinoa leaves exerted an inhibitory effect on rat prostate cancer AT-2 cell proliferation and motility (Gawlik-Dziki *et al*., 2013). Recent data support the anti-inflammatory activity of saponins from quinoa seeds in lipopolysaccharide-stimulated mouse macrophages (RAW 264.7 cells) (Yao *et al*., 2014). A critical overview of *in vitro* studies related to the potential antiproliferative effects clearly points out that the concentrations used in these studies are much higher than the potential reachable physiological concentration.

Moreover, cereal-derived peptides such as lunasin have received the most attention and appear to exert their action through different molecular mechanisms from those of phytochemicals (Silva-Sánchez *et al*., 2008; Ortiz-Martinez *et al*., 2014). Lunasin seemed to exert biological effects at the genomic level, inhibiting colony formation and histone acetylation in mouse (stably *ras* oncogen transfected) fibroblasts NIH3T3 and MCF-7 human breast cancer cells (Jeong *et al*., 2002), as well as inhibiting the cyclooxygenase-2 and inducible nitric oxide synthase associated with the inhibited activation of the nuclear transcription factor kappa B (de Mejia and Dia, 2010). Similarly, the MPI protein isolated from *A. mantegazzianus* showed an antiproliferative effect with osteoblasts (MC3T3E1 and UMR106) and intestinal cancer cell lines (Caco-2, and TC7) (Barrio and Añón, 2010). Proteins and peptides from buckwheat have also been shown to exert antiproliferative effects on a wide range of cancer cell lines (Leung and Ng, 2007). These effects are associated with downregulation of the expression (mRNA) of genes (*c-myc* and *c-fos*) involved in colon cancer development (Buzzi *et al*., 2009) as well as increased DNA fragmentation and expression of cytosolic cytochrome c, proapoptotic factors such as Bax and Bak, caspase-3 and -9 activity and disruption of mitochondrial membrane potential (Li *et al*., 2009; de Mejia and Dia, 2010).

Data from a few experimental models demonstrate the anti-inflammatory (Ishii *et al*., 2008) and anticarcinogenic (Liu *et al*., 2001) effects of buckwheat sprouts and extracts. Oral administration of buckwheat sprouts (ExtBS) was found to exert significant anti-inflammatory activity, reducing the production of IL-6 and TNF- in mice treated with the potent inflammatory lipopolysaccharide (LPS) from gram-negative bacteria (Ishii *et al*., 2008). IL-6 stimulates inflammatory and autoimmune processes in many diseases and has been found at higher levels in patients suffering advanced / metastatic cancers. Dietary buckwheat protein (net protein level, 200 g/kg; n=20/group, for 124 days) has

demonstrated its protective effects against 1,2-dimethylhydrazine-induced colon carcinogenesis in rats by reducing cell proliferation (Liu *et al.*, 2001). However, the potential contribution of several different buckwheat (*Fagopyrum esculentum* Moench)-derived compounds can be assumed because different fractions (dosed at 25–50 mg/kg) obtained with n-hexane, chloroform, ethyl acetate, but not with water from a 70% ethanol extract, were able to decrease (by 20% and 42%, respectively) tumour formation in sarcoma-180 implanted Balb/c mice (Kim *et al.*, 2007).

The identity of biologically active components in cereals and pseudocereals responsible for the effects observed remains unknown and therefore the exact underlying molecular mechanisms are also unknown. Considering the existing data, future research could be directed to determine the potential metabolic transformation of biologically active components derived from pseudocereals by environmental factors such as gut microbiota and the proportion of those able to reach the target organs.

10.9 Conclusions

Cereal and pseudocereal consumption has been linked to a wide spectrum of beneficial effects beyond its mere nutritional value and in relation to immune, inflammatory, antioxidant and metabolic disorders, including preventive anticancer effects. Many of these beneficial effects have been associated with their prebiotic effect but also with particular biologically active compounds. Newly discovered mechanisms of action may be responsible for these effects. However, some of the current studies did not take into consideration key aspects such as the bioavailability of the bioactive compounds. These studies used higher concentrations than were physiologically relevant. Future studies therefore need to be carefully designed so that the results can help to clarify the cellular and molecular mechanism underlying the beneficial effects attributed to individual components of pseudocereals. The important consequences for health derived from the consumption of pseudocereals and the remaining open questions, such as the extent to which they can contribute to improving human health, deserve further studies in humans.

