Bioactive Compounds in Quinoa (*Chenopodium quinoa*) and Kañiwa (*Chenopodium pallidicaule*)

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Abstract

Quinoa (*Chenopodium quinoa* Willd.) and kañiwa (*Chenopodium pallidicaule*) are very nutritious crops native to the Andean region of South America. Both grains contain good-quality proteins and micronutrients such as iron, calcium and vitamins. Their fat content is relatively high, making them a source of essential fatty acids and tocopherols. Kañiwa has a particularly high dietary fibre content, thus being beneficial for human health. Quinoa and kañiwa seeds are major sources of flavonoids which consist mainly of glycosides of the flavonols kaempferol and quercetin. Processing Andean grains can lead to changes in the content of beneficial bioactive compounds; precautions must thus be taken to avoid losses. The traditional way to process Andean grains is cooking and roasting. It has been reported that it is possible to maintain the level of phenolic compounds in quinoa after cooking, if the cooking water is not discarded. Heat treatments can cause the release of phenolic compounds from the grain matrix, making them more bioavailable. During the milling of Andean grains, the bran fraction should be collected and used in food products because the majority of bioactive compounds are concentrated in this fraction.

Keywords

Pseudocereals · Native crops · Phenolic compounds

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12.1 Introduction

The Andean area of South America is an important centre of domestication of edible crops. The great diversity of landscapes and agro-ecological zones is due to the variation in climate and altitude (1500–4200 m above sea level). In this area, it is very difficult to find flat, fertile and well-watered soil. The people in Andean areas have cultivated their crops for centuries on small plots on mountainsides rising thousands of metres. At the time of the Spanish invasion, the Incas cultivated and used almost as many species of crops as the farmers in Asia and Europe. It has been estimated that Andean native peoples domesticated as many as 70 separate crop species (National Research Council 1989). The cultivation of many of these plants was reduced dramatically after the arrival of the Europeans. Until recently, these plants have been neglected and have not received major scientific or commercial interest.

Quinoa (*Chenopodium quinoa* Willd.) is a seed crop of the Amaranthaceae family. It was a very important crop for the ancient cultures of Peru and Bolivia. 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 varieties and landraces of quinoa, which have adapted to distinct environmental conditions, for example, to high plateau, Andean valley and coastal areas. The seeds of quinoa are small, about 2 mm in diameter, and can be of various colours: white, cream, purple, yellow, red or black (Fig. 12.1a, b).

Kañiwa (*Chenopodium pallidicaule* Aellen) is a relative of quinoa, and it was considered a variety 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*, and is more resistant than quinoa to frost. In its native area, the temperature average is less than 10 °C, and frost can occur for at least 9 months of the year. For highland farmers, kañiwa is very important because it is the only crop that can resist during the frost. The most intensive production of kañiwa occurs in the southern Andes of Peru and Bolivia in the surroundings of Lake Titicaca. Kañiwa is a small plant and its seeds are smaller (approx. 1 mm) than those of quinoa. They are usually grey or brown, but there are some coloured ecotypes as well (Fig. 12.1c, d).

12.2 Nutritional Composition and Bioactive Compounds

Table 12.1 shows the proximate composition of quinoa and kañiwa seeds. The protein content of quinoa samples ranges between 13 and 17.9%, the black variety having the highest values. In the case of kañiwa, these values are between 14.4 and 16.9%. The protein of both grains is of good biological quality because of the balanced essential amino acid composition, especially because of the high lysine content. Quinoa protein is higher not only in lysine but in another important essential amino acid, methionine, than any other cereal (Arendt and Zannini 2013). These amino acids are especially important for vegetarian or vegan diets because they are

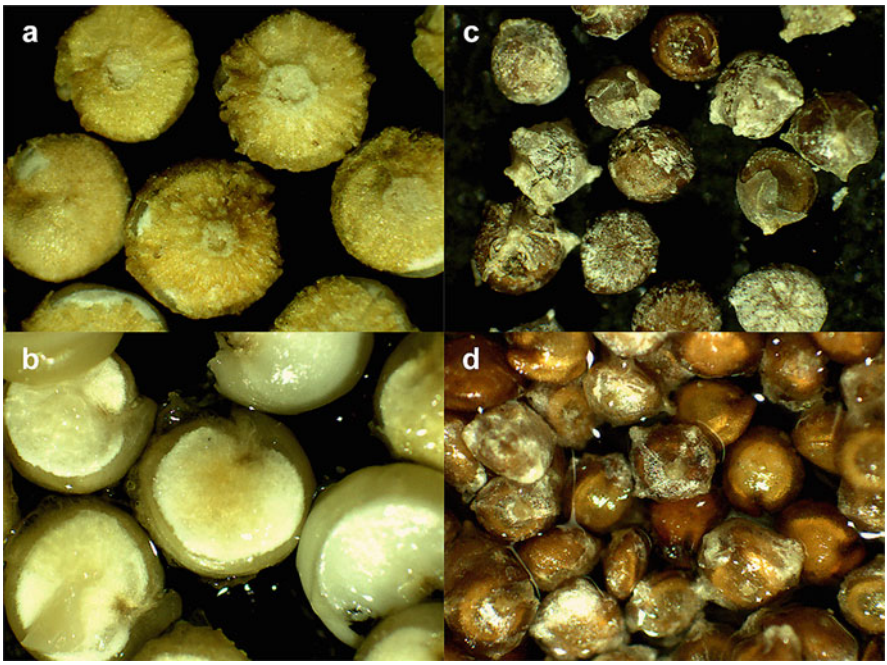

Fig. 12.1 Quinoa grain Amarilla Sacaca variety: (**a**) raw and (**b**) washed. Kañiwa grain Cupi variety: (**c**) raw and (**d**) washed (R. Repo-Carrasco-Valencia Unpublished)

limiting amino acids in vegetable proteins: cereals are limiting in lysine and legumes in methionine. Thus, quinoa and kañiwa can be used as a complement in products based on cereal and legume proteins.

