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Research Article

Antioxidant potential and fatty acid profile of different canihua (*Chenopodium pallidicaule*) cultivars, raised in Bolivian Altiplano

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Abstract
Though widely used in the Andes in the ancient times, canihua has been considered a forgotten crop for a long time. Only lately, due to increasing demand in European countries, canihua reveals significantly growing market potential. With the current scarcity of research about the composition, nutritional and healthy profile, this study aimed to provide new information about the antioxidant capacity and the fatty acid profile of Bolivian canihua cultivars with different grain colour. Samples of 28 cultivars were used in the study, divided into three groups according to the grain colour - light brown, pink and dark brown. Total antioxidant capacity, content of the total phenols and flavonoids, as well as fatty acid composition were quantified for the groups. The cultivars with light brown grains displayed the strongest antioxidant potential and the highest content of phenols and flavonoids. Regardless of the colour, canihua cultivars were rich in saturated fatty acids, linoleic and oleic acid. The pink grained cultivars displayed the most favourable fatty acid profile, with lowest amount of C16:0. Correlation analysis showed that total phenols and flavonoids, as well as saturated and monounsaturated fatty acids had strong and positive contribution for the antioxidant potential of the canihua grains.

Keywords
canihua (*Chenopodium pallidicaule*), grains, color, antioxidants, fatty acids

Abbreviations
ABTS – 2,2'-azino-bis (3-ethylbenzothiazoline-6-sulphonic) acid; DPPH – 2,2-diphenyl-1-picrylhydrazyl; FAME – fatty acid methyl esters; FCR –Folin–Ciocalteu reagent; FRAP – ferric reducing antioxidant power; MUFA – monounsaturated fatty acids; PUFA – polyunsaturated fatty acids; SFA – saturated fatty acids; TAC – total antioxidant capacity; TEAC – Trolox equivalent antioxidant activity; TF – flavonoids; TPH – content of the total phenolic compounds

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Introduction

According to FAO, more than 50,000 edible plant species in the world, only a few hundred contribute significantly to food supplies (Killian 2012). Moreover, just 15 crop plants provide 90 % of the world's food energy intake, with rice, maize and wheat - making up two-thirds of this. Despite this, thousands of neglected and underutilized plant species are still collected or cultivated being of great importance for the biodiversity (IPGRI 2002). A typical example of underutilized plant species are the Andean grains. The most common are quinoa (*Chenopodium quinoa*), cañahua or kañiwa (*Chenopodium pallidicaule*), amaranth [kiwicha] (*Amaranthus caudatus*) and lupin [tarwi] (*Lupinus mutabilis*). They have been selected and bred by the marginal farmers in the Andes and have a long history of safe use, contributing to the well-being of the local populations and their nutrition for centuries (Repo-Carrasco-Valencia et al. 2010; Gotor et al. 2017). Among the Andean grains, canihua has been the most neglected and endangered (Aroni et al. 2012). With more than 200 cultivars, it only grows in Peruvian and Bolivian highlands, the primary production area of the crop is located around Lake Titicaca and it is not distributed outside the Altiplano (Rodriguez et al. 2020). Many farmers only maintain canihua due to its high tolerance to frost, drought, saline soils and pests (Rodriguez et al. 2017). Yet, canihua has been recently gaining much attention and is considered emerging super food (Gomez Cahuata et al. 2022). In the traditional culture, canihua grains have been mostly converted into flour known as "canihuako" in Peru and "pito" in Bolivia (Rodriguez et al. 2020) that can be either used in hot and cold drinks, or mixed with wheat and used in making bread, pasta, snacks (Paez and Eyzaguirre 2004; Bustos et al. 2019). Moreover, the flour prepared by canihua might be consumed by people that have gluten intolerance (Paez and Eyzaguirre 2004). Studies focused on the nutritional profile of canihua showed that it is a good source of proteins and fibers (Villa et al. 2014). It has been demonstrated that canihua grains contain high amounts of iron, zinc, calcium and magnesium (Repo-Carrasco-Valencia et al. 2010; Repo-Carrasco-Valencia 2020). Earlier study of Peñarrieta et al. (2008) showed strong antioxidant capacity in samples of canihua grains, stems and leaves. Another important component of the dietetic and healthy value of foods is their fatty acid profile. It is known that fatty acids have many important functions in the body and influence the risk of development of various diseases and health conditions. So far, the studies on the fatty acid composition of canihua remain scarce. While Salas-Valero et al. (2014), provided information on the fatty acid profile of canihua flours, a new study of Mérida-López et al. (2023) presented data about the fatty acids in some canihua cultivars as a whole grain product and after dehulling. Both studies however, showed that canihua is rich in oleic (C18:1n-9) and linoleic acid (C18:2n-6). From the above said, it becomes clear that canihua has valuable qualities and responds to the increasing demands of the consumers towards healthy diet. The studies so far did not emphasize on particular traits that distinguish the canihua cultivars. Hence, our aim was to analyse and provide information about the antioxidant activities and fatty acid profile of various canihua cultivars, originating from Bolivia, according to the colour of the grain.

