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Nutritional Value and Bioactive Compounds in Andean Ancient Grains †

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Abstract: Quinoa (*Cheopodium quinoa*), kañiwa (*Cheopodium pallidicaule*), kiwicha (*Amaranthus caudatus*) and tarwi (*Lupinus mutabilis*) are ancient crops from the Andean region of South America. Recently, interest in these crops has grown, and worldwide demand for them has increased considerably. The aim of this study was to study the bioactive compounds and nutritional compositions of different varieties/ecotypes of quinoa, kañiwa, kiwicha and tarwi. Proximate, mineral, dietary fibre, fatty acid and amino acid compositions were evaluated. The content of phenolic compounds, tocopherols and phytosterols, and the folic acid and antioxidant capacity, were determined as well. The protein content of the grains was between 13.00% and 20.00%. More important than protein quantity is protein quality, which is demonstrated by the composition of the amino acids. All analysed grains, and especially the kañiwa, had very high lysine content. This amino acid is especially important in vegetarian diets because it is the limiting amino acid in cereal protein. The content of the total phenolic compounds in the studied grains was 27–58 mg gallic acid/100 g of sample. In quinoa, the principal flavonoids found were quercetin and kaempferol, in kañiwa quercetin and isorhamnetin. In kiwicha, no detectable amounts of flavonoids were found. Plant sterols (phytosterols) were another group of biologically active compounds detected. Andean lupin, tarwi, is very rich in oil, which has a beneficial nutritional composition. In conclusion, all studied grains have a very high nutritional value, are interesting sources of bioactive compounds and could be used as ingredients in health-promoting functional foods.

Keywords: quinoa; kañiwa; kiwicha; tarwi

1. Introduction

The Andean region of South America is an important center of the domestication of food crops. This area has a diversity of landscapes and agroecological zones, due to several climates and altitude differences (1500–4200 m). Compared with other regions in the world where crops have been domesticated, the Andean region has its own characteristics. There are no vast, unending plains of uniformly fertile, well-watered land, as in Asia, Europe and the Middle East. Instead, there is an almost total lack of flat, fertile, well-watered soil. The Andean people have always cultivated their crops on tiny plots, one above another up mountain sides, rising thousands of meters [1].

At the time of the European conquest, the Incas cultivated almost as many species of plants as the farmers of all Asia or Europe. It has been estimated that Andean native people domesticated as many as 70 separate crop species [1]. On mountain sides up to four km high along the whole continent, and in climates varying from tropical to polar, they grew roots, grains, legumes, vegetables, fruits and nuts.

Andean indigenous grains, such as quinoa (*Chenopodium quinoa*), kañiwa (*Chenopodium pallidicaule),* kiwicha (*Amaranthus caudatus*) and tarwi (*Lupinus mutabilis),* are good sources of high-quality proteins. They contain also dietary fibre and oil with polyunsaturated fatty acids. Dietary fibre is especially important in diets designated for disease risk reduction and the prevention of diabetes and heart disease. Quinoa, kañiwa and kiwicha are sometimes called pseudocereals because of their similarity in chemical composition with common cereals, such as wheat and rice. Tarwi is a leguminous seed grown mainly in Andean highlands.

The Andean indigenous food crops have enormous potential to be used as functional foods in the prevention of chronic diseases, such as cardiovascular diseases, cancer and diabetes. High variability, not only in colours and shapes, but also in primary nutrient constituents and bioactive compounds, has recently been reported. The health-related properties of Andean crops claimed by local people could be partially attributed to the presence of these bioactive compounds.

The objective of this research was to study the chemical composition and some bioactive compounds of different varieties/ecotypes of quinoa, kañiwa, kiwicha and tarwi.

2. Materials and Methods

Two varieties of quinoa and kiwicha and one variety of tarwi and kañiwa were acquired from the southern Andes of Peru.

Water content, proteins (N × 6.25), fat, crude fibre and ashes were determined according to American Association of Cereal Chemists, AACC (2005) [2].

The total dietary fibre was analysed by an enzymatic-gravimetric method according to the Approved Method of AACC (2005) [2] using the TDF-100 kit from Sigma Chemical Company (St. Louis, MO, USA)

Radical scavenging activity was determined according to the method of Brand-Williams et al. [3] (217) based on the decrease of absorbance at 515 nm produced by reduction of DPPH (2, 2Diphenyl-1-picrylhydrazyl) by an antioxidant. Trolox was used as the reference compound.