Bioactive peptides in Andean grains have been studied by Chirinos et al. (2018) and Vilcacundo et al. (2017). These peptides show antidiabetic, antioxidant and antihypertensive properties in vitro. These results indicate that seed protein is a potential source of bioactive peptides that could be used as raw material in the nutraceutical and functional food markets.

The fat content of all the grains is between 5.7 and 7.3%, and it is mainly located in the embryo. The oil content in Andean grains is considerably higher than that in common cereal grains (6–7% versus 2–4%, respectively). The oil in Andean grains is of high nutritional quality, containing the essential fatty acids linoleic and linolenic acids in adequate proportions. A diet with a high n-6/n-3 ratio (linoleic/linolenic acid ratio) can promote many chronic diseases, such as cardiovascular disease, cancer and osteoporosis, as well as inflammatory and autoimmune diseases. An increased n-3 fatty acid intake in diet reduces the biological markers associated with the above-mentioned diseases. The current n-6/n-3 ratio in Western countries has been estimated to be in the range 14:1–20:1 and is far from the recommended levels of 5:1–10:1. Quinoa's n-6/n-3 ratio, at 6.2, falls within the recommended

Table 12.1 Proximate composition of quinoa and kañiwa varieties

Grain	Moisture (g/100 g dw)	Fat (g/100 g dw)	Protein (g/100 g dw)	Crude fibre (g/100 g dw)	Ash (g/100 g dw)	Carbohydrates (g/100 g dw)
Black quinoa[a]	10.9	7.0	17.9	4.2	3.1	72.1
White quinoa Kancolla variety[a]	11.6	6.8	13.0	2.3	3.2	76.9
White quinoa INIA Salcedo variety[a]	10.6	7.3	14.4	2.5	2.6	75.7
Kañiwa, commercial sample[a]	11.2	8.9	16.9	4.9	3.8	70.2
Kañiwa Cupi variety[b]	10.4	5.7	14.4	11.2	5.0	63.6
Kañiwa Ramis variety[b]	11.8	7.0	14.9	8.2	4.3	65.6

[a]Data from Repo-Carrasco-Valencia et al. (2019)
[b]Data from Repo-Carrasco-Valencia et al. (2009). *dw* dry weight

Table 12.2 Dietary fibre in Andean grains

Sample	TDF (g/100 g)	IDF (g/100 g)	SDF (g/100 g)
Black quinoa/Negra Collana	18.06	16.10	1.95
Quinoa/white grain from highlands	12.35	11.12	1.22
Quinoa/white grain from coast	8.35	6.43	1.91
Quinoa/Kancolla	9.94	7.81	2.14
Quinoa/INIA Salcedo	12.33	9.38	2.95
Kañiwa/commercial	20.85	18.29	2.56

Data from Repo-Carrasco-Valencia et al. (2019). *TDF* total dietary fibre, *IDF* insoluble dietary fibre, *SDF* soluble dietary fibre

values (Alvarez-Jubete et al. 2009). Quinoa and kañiwa could serve as raw materials to produce healthy edible oils.

The total carbohydrate content in common cereals and Andean grains is similar at about 60–75%, starch being the main carbohydrate in all of these grains. The starch found in Andean grains has some very interesting chemical and rheological properties, which could have industrial applications, for example, in gluten-free baking (Vidaurre-Ruiz et al. 2020).

Andean grains are important sources of dietary fibre as can be seen in Table 12.2. Kañiwa is especially high in this compound. The highest dietary fibre content is found in black quinoa. The fibre is mainly insoluble, as is common in all grains. Varietal differences in dietary fibre content are common in grains. This variation

Table 12.3 Pentosan content in Andean grains

Sample	Dry matter	Pentosans % dw
Quinoa/Negra Collana	90.23	1.91
Quinoa/white grain from highlands	90.24	2.20
Quinoa/white grain from coast	90.82	1.85
Quinoa/Kancolla	88.48	1.87
Quinoa/INIA Salcedo	88.85	1.70
Kañiwa/commercial	89.55	2.35

Data from Repo-Carrasco-Valencia et al. (2019). *dw* dry weight

may be related to environmental conditions, such as soil nutrient content and water availability. Interactions between the genotype and environment may occur, resulting in different impacts on the concentrations of components (Shewry 2009).

Pentosans are one of the important soluble dietary fibre components in cereals. They consist mainly of the pentosan sugars L-arabinose and D-xylose. Pentosans decrease the absorption of lipid and cholesterol in the human body and can help to prevent cardiovascular diseases. They have a positive effect on food processing as well, for example, on dough rheological characteristics and in macaroni processing. Table 12.3 presents the pentosan content in Andean grains.