Materials and Methods

Canihua cultivars. The samples of the canihua cultivars with distinct colour of the grains (Fig. 1) were collected at the altitudes ranging from 3445 m to 4025 m in La Paz and Oruro Departments in Bolivia. Detailed description of the cultivars is provided in Table 1. Canihua cultivars were divided according to the colour of the grains forming three groups - light brown, pink and dark brown used in the statistical evaluation. For the purpose of the analysis, the grains were ground to fine dry powder and mixed to obtain homogenous samples.

Sample preparation for TAC, TPH and TF. Samples (3 g) of each canihua cultivar were extracted with 27 mL of methanol: water (9:1, by volume) by vortexing, followed by sonication of the sample in an ice-water bath (0℃, 15 min). The mixture was centrifuged in a Centurion Scientific K241 Medium Primemachine with an BRK5206 rotor (Centurion Scientific Ltd., Chichester, United Kingdom) at 20,000 g for 30 min at 4℃, and then the aspirated supernatant was stored at -80℃. The supernatants were further subjected to analysis of TAC, TPH and TF, as described previously (Peñarrieta et al. 2011; Tejeda et al. 2014).

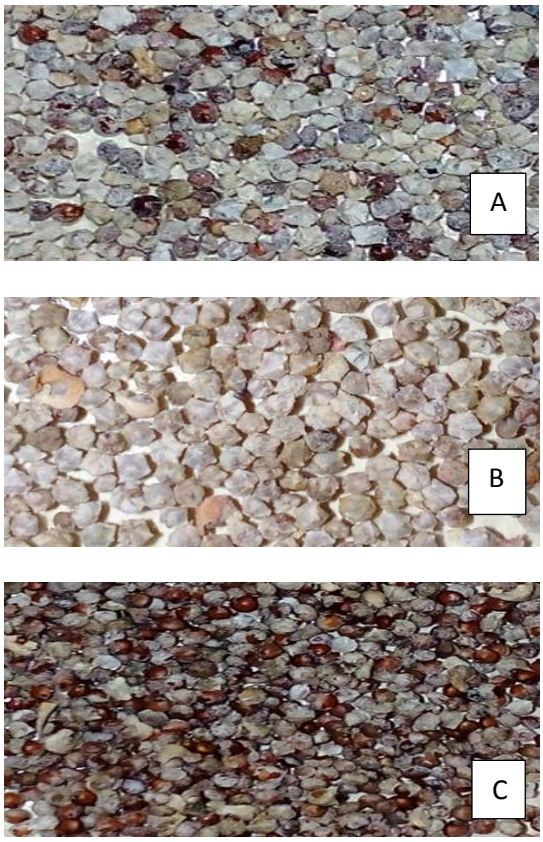

Figure 1. Light brown (A), pink (B) and dark brown (C) colours of canihua cultivar grains

TAC measurement. TAC was measured by the ABTS method (Re et al. 1999) and FRAP method modified by Benzie et al. (1996). The measurements were done through spectrophotometry using a Biotek Multi-Mode reader Cytation™ 3 Cell Imaging (Vermont, USA) using Trolox as a standard.

ABTS method. The colourless 2,2'-azino-bis (3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) (7 mmol.L^{-1}) was oxidized to the green ABTS + radical cation by adding K_2 S_2 O_8 (2.42 mmol.L^{-1}) and kept for 12 - 16 h in the dark at room temperature. For the analysis, ABTS+ solution was diluted with ethanol to an absorbance of 0.70 ± 0.02 at 734 nm. Further, 1.0 ml of the solution was added to 100 µl of the sample and the mixture was vortexed for 30 s. The absorbance readings were done at 734 nm and 25l ℃ for up to 6 min after the initial stirring. The decrease in the absorbance caused by the addition of the sample was compared with a standard curve made by use of Trolox (20 - 200 µmol.L^{-1}).

