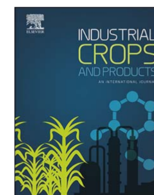
Industrial Crops & Products 111 (2018) 38–46

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop



Research Paper

Chemical, fatty acid, polyphenolic profile, techno-functional and antioxidant properties of flours obtained from quinoa (*Chenopodium quinoa* Willd) seeds

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A R T I C L E I N F O

Keywords:
Quinoa seeds
Flours
Fatty acids profiles
Polyphenolic profile
Antioxidant

A B S T R A C T

In the recent years, quinoa has gained a renewed relevance as an alternative crop to cereals due to its excellent nutritional value. Thus, the aims of this work were to determine the physico-chemical, techno-functional and *in vitro* antioxidant properties as well as the total phenolic and flavonid contents of six quinoa flours. On the different samples proximal compositions and polyphenolic, sugar and organic acids profiles were also determined. Quinoa flours showed a protein content ranged between 11.62 and 13.66 g/100 g while the fat content was comprised between 4.87 and 6.48 g/100 g. The TDF content ranged from 12.71 to 18.59 g/100 g with ratios IDF:SDF higher than 8:1. In all samples analyzed four organic acids (oxalic, ciltric, malic, and succinic) and three sugars (sucrose, glucose, and fructose) were determined. As regards to techno-functional propreties, all quinoa flours showed lower water and oil holding capacities with values of 1.44–1.80 g water/g sample and 0.89–1.04 g oil/g sample, respectively. However, all samples showed a high swelling capacity with values ranged from 8.55 to 9.57 mL/g. The chemical profiles identification allowed to exposed major concentrations of 4-hydroxibenzoic acid and interesting concentrations of the other phenolic compounds and interesting contents of Ω3 fatty acids, compounds with renewed biological properties in terms of antioxidant activity and control diseases. In addition, the antioxidant activity assessed allowed to establish their antioxidant capacity of this product and the good correlations with total phenolic and flavonoid contents. The results of this study suggested that quinoa flours is a valid source of natural compounds with significant antioxidant activity and biological properties. Further investigations should be undertaken in respect of target product, anyhow the present study allowed to increase the knowledge about this Andean region species.

1. Introduction

Quinoa (*Chenopodium quinoa* Willd) is a pseudocereal of Chenopodiacee family which was cultivated and consumed since 5000 years ago from the indigenous Andean region populations, to whom represented the sacred “mother grain” (Vega-Gálvez et al., 2010). In the recent years, quinoa has gained a renewed relevance as an alternative crop to cereals due to its excellent nutritional value. At present, this pseudocereal is mainly cultivated in Bolivia, Peru, Ecuador and Chile, from where it is exported (Fabio and Parraga, 2017). In Europe, small scale crop growing is also found. Therefore, during the past two decades quinoa gained growing attentions, arriving to be largely promoted also by the Food and Agriculture Organization of the United Nations, which dedicated year 2013 to this plant (Ruiz et al., 2014).

The traditional consumption of quinoa seeds is in soups or boiled. The seeds also can be utilized in dishes like other cereals or as main ingredient of hot or fermented beverages. The flours obtanined from de seeds, additionally can be used for elaborated bread or biscuits; furthermore, its leaves are eaten like salads or vegetables (Ridout et al., 1991). Nowadays, in the market, different products with a 20% content of quinoa are commercialy available: pre-coocked dishes, chocolates, snacks, pasta, backed products, muffins, drinks, breakfast cereales,

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http://dx.doi.org/10.1016/j.indcrop.2017.10.006
Received 11 July 2017; Received in revised form 3 October 2017; Accepted 5 October 2017
Available online 10 October 2017
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infant foods, diet supplements, gluten free products, edible films and emulsions stabilizers (Pellegrini and Agostoni, 2015; Wang and Zhu, 2016). Additionally, the gluten-free nature of quinoa seeds makes to this pseudocereal a valuable dietary source of digestible protein for people with gluten sensitivity and coeliac disease (Tang et al., 2015a).