The content of total phenolics was analysed according to the method of Swain and Hillis (220).

Tocopherols and tocotrienols were determined based on the direct hydrolysis method reported by Fratianni et al. [4].

The fatty acid composition of the fat fraction was determined after methylation using a modification of the procedure described by Slover and Lanza [5]. Profiling analysis of fatty acid methyl esters was conducted on a 6890N GC-FID gas chromatograph (Agilent) equipped with an Omegawax 250 fused silica capillary column (30 m × 0.25 mm × 0.25 μm, Supelco Inc., Bellefonte, PA, USA). The initial oven temperature was held at 160 °C for 1 min, raised to 240 °C at a rate of 4 °C/min, and kept there for 5 min. The injector and detector temperatures were 240 °C and 260 °C, respectively. Helium was used as the carrier gas at a flow rate of 1.1 mL/min. Identification of fatty acid methyl esters was carried out by comparing their retention times with those of standards (Sigma, USA). Results were expressed as percentage of total fatty acid methyl esters analysed.

Mineral: Ca, Mg, P, Fe. Samples were digested in concentrated nitric acid in a Tecator block digestor. ICP-OES = Inductively Coupled Plasma-Optical Emission Spectrometry was used for the determination of mineral and trace elements [6].

3. Results and Discussions

The proximate composition of the grains is presented in Table 1.

Table 1. Chemical composition of Andean grains (g/100 g).

Samples	Moisture	Protein	Fat	Ash	Dietary Fibre
Quinoa 1	10.9 ± 0.08	17.9 ± 0.11	7.0 ± 0.03	3.1 ± 0.02	12.4 ± 0.57
Quinoa 2	10.2 ± 0.09	15.3 ± 0.09	7.4 ± 0.04	3.3 ± 0.03	18.1 ± 0.81
Kañiwa	11.2 ± 0.08	17.0 ± 0.11	8.9 ± 0.02	3.8 ± 0.08	20.9 ± 0.46
Kiwicha 1	9.8 ± 0.04	14.8 ± 0.11	8.3 ± 0.03	2.2 ± 0.02	9.0 ± 0.30
Kiwicha 2	9.2 ± 0.07	15.0 ± 0.00	7.6 ± 0.05	3.0 ± 0.05	16.4 ± 0.55
Tarwi	8.2 ± 0.06	36.9 ± 0.15	18.4 ± 0.06	3.6 ± 0.05	37.0 ± 0.85

Analysis was made as triplicates.

The protein content of the three Andean grains was between 15.0% and 17.9%. The tarwi had a very high protein content (36.9%). The values of the proteins detected in this study are similar to the values found by Repo-Carrasco-Valencia [7]. The differences between the samples in protein content seem to be more related to the place of cultivation than to variety. The plants use the nitrogen from the soil to produce the proteins. If the soil is rich in nitrogen, the plant produces more proteins than a plant which has been cultivated in nitrogen-poor soil.

In the comparison of the proximate compositions of the Andean grains with the proximate compositions of common cereals, we can find some similarities and differences. The content of total carbohydrates in cereals and Andean grains is similar, about 60–75%. The main carbohydrate is starch in all grains. Thus, they could be used as materials for starch industries. The fat content in Andean grains is considerably higher than the fat content in common cereals (6–7% vs. 2–4%) [8]. The oil is of good nutritional quality, containing the essential fatty acids in proper proportions (see Table 2). Quinoa, kañiwa, kiwicha and tarwi could serve as raw materials to produce edible oils.

Table 2. Fatty acid composition of Andean grains (% of total fatty acids).