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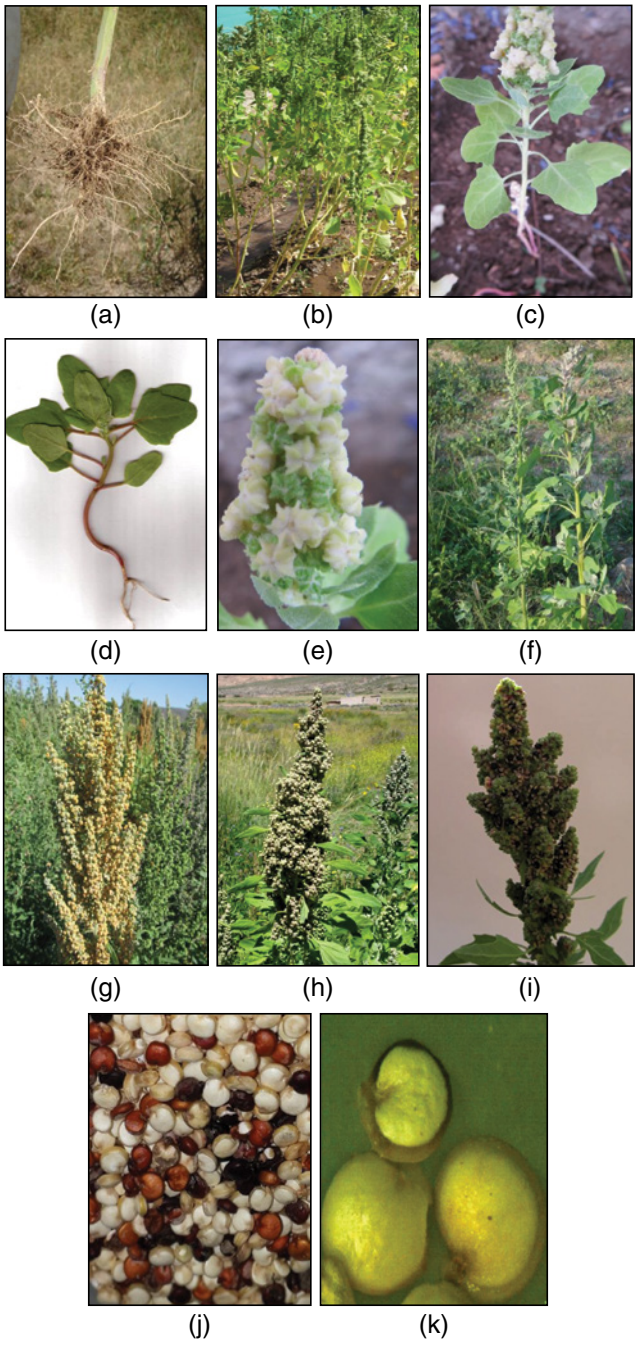

Figure 1.1 Development of quinoa plant: (a) taproot branched; (b) stem branched; (c) stem unbranched; (d) simple leaves; (e) small flowers; (f) panicle in training; (g) panicle amaranthiform; (h) compact panicle ; (i) mature panicle; (j) quinoa seeds; (k) seed.