This wide range applicability is due to is versatility as food ingredient, in addition, quinoa seeds represents also an interesting field of research due to the high content of different macromolecules and phytochemicals that these seed showed (Gordillo-Bastidas et al., 2016). Thus, different scientific works in fact, demonstrated that this pseudocereal contains high biological value proteins and bioavailable essential aminoacids, unsaturated lipids, dietary fiber, complex carbohydrates and other beneficial bioactive compounds such as polyphenolic compounds (phenolic acids, flavonoids, lignans, stilbenes, tannins) (Wu, 2015; Fischer et al., 2017). The main phenolic acids found in quinoa seeds are; ferulic, caffeic, *p*-coumaric and benzoic acids while the principal flavonoids are: kaempferol, myricetin and quercetin (Repo-Carrasco-Valencia et al., 2010; Gómez-Caravaca et al., 2012). Numerous studies have shown that the presence of polyphenolic compounds in plants or plants derivates can be particularly important for consumers, because of their beneficial health properties (Veberic et al., 2008). These substances have already shown different *in vitro* biological potentials (Alvarez-Jubete et al., 2010; Gawlik-Dziki et al., 2013) and *in vivo* activities against several diseases and metabolic conditinons (Graf et al., 2015; Gordillo-Bastidas et al., 2016).

The scientific literature contains several reviews that summarizes the different informations about chemistry, composition, functional and nutritional properties of quinoa as well as the antioxidant properties of quinoa seeds and leaves (Vega-Gálvez et al., 2010; Graf et al., 2015; Tang et al., 2015b; Gordillo-Bastidas et al., 2016). As already mentioned there are some studies on single seed varieties (Ogungbenle, 2003) or focused only on nutritional properties (Wu, 2015), protein isolates (Abugoch et al., 2008), chemical profiles identifications or physico-chemical and functional properties (Ahamed et al., 1996; Repo-Carrasco-Valencia et al., 2010).

Thus, the aim of this work was evaluated the (*i*) physico-chemical, (*ii*) techno-functional (*iii*) chemical (*iv*) antioxidant properties (*v*) polyphenolic compounds, (*vi*) organic acids and sugars and (*vii*) fatty acids profile on six quinoa flours with different seed colour and origin.

2. Material and methods

2.1. Plant material

The analyses were performed on six different quinoas obtained from the local market: white Spanish quinoa obtained from organic farming (WSQ); two distinct brands of white Bolivian Real quinoa obtained from organic farming (WBQI and WBQII); white Peruvian quinoa (WPQ); red Bolivian Real quinoa obtained from organic farming (RBQ); black Bolivian Real quinoa obtained from organic farming (BBQ). From quinoa seeds were obtained flour samples by grinding with a blender for 20 s the seeds; depending on the analysis, the samples were subjected to different treatments or extractions, reported in detail in respective paragraph.

2.2. Chemical proximal composition

Moisture, protein (using N × 6.25 as conversion factor) fat and ash contents were determined according to Official Methods (AOAC, 2000). Total (TDF) and insoluble dietary fibre (IDF) expressed as g TDF or IDF/100 g; were determined following the enzymatic-gravimetric AOAC method 985.29. Soluble dietary fibre (SDF) was calculated by subtracting the IDF proportion from TDF. All values were expressed in fresh matter.

2.3. Physico-chemical properties

The pH was measured in a suspension resulting from blending 1 g sample with 20 mL of deionized water for 3 min, using a pH meter (model pH/Ion 510, Eutech Instruments Pte Ltd., Singapore). The water activity (aw) was determined in a Novasina Thermoconstanter Sprint TH-500 (Pfäffikon, Switzerland) at 25 °C. The colour was studied in the CIEL*a*b* colour space using a Minolta CM-700 (Minolta Camera Co., Osaka, Japan), with illuminant $D_{65,}$ SCI mode and an observer angle of 10°. Low reflectance glass (Minolta CR-A51/1829-752) was placed between the samples and the equipment. The CIEL*a*b* coordinates determined were: lightness (L*), redness (a*, coordinate red/green), and yellowness (b*, coordinate yellow-blue) and the psychophysical parameters h_{ab} (hue) and C_{ab*} (chroma) which were calculated as follows:

$$h_{ab} = arctg\frac{b^*}{a^*}\ C^*_{ab} = \sqrt{a^{*2} + b^{*2}}$$

2.4. Techno-functional properties

Water-holding capacity (WHC) and oil-holding capacity (OHC), expressed as g of water and oil, respectively held per g of quinoa flour; swelling capacity (SWC) expressed as mL of volume increase per g quinoa flour were determined according to Vázquez-Ovando et al. (2009). In addition, the emulsifying activity (EA) and emulsion stability (ES) were also analysed following the recommendations of Vázquez-Ovando et al. (2009) with some modifications. For EA a suspension of 2 g of quinoa flour in 100 mL of water was homogenized at 11,000 r.p.m. for 30 s using the IKA T25 homogenizer (IKA, Staufen, Germany). One hundred milliliters of sunflower oil was added and homogenized for 1 min. The emulsions were centrifuged in graduated centrifuged tubes at 1200*g* for 5 min, and the emulsion volume was measured. Emulsion activity was expressed as the mL of the emulsified layer volume of the entire volume in the centrifuge tube. ES was determined by heating the emulsions at 80 °C during 30 min, cooling them and centrifuging again. Emulsion stability was calculated as volume of the remaining emulsified layer/original emulsion volume layer in the tube.

2.5. Total phenol, and total flavonoid content

The total phenol content (TPC) of quinoa flours was estimated using the Folin-Ciocalteu's reagent following the recommendations of Singleton and Rossi (1965). Gallic acid (GA) was employed as reference standard and results were expressed as mg GA eq./g of quinoa flour. The total flavonoid content (TFC) was established by means of the method described by Blasa et al. (2006). The reference standard was Rutin and results were expressed as mg rutin eq. (RE)/g of quinoa flour.

2.6. Organic acids and sugar profiles identifications

For organic acids and sugar profiles identifications, 1 g of each sample was subjected to: ultra-sonication extraction for 30 min with 5 mL of Milli-Q water, centrifugation at 12,000 rpm for 10 min and 0.45 μm filtrations with nylon Filter-Lab® syringe filters (Filtros Anoia SA, Barcelona, Spain).

The LC-DAD-RID analyses were performed with an 1100 series Hewlett-Packard HPLC (Woldbronn, Germany) coupled with a UV–vis Diode Array Detector G1315A, set at 210 nm, and a refractive index detector G-1362. The separation module was equipped with a Supelcogel C-610H column (300 × 7.8 mm) (Supelco-Bellefonte, USA) and a Supelguard-H pre-column (50 × 4.6 mm) (Supelco-Bellefonte, USA). The separation was achieved by means of the method described by Doughty (1995), the injection volume was 10 μL, the mobile phase was 0.1% of phosphoric acid acidified water, the flow was set to a rate of 0.5 mL/min and the column oven was set at 30 °C. The selected organic acids (L-ascorbic, malic, tartaric, citric, oxalic, fumaric, and

succinic acids) and monosaccharides (glucose, fructose, and sucrose) standards were obtained from Sigma Aldrich (Missouri, USA). Each compound was identified comparing retention times with references standards ones and unknown concentrations were calculated by means of standard calibration curve equation.

The sugar concentrations were reported as g/100 g of sample, while the organic acid ones as mg/100 g of sample.

2.7. LC-ESI–MS/MS phenolic profile identification

For LC–MS phenolic profile, the samples were extracted with two consecutive ultrasonic extractions of 15 min, with 80% methanol and 70% acetone, the mixtures were centrifuged at 12,000 rpm for 10 min, the supernatants were combined, evaporated, resuspended with 5 mL of UHPLC-grade methanol and filtered with RC syringe filter of 0.20 μm (Sartorious-Göttingen, Germany).