Quinoa and kañiwa are particularly good sources of tocopherols (Repo-Carrasco et al. 2003). Tocopherols are compounds with high antioxidant capacity and other important physiological functions; some of them have the function of vitamin E. Tocopherols exist as four different isomers with antioxidant power, that is, in decreasing order, $\delta > \gamma > \beta > \alpha$. Both grains have α-tocopherols and γ-tocopherols, γ-tocopherols being the main compounds. Black quinoa and kañiwa seem to be the best sources of these compounds (Repo-Carrasco-Valencia et al. 2019). The tocopherol content in quinoa and kañiwa is superior to that in common cereals.

Schoenlechner et al. (2010) analysed the folate content in quinoa and its products. They found that the content of this vitamin was 0.13 μg/100 g, about ten times as much as in wheat. The bran fractions contained on average 124% of total folate, while only 57% on average was present in the flour fractions. Repo-Carrasco-Valencia et al. (2019) analysed folic acid in quinoa and kañiwa samples and found 20–47 μg/100 g in different varieties.

Quinoa and kañiwa are good sources of some important minerals such as calcium, magnesium and iron (Kozioł 1992; Repo-Carrasco-Valencia et al. 2019). According to Nascimento et al. (2014), 100 g of quinoa could contribute more than 50% of the dietary reference intake of copper, iron, manganese, magnesium and phosphorus established by the Institute of Medicine (IOM) of the U.S. National Academies.

Like most grains, quinoa contains phytic acid. Phytate forms complexes with multivalent metal ions such as iron, calcium, magnesium and zinc, reducing their bioavailability. According to Ruales and Nair (1993), the phytic acid content in quinoa seeds is about 1% of the dry matter. Scrubbing and washing reduce the phytic acid content of the seeds by about 30%. These authors detected neither protease inhibitors nor tannins in grains.

Repo-Carrasco et al. (2010) studied the effect of wet and dry processing on the iron, calcium and zinc content of raw and processed seeds. Regarding zinc and calcium, quinoa grains contained the highest levels of both minerals. There was a significant decrease in iron content during the cooking process in all samples. Wet processing procedures in general cause a loss of dry matter and iron. Cooking reduced the zinc content in quinoa and kañiwa. Roasting negatively affected the calcium content in quinoa but not in kañiwa.

Quinoa contains saponins which are glycosylated secondary metabolites found in many plants. Saponins are soluble in methanol or water. They produce stable foams in aqueous solutions and haemolyse red blood cells (Ruales and Nair 1993). Seed contains three or four different sapogenins, oleanolic acid, hederagenin, phytolaccagenic acid and sometimes deoxyphytolaccagenic acid, depending on the variety (Ridout et al. 1991; Cuadrado et al. 1995). Glucose, arabinose and occasionally galactose are the sugars bound to the sapogenins. Saponins are considered to be antinutritional compounds; however, they have some interesting health-promoting properties such as reducing serum cholesterol levels, possessing anti-inflammatory and antioxidant activity and exhibiting insecticidal, antibiotic and fungicidal properties.

Polyphenol compounds have been extensively researched for health-promoting properties such as their role in the prevention of degenerative diseases which include cancer and cardiovascular disease. The most important phenolic compounds in cereals are phenolic acids, alkylresorcinols and flavonoids. These phytochemicals in whole grains are complementary to those in fruits and vegetables when consumed together. Quinoa and kañiwa seeds are abundant sources of flavonoids, which consist mainly of glycosides of the flavonols kaempferol and quercetin (Peñarrieta et al. 2008; Alvarez-Jubete et al. 2010b). Kañiwa is exceptionally rich in resorcinols, compounds not very common in plants. Of the major cereals, resorcinols have been reported to be present 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. ARs have also been reported to have antioxidant activity (Ross et al. 2003).

Repo-Carrasco et al. (2010) studied the profile of phenolic compounds in quinoa and kañiwa varieties. The flavonoid content of *Chenopodium* species was exceptionally high, varying from 36.2 to 144.3 mg/100 g. The predominant flavonoids in quinoa samples were quercetin and kaempferol, while 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. Both in phenolic acid and flavonoid contents, much variation was found between different samples (varieties). Berries have been considered as an excellent source of flavonols, especially quercetin and myricetin. When compared on a dry weight basis, the flavonoid content in berries and *Chenopodium* samples are of the same magnitude.

Pilco-Quesada et al. (2020) studied the effect of germination and kilning on the phenolic compound content in quinoa and amaranth. Altogether, 21 phenolic

compounds, mainly hydroxybenzoic acids, hydroxycinnamic acids and flavonols, were identified in the samples. The main flavonols were quercetin and kaempferol. Hydroxycinnamic acids identified from seeds mainly contained derivatives of coumaric and ferulic acids. Hemalatha et al. (2016) and Tang et al. (2015) quantified hydroxybenzoic acid derivatives from the extracts of (white, red and black) quinoa grains at high levels; these included gallic acid, *p*-hydroxybenzoic acid, 3,4-dihydroxybenzoic acid, vanillic acid and vanillic acid 4-glucoside. Abderrahim et al. (2012) studied the effect of germination on total phenolic compounds, total antioxidant capacity, Maillard reaction products and oxidative stress markers in kañiwa. They found that germination can enhance the total antioxidant capacity in kañiwa. Based on these studies, germination can improve the nutritional composition of Andean native grains by increasing the total phenolic compound content. The results encourage the application of germinated and kilned quinoa as potential ingredients for the development of innovative and nutritious products.