FRAP method. The FRAP reagent used for the analysis was prepared by mixing 0.1 mol.L^{-1} sodium acetate buffer (pH 3.6), 10 mmol.L^{-1} 2,4,6-Tripyridyl-s-triazine and 20 mmol.L^{-1} ferric chloride (10: 1: 1 v/ v /v). Distilled water (90 µl) and sample (30 µL) were added to the prepared reagent (900 µl of). The absorbance was read at 593 nm for up to 10 min, using blank composed of 120 µl of water and 900 µl of FRAP reagent. The final absorbance of each sample was compared to that of a standard curve made using Trolox (100 - 1000 µmol.L^{-1}). The results were expressed as µmol Trolox equivalents. g^{-1} dry matter. To assess the TAC of the reference compounds, the latter were dissolved in ethanol at 25 - 180 µmol.L^{-1}.

Measurement of TPH. The content of TPH was determined using Folin-Ciocalteu reagent. After 10 times dilution, the reagent (2.5 ml), 2 ml of saturated sodium carbonate (75 g.L^{-1}) and 50 µl of the sample (diluted ten times) were mixed for 10 s and warmed for 30 min at 45℃. After cooling at room temperature, the absorbance of each sample was read at 765 nm and compared with those from the standard curve made using gallic acid (235 - 1176 µmol.L^{-1}). The data were expressed as µmol gallic acid equivalents (GAE).g^{-1} dry matter.

Measurement of TF. A reagent containing aluminium chloride and sodium nitrite was used for determination of the TF content (Zhishen et al. 1999). A solution containing 30 µl of sodium nitrite (10%), 60 µl of aluminium chloride hexahydrate (20%), 200 µl of NaOH (1 M) and 400 µl of water was added to 100 µl of the sample. The absorbance readings were done at 510 nm starting 5 min after the addition of the sample. The final absorbance of each sample was compared with a standard curve made from catechin (69 - 689 µ.L^{-1}). The data were presented as µmol catechin equivalents (CE).g^{-1} dry matter.

Fatty acid analysis. For the fatty acid analysis, total lipids of canihua were extracted according the method of Bligh and Dyer (1959) with slight modifications, as described by Vargas-Ramella et al. (2020). Briefly, 10 g of the grain sample were homogenized with 10 ml of chloroform and 20 ml of methanol for 30 s using Polytron homogeniser. Then 10 ml of chloroform and 10 ml of NaCl (1% in distilled water) were added to the mixture and homogenized again for 30 s.

Table 1. Canihua cultivars evaluated in the study

Sample	Variety	Colour	Attitude	Coordinates	Place
JL1	Q7	light brown	3800	-17.2500, -67.9166	Prov. Camacho/ Chojñacota La Paz -
JL2	Q2	light brown	3800	-17.2500, -67.9166	Prov. Camacho/ Chojñacota , La Paz
JL3	Q8	light brown	3800	-17.2500, -67.9166	Prov. Camacho/ Chojñacota La Paz
JL4	WILLA	light brown	3823	-17.6483, -67.2072	Saucari, Oruro
JL5	ILLIMANI	light brown	3845	-15.7472, -68.8091	Jancohanque Abajo/Jesus de Machaca, La Paz
JL6	ILLIMANI	light brown	3845	-15.7472, -68.8091	Jancohanque Abajo/Jesus de Machaca, La Paz
JL7	WILLA CANAGUA	pink	3721	-17.8241, -67.7702	Toledo Oruro
JL8	JANCO	pink	4025	-17.7850, -68.1447	Toledo Oruro
JL9	ILLIMANI	dark brown	3845	-15.7472, -68.8091	Jancohanque Abajo/Jesus de Machaca, La Paz
JL10	SAMIRI	pink	3721	-17.8241, -67.7702	Toledo- Oruro
JL11	LINEA 3	dark brown	3445	-16.5344, -68.0622	Quipaquipani/PROINPA,La Paz
JL12	LINEA 4	dark brown	3707	-18.2166, -67.0333	Quipaquipani/PROINPA,La Paz
JL13	LINEA 7	dark brown	3445	-16.5344, -68.0622	Quipaquipani/PROINPA,La Paz
JL14	LASTA	dark brown	3445	-16.5344, -68.0622	Quipaquipani/PROINPA,La Paz
JL15	ILLIMANI	dark brown	3445	-16.5344, -68.0622	Quipaquipani/PROINPA,La Paz
JL16	SAYWA	dark brown	3445	-16.5344, -68.0622	Quipaquipani/PROINPA,La Paz
JL17	V 2	pink	3900	-16.6740, -68.3183	Centro Quipaquipani/PROINPA,La Paz
JL19	V7	pink	3445	-16.5344, -68.0622	Quipaquipani/PROINPA,La Paz
JL20	SAIHUA 7	pink	3900	-16.6740, -68.3183	Quipaquipani/PROINPA,La Paz
JL21	SAIHUA 39	pink	3900	-16.6740, -68.3183	Quipaquipani/PROINPA,La Paz
JL22	SAIHUA 37	pink	3900	-16.6740, -68.3183	Quipaquipani/PROINPA,La Paz
JL23	RAMIS	pink	3900	-16.6740, -68.3183	Quipaquipani/PROINPA,La Paz
JL24	SAIHUA 12	pink	3900	-16.6740, -68.3183	Quipaquipani/PROINPA,La Paz
JL25	SAIHUA 32	pink	3900	-16.6740, -68.3183	Quipaquipani/PROINPA,La Paz