The phenolic profile identification was achieved by means of a Nexera XR UHPLC system (Shimadzu – Tokyo, Japan) coupled with a Qtrap 4500 (Sciex − Toronto, Canada) fitted with a heated electrospray ionization source (ESI V-source). The separation module was equipped with an ACE Excel 2 C18-PFP column (10 cm × 2.1 mm ID, 2 μm; ACE – Aberdeen, UK). The mobile phase was 0.1% (v/v) aqueous formic acid (A) and acetonitrile (B), with a flow rate of 0.3 mL/min. The separation of the analytes was obtained with a mobile phase gradient programmed as follow: B from 5% to 100% in 5 min, an isocratic step at 100% for 1 min and then switched back to the initial 5% in 3 min. Quantitation was performed by the additional standard method and peak areas for the selected ions were assessed trough the Sciex MultiQuant software. The negative ionization mode was set as follows: −4.5 kV of ion spray voltage, 40 psi of nebulizer gas (air), 40 psi of turbo gas (nitrogen), and temperature of 500 °C. The acquisition was performed in Multi Reaction Monitoring (MRM) mode with the precursor ion/fragment ion transitions listed in Table 1 of supplementary material section. Results were reported as μg per gram of sample on FW.

2.8. Fatty acid composition

Quinoa oil was extracted from 25 g of samples using *n*-hexane, by means of an ultrasonic extraction at room temperature for 30 min (solid-liquid ratio of 1:4). After the extraction, the liquid was collected in a flask and the solvent was removed through a rotary vacuum evaporator.

Fatty acid composition identification was obtained by transesterification of fats with methanol, producing fatty acids methyl esters (FAME) as described by Golay and Moulin (2016). Gas Chromatography (GC) analysis were carried out on an autosystem chromatographer (Perkin Elmer – Beaconsfield, UK) equipped with a VF–23 ms fused silica capillary column (30 × 0.25 mm × 0.25 μm film thickness, Varian – Middelburg, The Netherlands) and a flame ionization detector (FID). The column was maintained at 60 °C for 1 min after injection, the temperature was set at 10 °C/min at 130 °C, then the temperature was set at 3 °C/min at 170 °C and the last ramp at 10 °C/min at 230 °C, hold 5 min. Helium was used as a carrier gas with a column inlet pressure set at 20 psi and a split ratio of 1:20. The injection volume was 0.5 μL. The total race time was 32 min. The injector and detector temperatures were set at 250 °C and 270 °C, respectively. Response factors were calculated using a reference fat (BCR-164) (Fedelco Inc., Madrid, Spain). For determination and quantification of FAME, Tritridecanoin was used as an internal standard. All analyses were performed in triplicate and results were expressed as g/100 g of oil.

2.9. In vitro antioxidant activity

The antioxidant activity was assessed through the employment of different *in vitro* spectrophotometric assays presented below. For thus, the samples were extracted with two consecutive ultrasonic extractions of 15 min, with 80% methanol and 70% acetone, the mixtures were centrifuged at 8000*g* for 12 min at 4 °C, the supernatants were combined, evaporated, suspended with 5 mL of UHPLC-grade methanol and filtered with 0.45 μm nylon Filter-Lab® syringe filters.

2.9.1. DPPH radical scavenging assay

DPPH assay was performed by employing the stable radical 2,2-diphenyl-1-picrylhydrazyl, following the method proposed by Brand-Williams et al. (1995). Trolox was used as reference standard and results were expressed as mg Trolox Equivalents per gram of quinoa flour.

2.9.2. Ferric reducing antioxidant power

Ferric reducing antioxidant power (FRAP) was assessed by means of potassium ferricyanide-ferric chloride method described by Oyaizu (1986). Trolox was used as reference standard and results were expressed as mg Trolox Equivalents per gram of quinoa flour.

2.9.3. ABTS radical cation ($ABTS^{\bullet+}$) scavenging activity assay

TEAC-ABTS assay was established trough the method proposed by Gullón et al. (2015). Trolox was used as reference standard and results were expressed as mg Trolox Equivalents per gram of quinoa flour.