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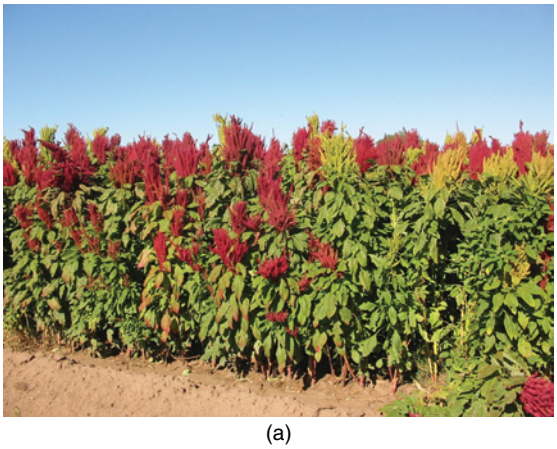
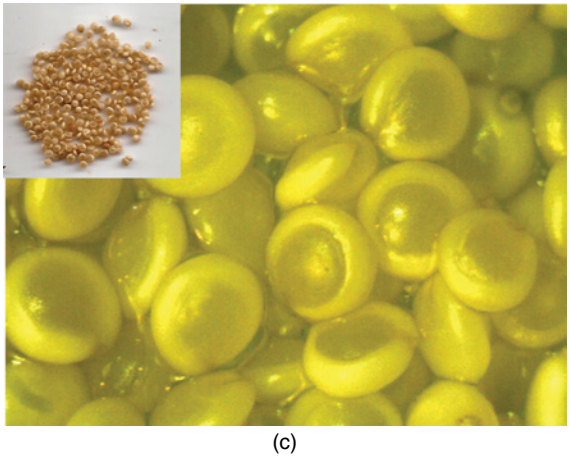
Figure 1.2 Quinoa cultivation, harvest and diseases: (a) quinoa in the South American Andes; (b) manual tools; (c) vegetable seeders; (d) fine grain seeders; (e) grain maturation; (f) harvest; (g) mildew; (h) abrupt leaf fall.



(a)

(b)



(c)

Figure 1.3 (a) Cultivation of amaranth; (b) inflorescence of amaranth; (c) amaranthus seeds.

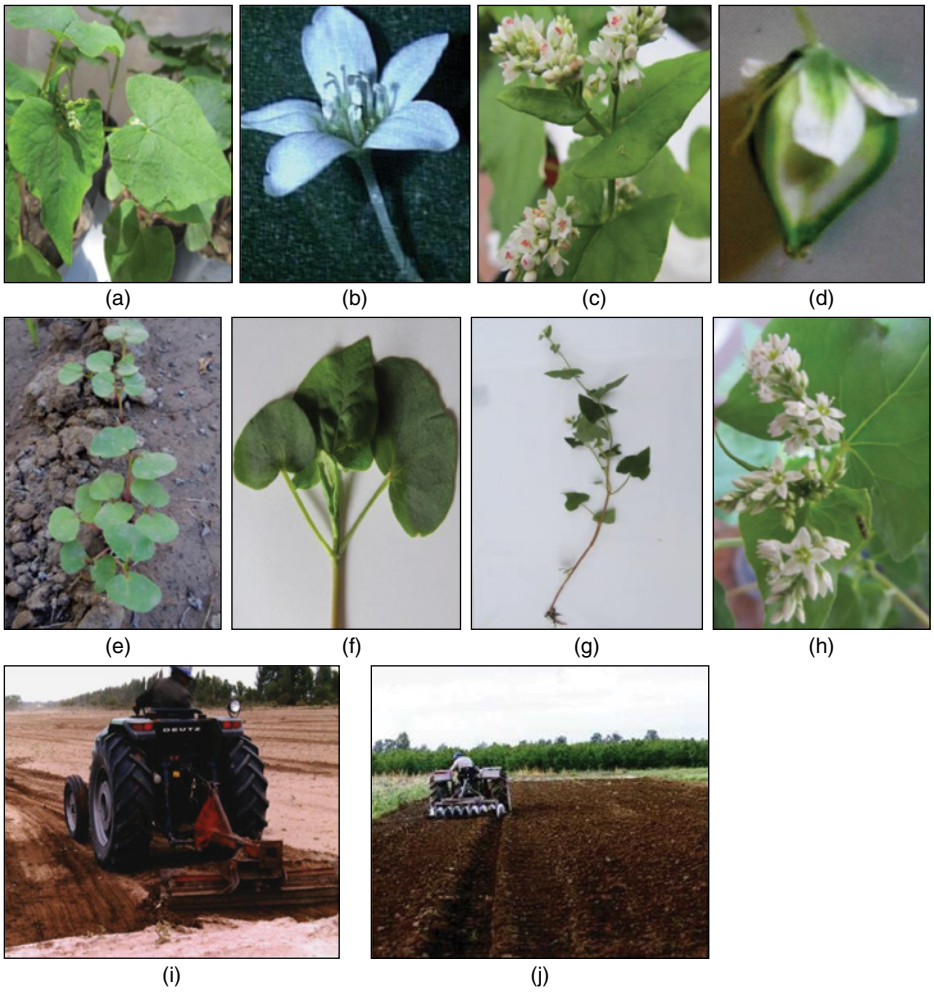
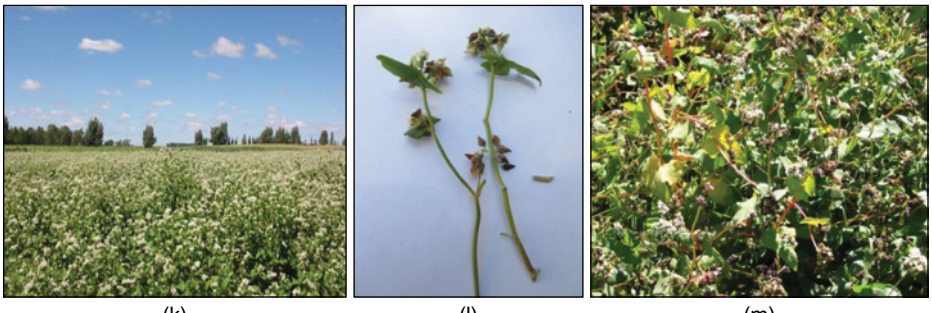