JL29	LASTA ROSADA	pink	3900	-16.6740, -68.3183	Quipaquipani/PROINPA,La Paz
JL30	SAIHUA 10	dark brown	3900	-16.6740, -68.3183	Quipaquipani/PROINPA,La Paz
JL31	SAHUA ROSADA	pink	3445	-16.5344, -68.0622	Quipaquipani/PROINPA,La Paz
JL33	SAIHUA 22	pink	3900	-16.6740, -68.3183	Quipaquipani/PROINPA,La Paz

The homogenized samples were centrifuged (4000 rpm for 10 min) and finally the chloroform layer was evaporated. The methyl esters of the fatty acids were obtained following the procedure of Domínguez et al. (2015) and modified by Barros et al. (2020). Briefly, the extracted fat (20 mg) was dissolved in 1 mL of toluene and mixed with 2 ml of a sodium methoxide (0.5 N) solution. The mixture was then vortexed for 10 s and left for 15 min at room temperature. Then, 4 ml of a H_2SO_4 solution (10% of H_2SO_4 in methanol) was added, to the sample, stirred for 10 s and left for 5 min before adding 2 ml of saturated sodium bicarbonate solution. Fatty acid methyl esters were extracted through adding 1 ml of hexane to the samples, vortexing for 10 s and transferring the organic phase to an appropriate GC vial. FAMEs were separated and quantified by gas chromatograph (GC-Agilent 7890A, Agilent Technologies, Santa Clara, CA, USA) equipped with DB-WAX capillary column (30m x 0.25mm x 0.25 um) and helium as carrier gas. The oven temperature was first set to 160℃ for 0.2 min, then raised until 235℃ at a rate of 5℃. min^{-1} and then held for 15 min. The temperatures of the detector and injector were 250℃. Methyl esters were identified through comparison to the retention times of the standards. Fatty acids were presented as percentages of the total amount of the methyl esters (FAME) identified.

Statistical analysis. The analyses of the examined traits were done in triplicates and the results were presented as mean values ± standard deviations. The statistical evaluation was done through one way ANOVA procedure of JMP v.7 software package. The normality of distribution of the data and homogeneity of variances were checked by Shapiro-Wilk and Brown-Forsythe tests prior ANOVA. Tukey HSD test at $P<0.05$ was applied to assess the differences among means of the colour groups regarding each examined trait. Pearson's r correlation coefficients were calculated to determine the correlations among variables.

Results and Discussion

Total antioxidant capacity of the cultivars. The antioxidant capacity measured by the ABTS method (Table 2) differed significantly between the colour groups ($P<0.05$). It showed maximum values in the cultivars with light brown grains (0.810 $\mu mol.g^{-1}$), while the lowest values were found in the dark brown grained cultivars (0.145 $\mu mol.g^{-1}$). This was also observed in regard to the antioxidant capacity measured by FRAP method, showing highest levels in the light brown (2.898 $\mu mol.g^{-1}$) and lowest in the dark brown grains (1.910 $\mu mol.g^{-1}$) ($P<0.05$). The antioxidant capacity of the pink grained group was at intermediary position as measured by both methods. The antioxidant activity in our study is lower that the reported by Peñarrieta et al. (2008) when evaluating 10 cultivars of canihua from Bolivia. Furthermore, Huamaini et al. (2020) when presenting the nutritional profile and antioxidants in three cultivars of canihua in Peru, with light gray, orange and red grains, showed significant antioxidant activity, measured by radical scavenging activity in favour of the plant with the light grey seeds.