2.9.4. Ferrous ion-chelating ability assay

Ferrous ions chelating activity (FIC) was determined establishing the inhibition of Fe^{2+}-ferrozine complex formation after adding to test material Fe^{2+} by means of the method described by Carter (1971). EDTA was used as reference standard and results were expressed as mg EDTA per gram of quinoa flour.

2.10. Statistical analysis

The results were expressed as the mean ± SD of 2 parallel trials ($n = 4$) and compared through statistical program JMP 13.1.0 (SAS Institute Inc., Cary, USA). The mean values of the different analysis results were analyzed by one-way analysis of variance (ANOVA). The Tukey's post hoc test was applied for comparisons of means and differences were considered significant at $p < 0.05$. Total phenolic and flavonoids content were compared with antioxidant activity results through Pearson’s correlation test: the positive/negative strength of correlation was considered: low for $+/-0.1 < r < +/-0.3$, moderate for $+/-0.3 < r < +/-0.7$, and strong for $r > +/-07$; for values of $r < +/- 0.1$ the variables were considered not correlated

3. Results and discussion

3.1. Chemical composition

The chemical composition of quinoa flours analyses were showed in Table 1. Regarding the ash content, highest value was obtained for WPQ, followed by RBQ and BBQ however no statistical differences were found ($p > 0.05$) between the samples analyzed except for WBQII that had the lowest ($p < 0.05$) value. WPQ showed also the highest content ($p < 0.05$) of protein, no statistical differences were found between WBQI, WBQII, RBQ and BBQ while WSQ showed the lowest content with no statistical differences ($p > 0.05$) with WBQII, RBQ and BBQ. In reference to fat contents, there were no significant differences ($p > 0.05$) among the samples, except for RBQ that showed highest values ($p < 0.05$) followed by WBQII. In reference to moisture content, the highest values ($p < 0.05$) were obtained for WSQ and WBQI with no statistical differences ($p > 0.05$) between them, while the lowest ($p < 0.05$) was obtained for BBQ. These contents of moisture, ash, lipid and protein of grain quinoa flour generally were in agreement with different work on quinoa seeds flours (Miranda et al., 2011; Nowak et al., 2016; Li and Zhu 2017).

As regards to total dietary fiber (TDF), insoluble dietary fiber (IDF) and soluble dietary fiber (SDF) the results obtained were showed in

Fig. 1. The TDF content ranged ($p < 0.05$) from 18.59 g/100 g in WSQ to 12.71 g/100 g in WBQII. The values obtained in this work were higher, than those reported for quinoa seeds cultivated in Bolivia (10.00 g/100 g), Canada (9.50 g/100 g) or Peru (10.50 g/100 g) (Wright et al., 2002; Ogungbenle, 2003; Lamothe et al., 2015). High contents of IDF (> 90%) was obtained for WSQ, RBQ and BBQ while high contents of SDF were recorded for WPQ and WBQII ($p < 0.05$). Flours rich in dietary fiber could be used as functional ingredients due to, as mentioned Viuda-Martos et al. (2010) dietary fiber provide numerous health benefits such as their ability to decrease cholesterol levels, improve glucose tolerance and the insulin response, reduce hyperlipidemia and hypertension, contribute to gastrointestinal health and the prevention of certain cancers such as colon cancer. For all the samples were calculated also the IDF:SDF ratios (Table 2 Supplementary material), the results obtained showed high ratios (IDF:SDF > 8:1), for all quinoas seeds flours analyzed except for WPQ and WBQII that showed lowest values ($p < 0.05$). Anyhow, all the obtained ratios are higher than the optimal 3:1 ratio recommended by the American Dietetic Association (Borderias et al., 2005).