Figure 1.4 Buckwheat: (a) simple leaves; (b) hermaphrodite flower; (c) inflorescence; (d) fruit achene; (e) emergence; (f) first leaves; (g) branches begin; (h) corymbose; (i) levelling; (j) soil preparation; (k) crop uniformity; (l) forms the fruits; (m) seed is mature; (n) harvest; (o) clean fruit.



(k) (l) (m)

(n) (o)

Figure 1.4 (Continued)

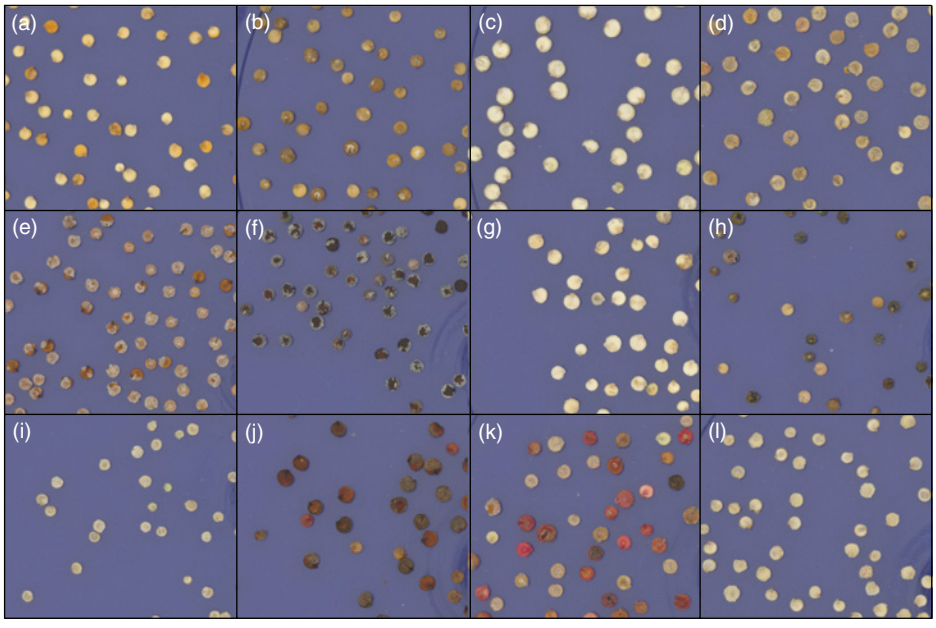


Figure 2.3 Quinoa seeds are diverse in size (1–2.6 mm), colour (green, white, off-white, opaque white, yellow, bright yellow, orange, pink, red vermilion, cherry, coffee, gray and others), composition and shape (conical, cylindrical or ellipsoidal). (a) PI 510535; (b) PI 614987; (c) PI 614916; (d) PI 614886; (e) PI 614880; (f) PI 510549; (g) PI 510544; (h) PI 510536; (i) PI 510533; (j) PI 478415; (k) PI 470932; (l) PI 433232; accessions were obtained from the US National Plant Germplasm System (ARS-USDA, United States).