Measurement of TPH and TF. The content of the total phenolics measured in this study showed significant differences in the canihua cultivars according to their colour (Fig. 2). The content of total phenolic compounds and total flavonoids in this study are lower than the values reported by Peñarietta et al. (2008) in the Bolivian cultivars. Their analysis however was performed on the whole plant which may explain the considerable differences with our results. Huamani et al. (2020)

Table 2. Antioxidant capacity of the canihua cultivars according to their colour

Indicator	Canihua grain colour		
TAC	**Light brown**	**Pink**	**Dark brown**
ABTS	0.810±0.659[a]	0.493±0.121[ab]	0.145±0.071[b]
FRAP	2.898±0.990[a]	2.374±0.083[ab]	1.910±0.135[b]

Values are expressed as mean values ± standard deviations. Means connected with different letters differ significantly (P<0.05)

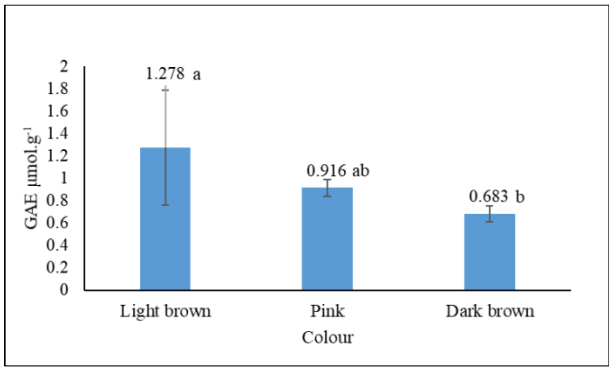

Figure 2. Content of total phenolic compounds (TPH) in the canihua cultivars according to the colour of the grains (means connected with different letters differ significantly at P<0.05)

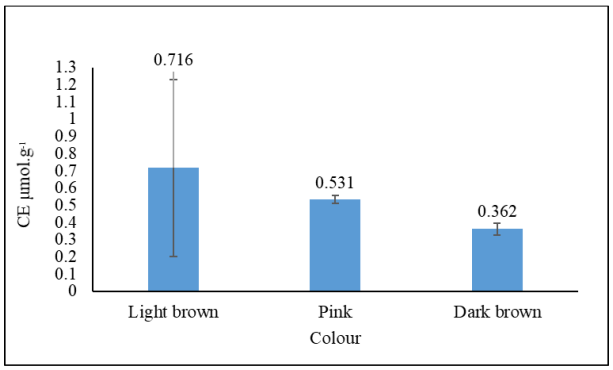

Figure 3. Content of total flavonoids (TF) in the canihua cultivars according to the colour of the grains

also reported higher values of phenolics (1.4 -1.9 mg eq. gallic acid.g^{-1}) and flavonoids (1-5 - 2.0 mg eq. catechin.100 g^{-1}), demonstrating superiority of red seeds vs. light grey. On the other hand, when evaluating the antioxidant capacity according to the intensity of the pelargonium colour, Callohuanca-Pariapaza et al. (2021), reported lower content of both phenolics and flavonoids. The authors reported the highest content of phenolics (10.66 mg eq. gallic acid.100g^{-1}) in the purple variety and the highest content of flavonoids in the black variety (32.58 mg eq. quercetin.100g^{-1}). Abderrahim et al. (2012) showed that considerable increase in the antioxidant activity, as well as the phenols and flavonoids is achieved at 72 h of germination.

Correlations between TAC, THP and TF. The correlations between the total phenols an flavonoids and the antioxidant capacity as measured by ABTS and FRAP were studied using Pearson's correlation coefficients (Table 3). The content of TPH showed high significant (P<0.001) positive correlation with ABTS (r=0.964) and FRAP (r=0.908). This was also observed in regard to the content of TF. The latter correlated positively with the TAC as measured by ABTS (r=0.970) and FRAP (r=0.977). Peñarrieta et al. (2008) found strong relationship between the total phenolics and flavonoids with FRAP, however the correlation between the phenolics and ABTS, though positive was not so strong. In quinoa, Park et al. (2017) showed positive and strong correlation between the flavonoids and the antioxidant activity as measured by FRAP and DPPH, however, the phenolic compounds showed weak and negative relation with the antioxidant assays. On the other hand, Li et al. (2021), reported strong and significant correlation between ABTS and FRAP with the total phenolic compounds in different quinoa varieties. In line with our results, strong correlation between the total phenolics and flavonoids was reported by Muflihah et al. (2021) in Indonesian herbs. The strong and positive correlations of the contents of the total phenolics and flavonoids with the ABTS and FRAP results show that these compounds equally contribute to the antioxidant capacity of canihua grains.