Plant sterols (phytosterols) are another group of biologically active components present in pseudocereal lipids. Phytosterols, which cannot be absorbed in the human intestine, have a very similar structure to cholesterol and inhibit intestinal cholesterol absorption, thereby lowering plasma total and low-density lipoprotein (LDL) cholesterol levels (Alvarez-Jubete et al. 2010a). Phytosterols have also shown antiviral and anti-tumour activity (Li and Zhang 2001). Black quinoa and kañiwa seem to be interesting sources of phytosterols (Repo-Carrasco-Valencia et al. 2019).

12.3 Effect of Processing on the Phenolic Compounds

The ways of consuming quinoa and kañiwa are very varied, and they can be consumed in the form of cooked whole grain or as flour to prepare snacks, bakery products, noodles, stews, desserts, drinks and soups (Repo-Carrasco-Valencia and Vidaurre-Ruiz 2019). As is known, the processing of food for consumption causes certain changes in the food matrix, and this can promote the increase or degradation of phenolic compounds.

12.3.1 Washing and Desaponification

The first stage of the processing to which the quinoa and kañiwa grains are subjected consists of the elimination of saponin and some waste such as dirt and sticks; this process can be carried out by using water or abrasion. Washing seeds with water for 15 min has been reported to increase the content of total phenolic compounds by 19.6% (116.77 $\pm$ 4.80 mg GAE/100 g dw) (Nickel et al. 2016), basically due to the release of bound bioactive compounds, which may be present in a good proportion in quinoa (Tang et al. 2016b). Although washing can be considered promising to increase the content of bioactive compounds, this process is often inefficient because a lot of water is wasted when it is necessary to eliminate the saponin from some bitter varieties of quinoa such as the *Amarilla sacaca* variety.

The pearling process (<15.89%) has also been reported to be appropriate for removing saponin from the grain and for maintaining its phytochemicals. With this percentage of abrasion, a 23.8% loss of total phenolic compounds (152.70 ± 1.20 mg GAE/100 g dw) and a 22.9% loss of flavonoids (173.10 ± 5.27 mg CE/100 g DW) are achieved (Han et al. 2019). Similar results have been reported by Gómez-Caravaca et al. (2014), who reported a small reduction of total free phenolic compounds, from 261.04 to 204.87 mg/100 g, and bound phenolic compounds, from 16.46 to 10.66 mg/100 g, when grains are pearled by 30%. The individual phenolic compounds that are lost the most during the pearling process are gallic acid, protocatechuic acid, chlorogenic acid, caffeic acid and vanillin (Han et al. 2019), although there is an increase in *p*-coumaric acid and certain flavonoids such as kaempferol, which can be present in the inner layers of the grain (Gómez-Caravaca et al. 2014).

12.3.2 Drying

After the washing process, an alternative to remove water from the grain is drying with hot air. It has been reported that drying of grains at high temperatures such as 60, 70 and 80 °C, respectively, with an air velocity of 2.0 ± 0.2 m/s, produces a notable loss of phenolic compounds; however, this does not affect the antioxidant capacity, since high antioxidant capacity has been reported when seeds are dried at 80 °C (Miranda et al. 2010). This effect may be related to the generation and accumulation of different antioxidant compounds which could show greater antioxidant capacity. Multari et al. (2018) expanded the research on the phenolic compounds present in grains (cultivated in Finland) after the drying process at temperatures of 40, 50, 60 and 70 °C, finding that the heat caused the degradation of free phenolic acids. The authors reported that the drying process carried out at 70 °C allowed the greatest recovery of total phenolic compounds, showing the presence of gallic acid at that process temperature.

12.3.3 Cooking

Another alternative in the processing of quinoa is that after washing, it is cooked so that the grain can be consumed. Dini et al. (2010) reported significant losses of total phenolic compounds and flavonoids when it is cooked in a 1:10 ratio (grains/water) for 20 min. The authors reported phenolic compound losses of 62.8% for sweet quinoa (28.7 ± 2.8 mg GAE/10 g dw) and 31.2% for bitter quinoa (59.4 ± 23.0 mg GAE/10 g dw); flavonoid compound losses were 77.8% for sweet quinoa (1.8 ± 0.7 mg CE/10 g dw) and 54.7% for bitter quinoa (6.3 ± 1.5 mg CE/10 g dw).

Nickel et al. (2016) reported that cooking grains for 11 min at atmospheric pressure, in a 1:3 ratio (grains/water), can increase total phenolic compounds by 13.5% (110.65 ± 3.43 mg GAE/100 g dw) and that cooking in a pressure cooker for

6 min can increase the total phenolic compound content in quinoa by up to 30.8% (127.54 ± 7.22 mg GAE/100 g dw).

A lower raw material/water ratio (1:1) during cooking has been reported by Rocchetti et al. (2019); the authors reported that it is possible to maintain the level of total phenolic compounds after cooking for 15 min (70.3 ± 2.5 mg GAE/100 g dw), being mainly flavonoids, phenolic acids and other polyphenols such as alkylphenols and hydroxyphenylpropenes, responsible for the differences in phenolic profile during cooking. These authors postulated that heat treatment is responsible for the solubilization of some flavonoids in the cooking water.

