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Flavonoids and other phenolic compounds in Andean indigenous grains: Quinoa (*Chenopodium quinoa*), kañiwa (*Chenopodium pallidicaule*) and kiwicha (*Amaranthus caudatus*)

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ABSTRACT

The amount of phenolic acids, flavonoids and betalains in Andean indigenous grains, quinoa (*Chenopodium quinoa*), kañiwa (*Chenopodium pallidicaule*) and kiwicha (*Amaranthus caudatus*), was determined. The total amount of phenolic acids varied from 16.8 to 59.7 mg/100 g and the proportion of soluble phenolic acids varied from 7% to 61%. The phenolic acid content in Andean crops was low compared with common cereals like wheat and rye, but was similar to levels found in oat, barley, corn and rice. The flavonoid content of quinoa and kañiwa was exceptionally high, varying from 36.2 to 144.3 mg/100 g. Kiwicha did not contain quantifiable amounts of these compounds. Only one variety of kiwicha contained low amounts of betalains. These compounds were not detected in kañiwa or quinoa. Our study demonstrates that Andean indigenous crops have excellent potential as sources of health-promoting bioactive compounds such as flavonoids.

1. Introduction

Quinoa (*Chenopodium quinoa*), kañiwa (*Chenopodium pallidicaule*) and kiwicha (*Amaranthus caudatus*) are nutritious grains that are grown in the Andean highlands. These crops were used by pre-Colombian cultures in South America for centuries. They were very important for the Incas together with corn and potatoes. These plants are cold- and drought-tolerant and can be cultivated in high mountains, particularly kañiwa, which can be grown at over 4000 masl. The genetic variability of quinoa, kañiwa and kiwicha is huge, with cultivars being adapted to growth from sea level to high mountains, and from cold, highland climates to subtropical conditions.

Quinoa, kañiwa and kiwicha are usually referred to as pseudocereals since they are not members of the grass family, but produce seeds that can be milled into flour and used like a cereal crop. Quinoa is mainly used in soups and also instead of rice in main courses. Kañiwa is usually toasted and milled and consumed as meal (*kañiwako*). Kiwicha is toasted to obtain "pop-kiwicha", a puffed product. It is consumed directly or used to make "turrones", a kind of snack bar. All these grains are gluten-free and can be used by persons who suffer from coeliac disease. They are also used in baby foods to make porridge.

Several studies have reported the nutritional value of quinoa. This crop contains proteins with a balanced essential amino acid composition that are of high biological value (Koziol, 1992; Ranhotra, Gelroth, Glaser, Lorenz, & Johnson, 1993; Repo-Carrasco, Espinoza, & Jacobsen, 2003). A close relative of quinoa, kañiwa, also has a relatively high protein content with adequate levels of essential amino acids (Repo-Carrasco et al., 2003). The high nutritional value of amaranth proteins was demonstrated by Bressani, De Martell, and Godinez (1993). Among the essential amino acids, the content of lysine in quinoa, kañiwa and kiwicha is notable. The consumption of quinoa and kañiwa has compensated the lack of animal protein, and they are still principal protein sources in many areas (Tapia, 1997). These crops are also very good sources of good quality edible oil (Berganza et al., 2003; Repo-Carrasco et al., 2003) and minerals, such as calcium and iron (Bressani, 1994). Starch is the most abundant component in quinoa, kañiwa and kiwicha seed, as in all cereal crops.

Polyphenols are bioactive secondary plant metabolites that are widely present in commonly consumed foods of plant origin. The three main types of polyphenols are flavonoids, phenolic acids and tannins, which act as powerful anti-oxidants *in vitro*. These compounds are considered to carry many potential beneficial health effects, e.g. in reduction of the risk of cardiovascular diseases, cancers, neurodegenerative diseases, diabetes, and osteoporosis. In food, polyphenols may contribute to bitterness,

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astringency, colour, flavour, and oxidative stability of products (Han, Shen, & Lou, 2007; Scalbert, Manach, Morand, & Rémésy, 2005; Shahidi & Naczk, 1995). Very little information exists concerning polyphenols in Andean cereals such as quinoa, kañiwa and kiwicha. A few articles concerning the isolation and characterisation of flavonoids in quinoa and kañiwa seeds have been published (De Simone, Dini, Pizza, Saturnino, & Scettino, 1990; Rastrelli, Saturnino, Schettino, & Dini, 1995; Zhu et al., 2001).

In addition, Peñarrieta, Alvarado, Åkesson, and Bergenståhl (2008) analysed levels of flavonoids and other phenolic compounds in *Chenopodium pallicaule* (edible part of the plant). Repo-Carrasco-Valencia, Peña, Kallio, and Salminen (2009) analysed the content of total phenolic compounds, phytic acid and anti-oxidant activity in two varieties of raw and extruded kiwicha. Anti-oxidant activity with the DPPH method for the raw kiwicha of the two varieties was 410.0 μmol trolox/g sample for Centenario and 398.1 μmol trolox/g sample for Oscar Blanco. With ABTS method those values were 827.6 and 670.1 μmol trolox/g sample for Centenario and Oscar Blanco, respectively. The content of total phenolics, phytic acid and the anti-oxidant activity decreased during the extrusion process.