Fatty acid composition. In this study a total of 15 fatty acids were identified (Fig. 4) in the groups of

Table 3. Pearson's correlation coefficients (r) of TAC, TPH and TF

	ABTS	FRAP	TPH	TF
ABTS	1			
P				
FRAP	0.982	1		
P	<0.0001			
TPH	0.964	0.980	1	
P	<0.0001	<0.0001		
TF	0.970	0.977	0.955	1
P	<0.0001	<0.0001	<0.0001	

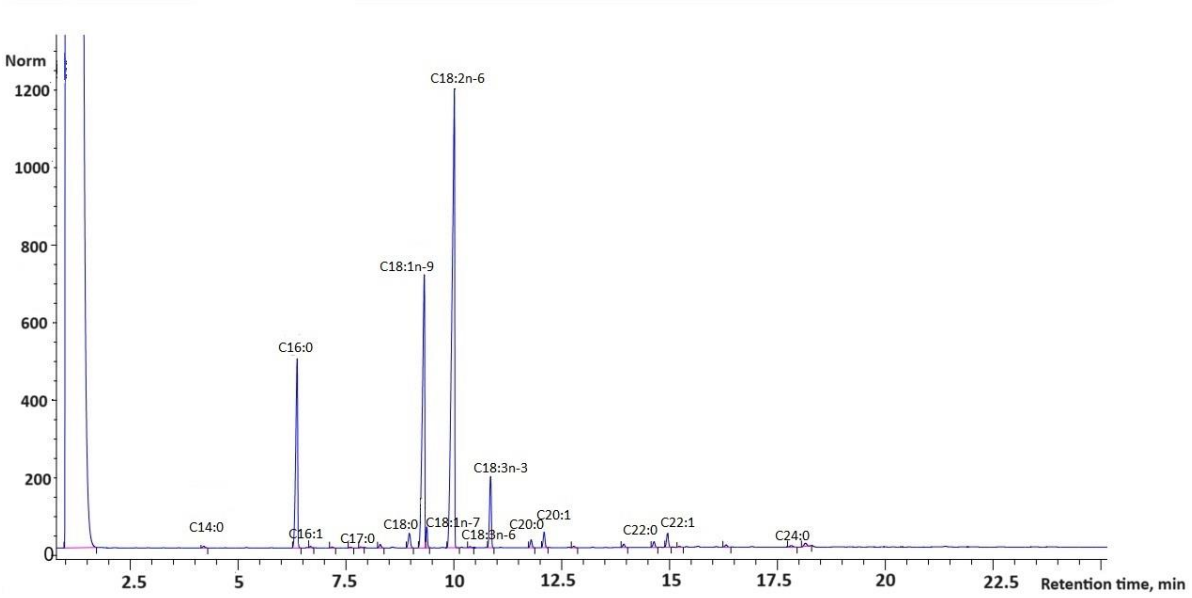

Figure 4. Gas chromatogram of the fatty acid composition of canihua (*Chenopodium pallidicaule*)

canihua cultivars (Table 4). Regardless of the colour, canihua grains exhibited high amounts of C16:0 (14.17 - 16.96%), C18:1n-9 (23.73 - 25.04%) and C18:2n-6 (47.91 - 49.78%). Significant differences among the colour groups were established mainly in regard to the saturated C16:0, C20:0, C22:0. The three fatty acids had the highest percentage in the cultivars with light brown grains. The lowest content of C16:0 was determined in the pink cultivars, while the cultivars with dark brown grains had the lowest percentage of C20:0 ($P<0.05$). Both cultivars exhibited equal and lower content of C22:0 in comparison to the light brown cultivars. Another fatty acid that differed significantly among the colour groups was C18:3n-3. Its percentage was higher in the pink and dark brown grained cultivars compared to the light brown ones. In regard to the total amounts, significant differences between the colour groups were observed in the saturated fatty acids (SFA) ($P<0.05$). The highest content of SFA was observed in the light brown grains. Despite the significant differences in the C18:3n-3 among the colour groups of canihua, they were not sufficient to affect the total amount of polyunsaturated fatty acids. On the other hand, the lower content of C18:3n-3 in the light brown grains was associated with significantly higher n-6/n-3 ratio in these cultivars compared to the dark brown and pink grained plants ($P<0.05$). The ratio between polyunsaturated and saturated fatty acids (P/S) also differed between group, showing highest value in the cultivars with pink grains, and lowest in the light brown ones ($P<0.05$). The dark brown grained cultivars were in the middle position in regard to this trait. The fatty acid profile of the foods is of crucial importance for their dietetic qualities and healthy value. The results of this study showed that the canihua cultivars, regardless of the colour are