12.3.4 Germination and Malting

Germination has proven to be an efficient and economical process to increase the phenolic compound content in grains (Alvarez-Jubete et al. 2010b; Abderrahim et al. 2012). An increase in total phenolic compounds of more than 100% (147.2 mg GAE/100 g dw) has been reported when sprouted at 10 °C for 84 h. Specifically, a more than 50% increase in flavonoids such as kaempferol glycosides (56 μmol/100 g) and quercetin (66.6 μmol/100 g) has been reported compared to non-germinated grain (Alvarez-Jubete et al. 2010b). Paucar-Menacho et al. (2018) reported that the optimum temperature and germination time are 20 °C and 42 h, respectively. Under these conditions, the total phenolic compound content can almost double. Specifically, the researchers identified the formation of *trans*-*p*-coumaroylhexoside acid, *trans*-feruloyl hexoside acid isomers and sinapoylhexoside acid, as well as reported the most notable increase in flavonoid compounds such as kaempferol-*O*-dirhamnosyl-galactopyranose and quercetin-*O*-glucuronide.

Among the commercial varieties, it has been reported that red quinoa (Pasankalla variety) and black quinoa (Collana variety) would be promising for the germination process because they show a 49% increase in total phenolic compounds and 18% increase in flavonoids (Aguilar et al. 2019). In a recent publication, Pilco-Quesada et al. (2020) reported that germination of Chullpi quinoa at 22 °C for 72 h increases phenolic compounds such as coumaric acid (1346.4 μg/g dw) and kaempferol-deoxyhexosido-deoxyhexosido-hexoside (725.8 μg/g dw) by more than 100%. Likewise, it has been reported that when the Real Quinoa variety from Bolivia is germinated at 20 °C for 72 h, the most notable increase in phenolic compounds was of *p*-coumaric and vanillic acids.

The formation of phenolic compounds during germination can be explained by the release of bound phenolic compounds, which can be released during the early stages of germination, basically due to the breakdown of proteins and carbohydrates in the cell wall. Likewise, the synthesis of new phenolic compounds occurs with increased germination time, with glucose being the main precursor (Gan et al. 2017).

12.3.5 Milling

The milling of desaponified grain is an alternative process for converting it into flour and its subsequent application in different processed foods such as bakery products and desserts (Repo-Carrasco-Valencia and Vidaurre-Ruiz 2019).

It has been reported that of the fractions obtained during the milling, the bran fraction has the highest content of total phenolic compounds (4.29 mg of ferulic acid equivalents/g) and flavonoids (2.35 mg of catechin equivalents/g), while milled grain has the lowest content of total phenolic compounds (1.92 mg of ferulic acid equivalents/g) and flavonoids (1.09 mg of catechin equivalents/g). The loss of bioactive compounds is close to 30–40% after the milling process; however, it has been reported to be much less than the losses of bioactive compounds from wheat and barley (Hemalatha et al. 2016).

The degree of milling of grain is also a factor that affects the phenolic compound content in the finished product. Han et al. (2019) have reported that there is a linear relationship between the increase in degree of milling (DOM) and the loss of total phenolics and flavonoids in both free and bound forms. With a DOM of 27.23% (the most aggressive), the content of free phenolic compounds can decrease by up to 31.5% (111.51 mg GAE/100 g dw) and that of bound phenolic compounds by 31.1% (25.85 mg GAE/100 g dw). Similarly, the free flavonoid content can be affected, decreasing by up to 35.7% (95.19 mg CE/100 g dw); in the case of bound flavonoids, it can decrease by up to 52.4% (36.48 mg CE/100 g dw). Compared to the loss of phenolic compounds after grinding other grains with a similar DOM, grain shows less loss after the process. This could indicate that phenolic compounds are distributed in a more balanced way in the quinoa grain than in other cereals (Gómez-Caravaca et al. 2014; Hemalatha et al. 2016; Han et al. 2019).

12.3.6 Fermentation

Fermentation, like germination, is a low-cost, low-energy processing method that can improve the functional aspect of Andean grains. Recent research has shown that fermentation for 72 h with *Lactobacillus* (*L. reuteri* and *L. plantarum*) significantly increases the total phenolic compound content, showing an increase of almost 2.6 times in comparison to the initial content (12–32 mg GAE/g dw) (Ayyash et al. 2019). The fermentation time is an important factor in achieving the increase in phenolic compounds, since the longer the fermentation time, the more hydrolysis of the so-called non-extractable polyphenols in the food matrix is promoted. Rocchetti et al. (2019) fermented grains with *L. paracasei* and *Pediococcus pentosaceus* and with a blend of both strains, finding that after 24 h of fermentation, a slight increase in total phenolic compounds was evident in the samples fermented with *P. pentosaceus* and *P. pentosaceus* + *L. paracasei* (70.9 and 74.8 mg GAE/100 g dw, respectively). Through metabolic analysis, the authors determined that the process of fermenting seeds with *L. paracasei* showed a maximum increase in phenolic compounds (fold change, FC = 1.5), improving the content of phenolic

acids and tyrosols, probably the result of hydrolysis of the linked polyphenols of higher molecular weight.

Yeast (*Saccharomyces cerevisiae*) used for brewing and baking has also been used for the fermentation of grains. In the research carried out by Carciochi et al. (2016), fermentation for 24 h produced a 55% increase in the content of total phenolic compounds, specifically a significant increase in *p*-OH-benzoic acid, vanillic acid and *p*-coumaric acid. The fungus *Rhizopus oligosporus* has also been used for the fermentation; Starzyńska-Janiszewska et al. (2016) performed a prolonged tempe-type fermentation of white, red and black quinoa for 30 and 40 h. The authors found that long-term fermentation increased the content of soluble phenols such as vanillic acid, protocatechuic acid and rutin.