Sample	Myristic C14:0	Palmitic C16:0	Stearic C18:0	Oleic C18:1	Linoleic C18:2w6	Linolenic C18:3w3
Quinua	0.14	10.08	0.66	26.15	46.83	8.21
Quinua	0.10	9.1	0.79	27.73	50.38	4.37
Kañiwa	0.12	12.89	1.31	24.86	48.37	5.25
Kiwicha	0.17	17.01	3.01	29.04	42.55	1.84
Kiwicha	0.15	16.64	3.84	30.27	42.17	0.83
Tarwi	n.d.	9.60	9.06	51.21	24.23	2.76

In Table 3, the contents of phenolic compounds and the antioxidant capacities of Andean grains can be observed. The kañiwa had the highest value compared with the other grains, followed by tarwi, and the kiwicha samples had the lowest values. This sample tendency can be observed in the values of antioxidant capacity. This demonstrates that the phenolic compounds are the main compounds responsible of the antioxidant activity of these Andean grains.

Tocopherols are compounds with a high antioxidant capacity and other important physiological functions. Some of them have the function of vitamin E. The contents of different tocopherols in the Andean grains are presented in Table 4. The highest content of tocopherols was found in black quinoa from Cusco. Kiwicha samples were low in α-tocopherol, but interestingly, high in γ-tocopherol. This tocopherol was found in high amounts in kañiwa as well. Wheat has about 1.3 mg/100 g of total α-tocopherol, and it does not contain γ-tocopherol [9]. Barley, oat, rye, rice and corn contain the following amounts of total tocopherols: 0.75–0.9, 0.6–1.3, 1.8, 0.2–0.6 and 4.4–5.1 mg/100 g, respectively [8]. Thus, in comparison with common cereals, the Andean grains could be considered good sources of these tocopherols.

Table 3. Phenolic compounds and antioxidant capacity in Andean grains.

Sample	Total Phenolics (mg Gallic Acid/100g of Sample)	Antioxidant Capacity with DPPH (µg of Trolox/g of Sample)
Quinoa 1	34.0	388.2
Quinoa 2	40.6	654.0
Kañiwa	57.9	1566.8
Kiwicha 1	17.4	172.7
Kiwicha 2	15.5	202.0
Tarwi	45.0	620.0

Table 4. Content of tocopherols in Andean grains.

Sample	α-Tocopherol mg/100 g dw	γ-Tocopherol mg/100 g dw	δ-Tocopherol mg/100 g dw
Quinoa 1	4.1	3.7	<0.2
Quinoa 2	2.3	5.8	0.6
Kañiwa	1.6	6.0	<0.2
Kiwicha 1	0.5	4.7	2.7
Kiwicha 2	0.6	3.9	2.0

The contents of some important minerals in Andean grains can be observed in Table 5. In comparison with quinoa and kañiwa samples, the kiwicha samples had the highest calcium content. The black kiwicha was exceptionally rich in this element. This sample had the highest iron and magnesium content, as well. The content of calcium and magnesium in Andean grains is higher than the content of these minerals in wheat, barley, oats and rice, whereas the content of iron is similar [9].

Table 5. Content of minerals in Andean grains.

Sample	Calcium (g/kg dw)	Magnesium (g/kg dw)	Iron (mg/kg dw)
Quinua 1	0.54	2.13	55
Quinua 2	0.49	2.29	50
Kañiwa	1.21	2.95	57
Kiwicha 1	1.37	2.11	54
Kiwicha 2	3.06	3.38	73

4. Conclusions

All Andean grains had a relatively high protein and fat content. The pink kiwicha had the highest oil content. This is interesting because kiwicha oil is a very good source of phytosterols, essential fatty acids and, according to the literature, of squalene. This compound is found in olive oil, as well. Squalene is a terpenoid compound and it has some health-promoting properties; in particular it lowers the cholesterol level in blood by inhibiting its synthesis in the liver. In addition, it is hypothesized that the decreased risk of various cancers associated with high olive oil consumption could be due to the presences of squalene. This variety could be an interesting material for producing edible high-quality oil, with bioactive compounds, such as squalene, essential fatty acids and phytosterols. Kañiwa's oil is very interesting, as well. It has a very high content of tocopherols and unsaturated fatty acids.

The best source of antioxidants (phenolic compounds) out of the studied grains was kañiwa. Andean grains contain flavonoids, a type of phenolic compound with important antioxidant activity. Berries, such as blueberries, are generally considered to be excellent sources of flavonoids. Regarding the content of tocopherols, in comparison with common cereals, the Andean grains could be considered good sources of these compounds. In general, these Andean native grains are very rich in health-promoting compounds, and should be explored in future studies on the bioavailability of these compounds.

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