Table 4. Fatty acid composition (% FAME) in the canihua cultivars according to the colour of the grain

Fatty acids	Canihua grain colour		
	Light brown	**Pink**	**Dark brown**
C14:0	0.20±0.05	0.18±0.13	0.13±0.01
C16:0	16.96±3.48[a]	14.17±0.44[b]	15.20±0.93[ab]
C16:1	0.10±0.01	0.09±0.01	0.10±0.02
C17:0	0.06±0.03	0.06±0.003	0.06±0.01
C18:0	1.46±0.24	1.31±0.16	1.59±1.11
C18:1n-9	24.06±1.98	25.04±1.52	23.73±1.02
C18:1n-7	1.13±0.22	0.99±0.09	1.02±0.07
C18:2n-6	47.91±5.81	49.78±1.47	49.47±2.43
C18:3n-6	0.09±0.05	0.07±0.03	0.11±0.03
C18:3n-3	4.59±0.86[a]	5.27±0.30[b]	5.43±0.46[b]
C20:0	0.68±0.09[a]	0.61±0.04[ab]	0.57±0.05[b]
C20:1	1.04±0.14	1.01±0.04	1.05±0.05
C22:0	0.52±0.13[a]	0.44±0.01[b]	0.44±0.02[b]
C22:1	0.99±0.33	0.79±0.14	0.92±0.16
C24:0	0.21±0.15	0.19±0.01	0.18±0.01
SFA	20.09±4.08[a]	16.96±0.40[b]	18.17±1.94[ab]
MUFA	27.32±2.42	27.92±1.56	26.82±1.01
PUFA	52.59±6.62	55.12±1.56	55.01±2.45
n-6/n-3	10.46±0.93[a]	9.46±0.55[b]	9.13±0.93[b]
P/S	2.62±0.70[a]	3.25±0.12[b]	3.03±0.38[ab]

Values are expressed as mean values ± standard deviations. Means connected with different letters differ significantly ($P<0.05$)

important source of polyunsaturated (PUFA) and monounsaturated (MUFA) fatty acids. A certain advantage in regard to the polyunsaturated fatty acids could be attributed to the cultivars with dark brown and pink coloured grains. The high content of PUFA in the canihua is mainly at the expense of C18:2n-6. On the other hand, the high MUFA content was exclusively due to C18:1n-9. The percentage of these fatty acids that were measured in this study are similar to those reported by Huamaní et al. (2020) in the Peruvian ecotypes, and also by Salas-Valero et al. (2014) in canihua flours from cultivars Cupi and Illpa-Inia. In regard to the content of C18:2n-6 and C18:1n-9 canihua lipids resemble the corn and soybean oil (Kostik et al. 2013). In addition, canihua grains displayed amounts of C18:3n-3 within the range of 4.59-5.43%. Both C18:2n-6 and C18:3n-3 are essential fatty acids for humans. They serve as precursors for the synthesis of the long-chain polyunsaturated fatty acids and numerous studies have emphasized on their effect for improving the cardiovascular health, the reduction of onset of diabetes (Marangoni et al. 2020), as well as some cancers (Chemberland and Moon 2015; Roy et al. 2017), and also impact the brain development and cognition (Nazir and Zahid 2023). On the other hand, diets containing too high content of C18:2n-6 but too low in n-3 fatty acids may lead to chronic inflammation, hypertension and blood clotting tendency, increasing the risk of heart attack and stroke (Kaur et al. 2014). The high amounts of C18:2n-6 in the canihua cultivars are

associated with elevated n-6/n-3 ratio (9.13 - 10.46), exceeding the recommended values of 4.0. In their study on whole grain and dehulled canihua cultivars Mérida-López et al. (2023) reported values of this ration ranging from 10.03-12.17. This indicates certain imbalance of the fatty acid profile of the canihua with regards to PUFA, however, on the other hand, the high content of C18:1n-9 compensates for this disadvantage due to the its benefits for the human health widely reviewed (Sales-Campos et al. 2013; Karakor and Cam 2015). Furthermore, although the canihua grains were rich in C16:0 and hence SFA, their content was lower than that of PUFA and MUFA, as the pink grain variety was superior in regard to these indicators. The content of C14:0 was also negligible in the three colour groups (0.13 - 0.20%). Both fatty acids have been shown to have negative impact on the health with C16:0 exerting direct pro-inflammatory and atherogenic effect (Wu 2014).