It is clear that the increase in phenolic compound content during the fermentation process can be mediated by microbial enzymes, which can induce the breakdown of the grain's cell wall structure and/or hydrolyse the esterified or insoluble phenolics; it is also possible that the microorganisms metabolize new phenolic compounds (Carciochi et al. 2016; Starzyńska-Janiszewska et al. 2016; Ayyash et al. 2019).

12.3.7 Phenolic Compounds in Products Made with Quinoa and Kañiwa

The inclusion of previously processed grains in the development of products with functional characteristics has gained interest in recent years (Pérez et al. 2016; Ludena Urquizo et al. 2017; Repo-Carrasco-Valencia and Vidaurre-Ruiz 2019). It has been reported that as the level of flour in food increases, the content of bioactive compounds, such as total phenolic compounds and flavonoids, increases.

Chlopicka et al. (2012) showed that replacing 30% of wheat flour with quinoa flour produces breads with 2.54 mg GAE/g of total phenolic compounds and 28.7 mg CE/g dw of flavonoids. Proportional amounts of total phenolic compounds have been reported by Xu et al. (2019), who found that the replacement of 0, 5, 10 and 15%, respectively, of wheat flour by quinoa flour increases the total phenolic compound values from 0.95 to 1.63 mg GAE/g in doughs and 0.63 to 1.01 mg GAE/g in breads. The authors noted that the loss of total phenolic compounds after baking was in the range of 30–37%. Alvarez-Jubete et al. (2010b) showed lower total phenolic compound values in gluten-free breads based on potato starch and with 50% substitution for quinoa flour; the total phenolic compound content after baking was 0.307 mg GAE/g. The authors also pointed out that losses of phenolic compounds are evident after baking and indicate that the presence of simple phenolics was not detected, but it was possible to detect flavonoids such as quercetin glycosides and kaempferol glycosides. In a recent investigation, Ballester-Sánchez et al. (2019) indicated that the replacement of 25% of wheat flour by quinoa flour (white, red and black organic quinoa Real) doubles the total phenolic compound content in breads (20.70–24.12 mg GAE/g dm), hydrolysable polyphenols (17.34–20.23 mg GAE/g dm) being found at a higher proportion in breads than extractable polyphenols (3.35–3.89 mg GAE/g dm).

Quinoa sprouts have recently been used to produce a dairy substitute and later in yogurt making. Joy Ujiroghene et al. (2019) reported that the maximum content of total phenolic compounds and flavonoids in yogurt produced with 100% fermented sprouted quinoa (Mengli 2 variety) was 276.9 mg GAE/100 g and 560.1 mg quercetin/100 g, respectively, while for yogurt produced with 50% v/v UHT milk/fermented sprouted quinoa milk, it was 144.7 mg GAE/100 g and 439.9 mg quercetin/100 g, respectively. The authors pointed out that phenolic compounds such as epicatechin, gallic acid, kaempferol, kaempferol-3-glucorhamnoside, kaempferol-3-*O*-rutinoside, quercetin, 7-hydroxycoumarin, methyl vanillate, morin, ferulic acids, dihydroartemisinic acid, artemisinic acid, gentisic acid, azelaic acid and protocatechuic acid were found in yogurts, as well as flavonoids such as kaempferol and quercetin.

Extruded quinoa products are also a source of phenolic compounds. Repo-Carrasco-Valencia and Serna (2011) reported that the total phenolic compound content in extrudates made from four varieties of quinoa (La Molina 89, Kcancolla, Blanca de Juli and Sajama) was between 1.66 and 3.28 mg GAE/g. Similar results have been reported by Kowalski et al. (2016) who reported that extrudates made with the Cherry Vanilla quinoa variety contain 11.81–20.22 mg GAE/g.

The inclusion of quinoa and kañiwa in pasta has also been investigated. Recently, Bustos et al. (2019) have reported that replacing 20% of wheat flour with kañiwa flour allowed them to obtain functional pasta with satisfactory cooking quality and good nutritional characteristics. Likewise, the phenolic compounds in a gluten-free commercial pasta after the cooking process have been analysed, and it has been reported that the free phenolic content after cooking does not decrease significantly compared to uncooked pasta (19.27 mg GAE/g); however, the authors showed a loss of bound phenolic compounds, which affects the antioxidant capacity of the pasta (Rocchetti et al. 2017). The authors stated that the lignans, followed by stilbenes and flavonoids, decreased during the pasta cooking process. However, phenolic acids and other phenolic compounds showed greater stability.

12.4 Effect of Processing on Antioxidant Activity

Reactive oxygen species (ROS) are known to be free radicals produced by endogenous oxidation-reduction (REDOX) reactions (Orona-Tamayo et al. 2019). When there is an imbalance in organism's ROS production, oxidative stress occurs, which can cause cell damage and macromolecular damage such as ageing, cancer, hypertension, neurodegenerative disorders and heart disease (Tang and Tsao 2017; Orona-Tamayo et al. 2019). Andean grains are sources of bioactive compounds such as phenols, carotenoids and bioactive peptides that show antioxidant activity. These compounds are capable of donating or receiving electrons to neutralize free radicals (Repo-Carrasco-Valencia et al. 2009; Tang and Tsao 2017; Multari et al. 2018; Ayyash et al. 2019).