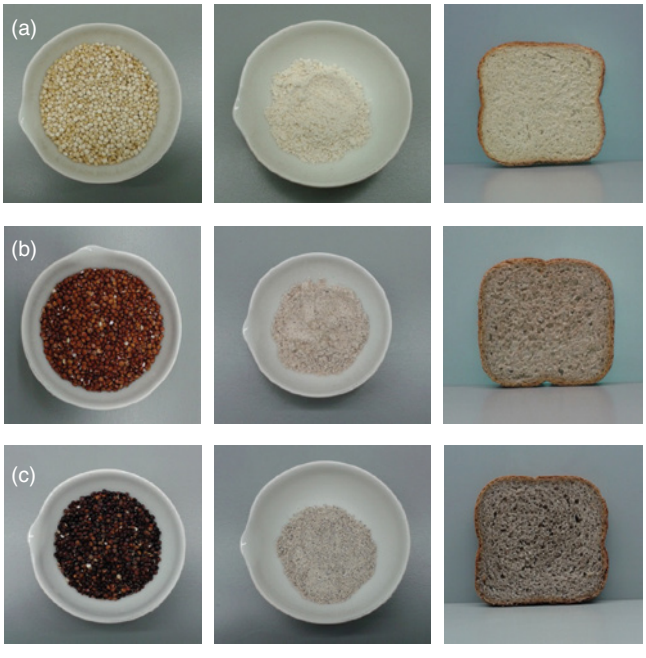


Figure 7.1 Quinoa grains, whole flour and crumb bread with 25% quinoa flour: (a) white quinoa; (b) red quinoa; (c) black quinoa.

Figure 7.5 Fractions obtained by quinoa wet-milling: (a) red quinoa; (b) fraction rich in Hull; (c) fraction rich in Germen and fibre; (d) fraction rich in protein; (e) fraction rich in starch (Gonzalez-Roberto *et al*., 2015).

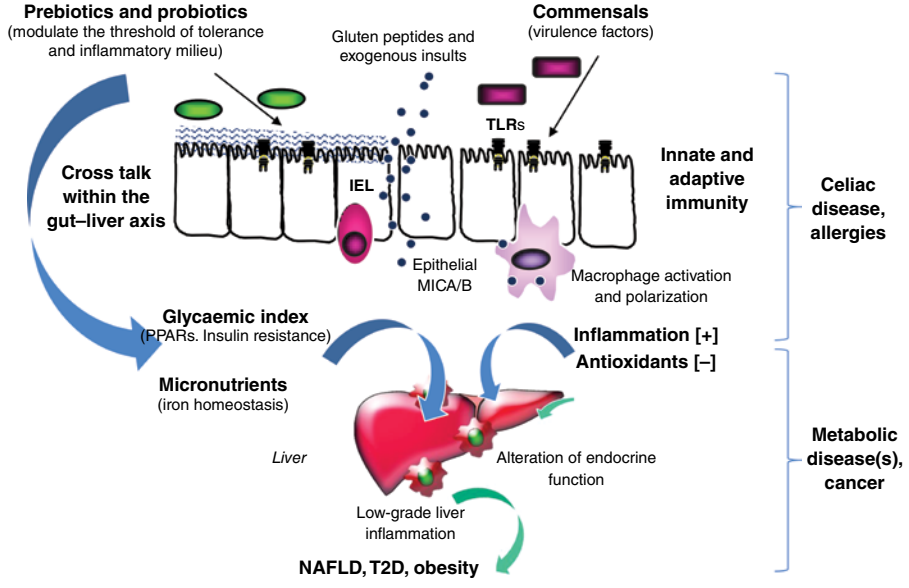


Figure 10.1 Functional interrrelationships within the gut–liver axis that can be modulated by biologically active compounds from pseudocereals.

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