3.2. Organic acids and sugar profiles identifications

Table 1 shows the organic acid and sugar content obtained from the six quinoa flours analysed. As far our knowledge, no studies have been published on the organic acid profile of quinoa. In all quinoa flour samples analysed four types of organic acids were identified. Succinic acid was the main organic acid present in all quinoa flour samples, with the highest concentration ($p < 0.05$) found in RBQ whilst WPQ had the lowest one ($p < 0.05$). Among the flours there were no significantly differences ($p > 0.05$) among the samples regarding malic and oxalic acids, except for WPQ that showed a higher content ($p < 0.05$) of both organic acids. Citric acid concentrations instead were found highest in WBQI ($p < 0.05$) on the other hand RBQ showed the lowest values ($p < 0.05$) for this organic acid. As mentioned above, apparently, in scientific literature there are not evidences about quinoa organic acids contents, however, the detected organic acids have been already detected in species belonging to *Chenopodiaceae* family (Marchyshyn et al., 2016).

With reference to sugar content, the results obtained reported in Table 1, showed that the sucrose was the main sugar found in quinoa flours analyzed. Thus, there were no statistical differences among the samples ($p > 0.05$), except for WPQ that showed lowest values ($p < 0.05$). In addition, the obtained results showed that all the flours analyzed had low values of glucose and fructose and these flours could be considered as low glycemic index foods. The sugars concentrations obtained were lower than those presented by Ogungbenle (2003). However, as reported Repo-Carrasco-Valencia and Arana, (2017) the different extraction method, analysis, ecotypes, origin of quinoa and cultivation or environmental stress affect the sugars concentration. Anyway, quinoa seeds, like the other Andean region grains (e.g. *Chenopodium pallidicaule* and *Amaranthus caudatus*), have higher sugar content than other common cereals (Repo-Carrasco-Valencia, and Arana, 2017).

3.3. Fatty acid composition

The oil content and composition of the major fatty acids obtained from six quinoa flours are shown in Table 2. The oil yield was different among the samples: from WSQ, WBQI and WPQ, were obtained yield values of 2.66, while for WBQII, RBQ and BBQ was recovered an oil yield of 4.01%. These results were slightly lower than what was reported by (Alvarez-Jubete et al., 2009). In all samples, the main fatty acids detected were linoleic acid (18:2*n*-6) > oleic acid (18:1*n*-9) > palmitic acid (16:0) > α-linolenic (18:3*n*-3) acid with statistical differences ($p < 0.05$) between them. These results were in agreement than those reported by Peiretti et al. (2013) and Tang et al. (2015a)

Table 1
Chemical composition, and organic acids and sugars contents obtained from different quinoa flours (mean ± standard deviation).

	Chemical composition				Organic acids				Sugars		
Id	Moisture	Ash	Proteins	Fat	Oxalic	Citric	Malic	Succinic	Sucrose	Glucose	Fructose
WSQ	8.40 ± 0.05^{a}	2.07 ± 0.29^{ab}	11.62 ± 0.17^{c}	5.11 ± 0.40^{c}	0.59 ± 0.07^{b}	0.53 ± 0.08^{ab}	0.18 ± 0.02^{b}	15.74 ± 2.39^{ab}	1.49 ± 0.04^{a}	0.75 ± 0.10^{a}	0.12 ± 0.00^{a}
WBQI	8.64 ± 0.01^{a}	2.28 ± 0.14^{ab}	12.84 ± 0.23^{b}	4.87 ± 0.33^{c}	0.62 ± 0.04^{b}	0.71 ± 0.04^{a}	0.22 ± 0.02^{b}	16.30 ± 1.94^{ab}	1.52 ± 0.05^{a}	0.59 ± 0.03^{a}	0.13 ± 0.02^{a}
WPQ	6.49 ± 0.14^{b}	2.63 ± 0.35^{a}	13.66 ± 0.18^{a}	5.20 ± 0.26^{c}	0.98 ± 0.03^{a}	0.43 ± 0.06^{ab}	0.36 ± 0.04^{a}	12.64 ± 0.03^{b}	1.11 ± 0.03^{b}	0.78 ± 0.00^{a}	0.11 ± 0.00^{a}
WBQII	6.14 ± 0.28^{bc}	1.74 ± 0.21^{b}	12.71 ± 0.15^{bc}	6.06 ± 0.14^{b}	0.50 ± 0.00^{b}	0.61 ± 0.13^{ab}	0.16 ± 0.05^{b}	15.45 ± 2.15^{ab}	1.48 ± 0.07^{a}	0.68 ± 0.0^{a}	0.11 ± 0.00^{a}
RBQ	6.29 ± 0.44^{b}	2.43 ± 0.51^{a}	12.52 ± 0.17^{bc}	6.48 ± 0.22^{a}	0.64 ± 0.08^{b}	0.40 ± 0.05^{b}	0.14 ± 0.01^{b}	21.19 ± 3.59^{a}	1.40 ± 0.02^{a}	0.80 ± 0.09^{a}	0.16 ± 0.03^{a}
BBQ	5.27 ± 0.17^{c}	2.37 ± 0.13^{a}	12.44 ± 0.25^{bc}	5.31 ± 0.41^{c}	0.56 ± 0.05^{b}	0.61 ± 0.05^{ab}	0.21 ± 0.02^{b}	20.72 ± 0.59^{ab}	1.45 ± 0.04^{a}	0.68 ± 0.01^{a}	0.16 ± 0.00^{a}