The most widely used chemical methods for evaluating the antioxidant activity of Andean grains are the DPPH free radical test, oxygen radical absorbance capacity

(ORAC), Trolox equivalent antioxidant capacity (TEAC), ferric reducing antioxidant power (FRAP) and ABTS radical scavenging assay (Peñarrieta et al. 2008; Tang and Tsao 2017; Liu 2019). Various investigations have correlated the phenolic compound content in Andean grains with antioxidant activity (Hemalatha et al. 2016; Pellegrini et al. 2017; Liu et al. 2020); in the same way, the antioxidant activity of Andean grains has been successfully correlated with the seeds' unsaturated fatty acid content, total carotenoid index and total tocopherol index (Tang et al. 2016a; Tang and Tsao 2017).

During the processing, certain changes may occur in the grains that can favour or harm their antioxidant capacity. A summary of the investigations carried out so far on how the different processes such as washing, drying, grinding, cooking, germination and fermentation can affect the antioxidant activity is shown in Table 12.4.

It is clear that the optimization of parameters such as time, temperature, type of microorganism used or technology used to process the grains plays an important role in preserving the antioxidant activity of Andean grains; however, much more research is needed regarding kañiwa which is still scarcely studied.

12.5 Health Benefits

In vitro studies have shown that many of the bioactive components of quinoa and kañiwa (phenolics, bioactive peptides, carotenoids, saponins, betalains, fatty acids, tocopherols and carotenoids) have beneficial effects on human health, showing different properties such as an antioxidant (Pellegrini et al. 2017; Šťastná et al. 2019), anti-inflammatory (Tang et al. 2016b; Capraro et al. 2020; Liu et al. 2020), antihypertensive (Chirinos et al. 2018), anti-carcinogenic (Paśko et al. 2019; Liu et al. 2020) and antidiabetic effects (Tang et al. 2016b).

However, scarce research has been done in vivo, with animals, or in clinical trials with people. Within animal studies, it has been possible to determine that quinoa intake has a positive association with weight loss, as well as being effective in improving the blood glucose response and keeping plasma free fatty acids (FFA) (Mithila and Khanum 2015). The quinoa diet has also been reported to decrease the mass of adipose tissue and significantly reduce the expression of inflammatory adipokines (Foucault et al. 2012). Paśko et al. (2010) pointed out that feeding rats with seeds for 5 weeks effectively reduces total serum cholesterol, LDL and triglycerides. Likewise, a significant reduction in the blood glucose level and total plasma protein level was evident.

The effect of intake of sprouted and fermented seeds on physical and biochemical parameters in Wistar rats has also been investigated; according to the research carried out by de Oliveira Lopes et al. (2019), they showed that diets with sprouted and fermented seeds reduce the glycaemic index of diets with high levels of simple carbohydrates. They also reduce glucose and lipid levels in the blood and the accumulation of epididymal adipose tissue. Products processed with quinoa have also been investigated with in vivo models. In a recent investigation, Carrizo et al. (2020) made pasta bio-enriched with B2, B9 and minerals using sourdough

Table 12.4 Effect of different types of process on the antioxidant activity of quinoa and kañiwa

Transformation process	Evaluation	Method	Antioxidant activity	Units	Findings	References
Milling	Influence of the degree of milling (DOM) of quinoa grains (0%, 8.45%, 15.9%, 21.17%, 27.23%)	ORAC	8.48–14.05	mg TE/g dw	As DOM increases, the antioxidant capacity of quinoa grains decreases. A high DOM is detrimental to the retention of quinoa's antioxidant activity	
		FRAP	116.54–196.43	mg TE/100 g dw		
	Different fractions of grinding quinoa (hulls, dehulled grain, milled grain and bran)	DPPH	9.84–31.90	IC_{50} (μg/mL)	Bran fractions and hulls exhibited stronger radical scavenging than milled quinoa grain	
		FRAP	3.85–10.15	mmol Fe^{2+} equiv/100 g		
Washing	Influence of manual rubbing of quinoa grains in running water for 15 min	DPPH	4830.72	IC_{50} (μg/mL)	Antioxidant capacity increased slightly compared to unwashed grains	
		DPPH	30.96	mg TE/100 g dw		
		FRAP	15.05	mg TE/100 g dw		
Drying	Influence of hot air drying of quinoa grains at 40, 50, 60, 70 and 80 °C	DPPH	≈2300–3200	IC_{50} (μg/mL)	High antioxidant capacity when quinoa grains are dried at 40, 50 and 80 °C instead of 60 and 70 °C	
Cooking	Effect of cooking bitter and sweet quinoa grains	DPPH	19.9–35.7	μmol TE/10 g	Bitter quinoa grains had a higher antioxidant capacity than sweet quinoa grains. Cooking caused a significant loss of antioxidant capacity	Dini et al. (2010)
		FRAP	12.4–47.7	μmol TE/10 g		

	Effect of cooking quinoa at atmospheric pressure	DPPH	3409.47	IC_{50} (μg/mL)	Cooking at atmospheric pressure increased antioxidant capacity due to the release of conjugated and individual phenolic compounds	Nickel et al. (2016)
		DPPH	32.13	mg TE/100 g dw		
		FRAP	17.44	mg TE/100 g dw		
	Effect of cooking quinoa grains	FRAP	178.5	μmol GAE/g dw	Increase in the elimination of FRAP and ORAC radicals in quinoa seeds after the cooking process due to alteration of the matrix and consequent release of bioactive compounds	Rocchetti et al. (2019)
		ORAC	14161.8	μmol TE/g dw		
Germination	Influence of germination time (78, 72 and 96 h) of kañiwa seeds	ABTS	100.94	mmol Trolox/kg dw	The optimal germination time to increase the antioxidant capacity of kañiwa was 72 h	Abderrahim et al. (2012)
	Optimization of germination time and temperature of quinoa seeds	ORAC	315.8–1410.42	mg TE/100 g dw	The best germination conditions were at 20 °C for 42 h, which caused a 130% increase in the antioxidant activity of sprouted quinoa compared to quinoa seeds	Paucar-Menacho et al. (2018)
Malting	Influence of malting on three varieties of quinoa	DPPH	22.9–58.1	% inhibition	The % inhibition of DPPH increased up to 34% for the Pasankalla Roja variety and 40% for the Negra Collana variety	Aguilar et al. (2019)
	Optimization of roasting temperature of sprouted quinoa seeds	DPPH	40.68–53.04	μmol TE/100 g	Maximum antioxidant activity was obtained by roasting sprouted quinoa seeds at 145 °C for 30 min	Carciochi et al. (2016)