Table 5. Correlations between the antioxidants and major fatty acids in canihua

	ABTS		FRAP		TPH		TF	
	r	**P**	**r**	**P**	**r**	**P**	**r**	**P**
SFA	0.754	0.0046	0.762	0.0039	0.794	0.0020	0.784	0.0025
C16:0	0.839	0.0006	0.851	0.0004	0.869	0.0002	0.869	0.0002
C18:0	0.072	0.8421	0.068	0.0833	0.169	0.7174	0.112	0.7290
MUFA	0.724	0.0077	0.756	0.0045	0.773	0.0032	0.820	0.0011
C18:1	0.678	0.0155	0.707	0.0101	0.728	0.0073	0.770	0.0034
PUFA	-0.833	0.0008	-0.852	0.0004	-0.881	0.0002	-0.892	<0.0001
C18:2n-6	-0.791	0.0022	-0.811	0.0014	-0.841	0.0006	-0.861	0.0003
C18:3n-3	-0.877	0.0002	-0.889	0.0001	-0.910	<0.0001	-0.876	0.0002

Correlations between the antioxidants and fatty acids in canihua. As shown in Table 5, the antioxidant activity and the content of the antioxidant components in the canihua seeds correlated strongly with its fatty acid profile. There was significant positive correlation between the total amount of the saturated fatty acids and antioxidant activity as measured by ABTS (r=0.754; P=0.0046) and FRAP (r=0.762, P=0.0039). This corresponds to the strong and positive correlations observed between the antioxidant activity and C16:0. However, there was no significant correlation between the antioxidant status and C18:0. Antioxidant activity also correlated strongly to the content of MUFA, showing that increase of the content of the monounsaturated fatty acids was associated with higher antioxidant capacity: ABTS (r=0.724; P=0.0155) and FRAP (r=0.756, P=0.0045). The content of total and individual SFA and MUFA, except C18:0 showed strong positive and significant correlations with the total phenols and flavonoids. On the other hand, the content of PUFA exhibited strong negative correlation with the antioxidant activity. This was found also with regard to the content of the two essential polyunsaturated fatty acids C18:2n-6 and C18:3n-3. This can be expected since the higher content of PUFA is associated with more oxidative susceptibility of the food matrix (Tao 2015). The content of the total phenolics and flavonoids also correlated negatively with PUFA, C18:2n-2 and C18:3n-3. Tang et al. (2016) showed strong positive correlation between the unsaturated fatty acids in amaranth and quinoa with the antioxidant capacity, thus demonstrating that UFAs can significantly contribute to the antioxidant activity. The correlations between the fatty acid profile and antioxidant activity in plants have been investigated, however, so far, the results are contradictory and differ between the plant species. Zhang et al. (2014) did not find any relationship between the fatty acids and the content of the antioxidants in lentils. On the other hand, in avocado, Villa-Rodriguez et al. (2011), reported

significant positive correlation between mono- and polyunsaturated fatty acids with antioxidant activity measured by DPPH and TEAC. In a recent study, Szabo et al. (2021) found that the total antioxidant capacities measured by FCR, FRAP and TEAC of grape seed pomace and the content of resveratrol as phenolic compound correlated positively with the C16:0, C18:1, C20:1. However, the content of rutin showed negative correlation. The latter also showed negative correlation with the content of C18:2n-6 and C18:3n-3.

Conclusions

Our results indicate that the canihua grains from cultivars raised in Bolivian Altiplano exhibit different antioxidant activity and fatty acid profile according to their colour. The cultivars with light brown grains had strongest antioxidant potential and were highest content of phenols and flavonoids. The cultivars with dark brown seeds showed lowest antioxidant capacity, while pink cultivars have intermediary values. The fatty acid composition, showed that regardless of the colour, canihua cultivars were rich in linoleic acid causing certain imbalance of the fatty acid profile. However, this can be compensated by the high amounts of oleic acid. The canihua cultivars with pink coloured grained displayed the most favourable fatty acid profile, with lowest amount of the hypercholesterolemic C16:0. The correlation analysis showed that total phenols and flavonoids, as well as SFA and MUFA contributed positively for the antioxidant potential of the canihua grains.

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