Moisture, ash, proteins and fat contents were expresses as g/100 g, organic acids content as mg/g and sugar contents as g/100 g of fresh weight. For each assessment, results followed by same case letter are not significantly different according to Tukey's HSD post-hoc test ($p > 0.05$). In the table: WSQ – white Spanish quinoa obtained from organic farming; WBQI and WBQII – two different brand of white Bolivian Real quinoa obtained from organic farming; WPQ – white Peruvian quinoa; RBQ – red Bolivian Real quinoa obtained from organic farming; BBQ – black Bolivian Real quinoa obtained from organic farming

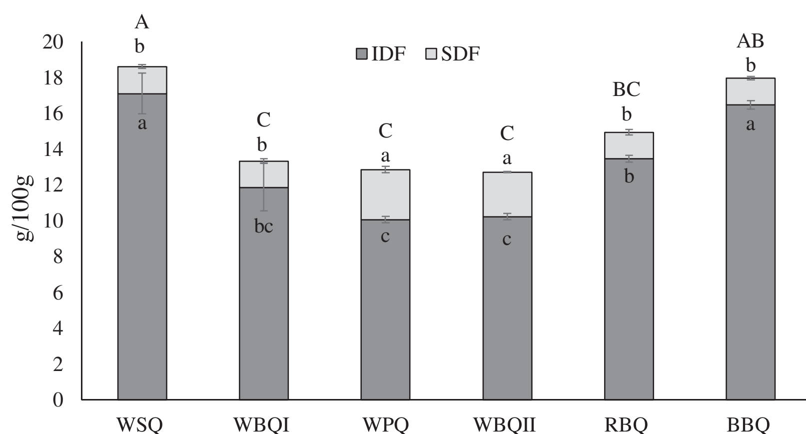

Fig. 1. Insoluble Dietary fiber (IDF) and soluble dietary fiber (SDF) obtained from the different samples. In the figure: WSQ – white Spanish quinoa obtained from organic farming; WBQI and WBQII – two different brand of white Bolivian Real quinoa obtained from organic farming; WPQ – white Peruvian quinoa; RBQ – red Bolivian Real quinoa obtained from organic farming; BBQ – black Bolivian Real quinoa obtained from organic farming. Low-case letters refers to the comparisons of IDF and SDF contents of the samples while upper-case letter refers to the comparison of total dietary fiber contents (TDF = IDF + SDF). Bars followed by same lower/upper-case letter are not significantly different according to Tukey's HSD post-hoc test ($p > 0.05$).

who reported that these fatty acids are the main components of quinoa oils.