(continued)

Table 12.4 (continued)

Transformation process	Evaluation	Method	Antioxidant activity	Units	Findings	References
Fermentation	Influence of fermentation time (0, 24, 48 and 72 h) of quinoa grains with three *Lactobacillus* strains on antioxidant capacity	DPPH	≈25–65	% inhibition	Grains fermented for 72 h with *Lactobacillus reuteri* K777 and *Lactobacillus plantarum* K779 had the highest % inhibition of DPPH and ABTS	Ayyash et al. (2019)
		ABTS	≈12–73	% inhibition		
	Effect of fermentation of quinoa seeds with lactic acid bacteria (*Lactobacillus paracasei* and *Pediococcus pentosaceus*)	ORAC	5967.7–7010.7	mg TE/100 g dw	The elimination of ORAC radicals from fermented quinoa seeds was higher than in raw seeds, with higher values reported by fermentation with *P. pentosaceus* and with the blend of *P. pentosaceus* + *L. paracasei*	Rocchetti et al. (2019)
	Effect of quinoa seed fermentation with baker's and brewer's yeasts (*Saccharomyces cerevisiae*)	DPPH	≈350–390	μmol TE/100 g	Fermentation with both *S. cerevisiae* strains showed increases in antioxidant activity compared to raw quinoa: 43% and 33% for DPPH, 22% and 27% for ABTS + and 51% and 50% for FRAP for baker's and brewer's yeast, respectively	Carciochi et al. (2016)
		ABTS	≈450–470	μmol TE/100 g		
		FRAP	≈190–200	μmol TE/100 g		
	Effect of prolonged tempe-type fermentation on white, red and black quinoas	DPPH	1.42–2.48	μmol TE/g dw	Quinoa fermented for 40 h had a more favourable antioxidant potential than standard products. Reducing power increased on average by 30% (red and white seeds) and 18% (black seeds), compared to fermentation for 30 h	Starzyńska-Janiszewska et al. (2016)
		ABTS	8.13–21.80	μmol TE/g dw		

(*L. plantarum* CRL 2107 + *L. plantarum* CRL 1964) and found that consumption of the pasta increased the levels of B2 and B9 in the blood of mice. Also, they had higher concentrations of minerals, haemoglobin and haematocrit compared to the group of mice that were deficient.

Intake of quinoa by obese diabetic mice improves or decreases the conditions associated with type 2 diabetes improving liver steatosis, plasma lipids and the state of inflammatory-oxidative stress in this type of animal (Noratto et al. 2019). It has recently been reported that a mixture of quinoa flour and sorghum flour has a high antioxidant capacity in vivo, which would be related to the high content of phenolic compounds (Medina Martinez et al. 2020).

There have been very few clinical trials assessing the effects of quinoa consumption. Ruales et al. (2002) found that twice-a-day intake of 100 g of porridge made from quinoa by preschool children (5 years old) for 15 days can increase the levels of growth factor similar to plasma insulin (IGF-1). This means that the consumption of quinoa promotes growth in children. Farinazzi-Machado et al. (2012) investigated the effects of consuming quinoa cereal bars (twice a day, for 30 days) in 22 students. The authors found that the consumption had beneficial effects in part of the studied population since the levels of total cholesterol, triglycerides and LDL-c were reduced. De Carvalho et al. (2014) carried out a prospective, double-blind study for 4 weeks with 35 overweight postmenopausal women who consumed 25 g of flakes or cornflakes daily. The results found indicate that the consumption of flakes manages to reduce total cholesterol and LDL cholesterol (LDL-c) and increase GSH, showing a possible beneficial effect of quinoa flakes.

12.6 Conclusions

Quinoa and kañiwa are relatively rich in protein and fat, with significant differences in nutritional composition among the different varieties of these two grains. The oil in Andean grains is of high nutritional quality, containing the essential fatty acids linoleic and linolenic acids in adequate proportions. Kañiwa oil is particularly notable because it is very rich in phytosterols, tocopherols and unsaturated fatty acids. Andean grains contain flavonoids, a type of phenolic compound with significant antioxidant activity. Plant sterols, phytosterols, are another group of biologically active components found in pseudocereal lipids. Black quinoa and kañiwa are interesting sources of these compounds. During the processing, certain changes may occur in the grains that can favour or harm their nutritional value. It is clear that the optimization of processing parameters such as time, temperature, type of microorganism used or technology used to process the grains plays an important role in preserving the nutritional value and content of bioactive compounds of Andean grains; however, much more research is needed especially regarding kañiwa which is still scarcely studied. In general, these Andean native grains are very rich in health-promoting compounds, and future studies should evaluate the bioavailability of these compounds.

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