To our knowledge, there are no previous data on the phenolic acid and flavonoid content in the seeds of *Chenopodium* species. Klimczak, Malecka, and Pacholek (2002) published results concerning the phenolic acid content of amaranth seeds. Another article concerning the phenolic and flavonoid content in amaranth (*Amaranthus hypochondriacus*) has also recently been published (Barba de la Rosa et al., 2009). Pasko et al. (2009) analysed the total polyphenol content and anti-oxidant activity in two amaranth varieties (*Amaranthus cruentus*) and quinoa seeds and sprouts. Anti-oxidant activity of the investigated seeds decreased in the following order: quinoa, amaranth v. Rawa, amaranth v. Aztek for FRAP and quinoa, amaranth v. Aztek, amaranth v. Rawa for both ABTS and DPPH. The data obtained by the three methods showed significant correlation between total polyphenols content in seed and sprouts.

Betalains are yellow and red compounds that are found in few selected plants such as beetroot, cactus pears and amaranthus. Chemically they can be divided into betaxanthins, which are condensation products of betalamic acid and various amino compounds, and betacyanins, which are conjugates of betalamic acid and *cyclo*-Dopa with various substitutions (Stintzing & Carle, 2004). The betalains from red beet have been extensively used as colourants in the modern food industry. Recently, several studies on the antiradical and anti-oxidant activity of betalains (mainly betanin) from beetroot (*Beta vulgaris*) have been published (Kanner, Harel, & Granit, 2001; Pedreno & Escribano, 2000). Cai, Sun, and Corke (2003) studied the anti-oxidant activity of betalains from plants of *Amaranthaceae*. They found that plants of the *Amaranthaceae*, containing betacyanins and betaxanthins, demonstrated very strong anti-oxidant activity.

The aim of this study was to determine the levels of flavonoids, phenolic acids and betalains in the Andean grains quinoa, kañiwa and kiwicha. In addition, the basic composition of these pseudocereals was analysed.

2. Materials and methods

2.1. Samples

Six ecotypes of Quinoa (*C. quinoa*) were obtained from the Agronomical Experimental Station-INIA Salcedo, Puno, Peru (03-21-1181, Witulla, Roja Coporaque, 03-21-0093, Huaripongo, Ccoito) and two varieties (INIA-415 Pasankalla, Salcedo INIA), and two commercial samples from Cusco were purchased for the study.

Table 1
Description of the quinoa, kañiwa and kiwicha samples.

Sample	Colour	Place cultivated
Quinoa		
Ccoito	Grey	Puno
INIA-415 Pasankalla	Grey/red	Puno
Roja de Coporaque	Red	Puno
Witulla	Red	Puno
03-21-0093	Red	Puno
Salcedo INIA	Cream	Puno
Commercial 1.	Red	Cusco
Commercial 2.	Black	Cusco
Huaripongo	Yellow	Puno
03-21-1181	Yellow	Puno
Kañiwa		
Kello	Yellow	Puno
Wila	Brown	Puno
Guinda	Brown	Puno
Ayara	Grey	Puno
Commercial sample	Brown	Cusco
Kiwicha		
1.	Black	Mollepata, Cusco
2.	Black	San Salvador, Cusco
3.	Pink	Mollepata, Cusco
4.	Cream	San Salvador, Cusco

Four ecotypes of kañiwa (*C. pallidicaule*) were obtained from the Agronomical Experimental Station-INIA Salcedo, Puno, Peru (Kello, Wila, Guinda and Ayara) and one commercial sample from Cusco was purchased. Black, pink and white grains of kiwicha (*A. caudatus*) were collected from Mollepata, Cusco and one black sample from San Salvador, Cusco.

See Table 1 for more details. All grain was from 2007 to 2008 growing season.

2.2. Proximate analysis

Water content, proteins, fat, crude fibre and ash were determined according to AOAC methods (1995). The carbohydrates were calculated by difference.

2.3. Flavonoids

Flavonoids were analysed as aglycones according to the method explained by Mattila, Astola, and Kumpulainen (2000). Briefly, a sample (0.3–1 g) was weighed into a 100-ml Erlenmeyer flask and dispersed in 40 ml of 62.5% aqueous methanol containing 2 g/l of 2,3-tert-butyl-4-hydroxyanisole (BHA). To this extract 10 ml of 6 M HCl was added. Hydrolysis was carried out in a shaking water bath at 90 °C for 2 h. After hydrolysis the sample was allowed to cool. Then it was filtered and made up to 100 ml with methanol. Before quantification by HPLC the sample was filtered through a 0.45 μm membrane filter.

The analytical HPLC system consisted of an Agilent 1100 Series high-performance liquid chromatograph equipped with a diode array detector. The HPLC pumps, autosampler, column oven, and diode array system were monitored and controlled using the HP Chem Station computer programme. Wavelengths used for identification and quantification of flavonoids with the diode array detector were 280 nm for eriodictyol, naringenin, and hesperetin, 329 nm for luteolin and apigenin and 370 nm for myricetin, kaempferol, quercetin and isorhamnetin. Flavonoid separation was done by an Inertsil (GL Sciences, Inc., Japan) ODS-3 (4.0 × 150 mm, 3 μm) column with a C-18 guard column. The temperature of the column oven was set at 35 °C. Gradient elution was employed for flavonoids with a mobile phase consisting of 50 mM H_3PO_4, pH 2.5 (solution A) and acetonitrile (solution B) as follows: isocratic elution 95% A, 0–5 min; linear gradient from 95% A to 50%