WPQ showed highest percentages of linoleic acid ($p < 0.05$), while RBQ the lowest ones ($p < 0.05$). However, for oleic acid its this quinoa flour (RBQ) which showed the highest values with statistical differences ($p < 0.05$) with all samples. At the other end WPQ and BBQ had the lowest values ($p < 0.05$) for this acid (oleic). Regarding palmitic acid, WPQ showed highest values ($p < 0.05$) whilst BBQ had the lowest ($p < 0.05$). However, for α-linolenic acid an opposite trend (BBQ > WPQ) was obtained. The other fatty acids represented the minor fractions (< 1.5%). The majority of the fatty acids detected in quinoa flours were unsaturated fatty acids (UFA). Approximately, 60% of the total content were polyunsaturated fatty acids (PUFA) and a 30% of monounsaturated fatty acids (MUFA); saturated fatty acids (SFA) represented the left 10%. These results were in concordance with found by Tang et al. (2015a) in three commercial quinoa seeds (white, red and black) originated from the Andes. In addition, all quinoa oils (Table 2) presented high Ω6 content, highest values ($p < 0.05$) were obtained from WPQ while lowest ($p < 0.05$) for RBQ, and a good Ω3 content, BBQ showed the best values ($p < 0.05$). These fatty acids exert biological activities; daily intakes of Ω3 fatty acids in fact, are associated with cardiovascular disease risk reduction and inflammatory responses suppression (Simopoulos, 2008). The balance between Ω6 and Ω3 is also highly important in health risk reduction. The Ω6 to Ω3 ratio in quinoa seeds was lower than 6.5 in all the samples, except for RBQ and WPQ which presented higher ratios ($p < 0.05$), 7.48 and 11.42 respectively. The optimal Ω6:Ω3 is different depending on the disease under consideration; however, a ratio should be from 1:1 to 4:1. Thus, in this case the ratio was higher and should not be related to the discussed biological activities.

Table 2
The oil content and composition of the major fatty acids obtained from six quinoa flours identified by means of GC–MS (means ± standard deviation).

ID	WSQ	WBQI	WPQ	WBQII	RBQ	BBQ
C14:0	$0.14 \pm 0.01^{iA.}$	$0.17 \pm 0.04^{hiA.}$	$0.17 \pm 0.01^{iA.}$	$0.19 \pm 0.03^{iA.}$	$0.14 \pm 0.02^{iA.}$	$0.09 \pm 0.04^{lA.}$
C14:1c9	0.08 ± 0.01^{iA}	0.06 ± 0.03^{iA}	0.05 ± 0.02^{jA}	0.08 ± 0.01^{ijA}	0.02 ± 0.03^{iA}	n.d.
C16:0	8.35 ± 0.04^{cBC}	8.51 ± 0.25^{cBC}	9.32 ± 0.05^{cA}	8.51 ± 0.02^{cBC}	8.86 ± 0.23^{cAB}	8.27 ± 0.02^{cC}
C17:0 i	0.18 ± 0.05^{iA}	0.17 ± 0.05^{hiA}	0.19 ± 0.02^{iA}	0.18 ± 0.05^{iA}	0.17 ± 0.05^{hiA}	0.09 ± 0.00^{lA}
C17:0 i	0.10 ± 0.02^{iA}	0.07 ± 0.02^{iA}	0.09 ± 0.01^{ijA}	0.16 ± 0.04^{iA}	0.08 ± 0.02^{iA}	0.10 ± 0.01^{lA}
C16:1 c9	0.12 ± 0.01^{iA}	0.08 ± 0.01^{iA}	0.09 ± 0.01^{ijA}	0.12 ± 0.01^{ijA}	0.09 ± 0.01^{iA}	0.11 ± 0.04^{klA}
C17.0	0.17 ± 0.01^{iA}	0.17 ± 0.02^{hiA}	0.18 ± 0.03^{iA}	0.21 ± 0.03^{iA}	0.18 ± 0.07^{hiA}	0.20 ± 0.00^{jA}
C17:1	0.11 ± 0.01^{iAB}	0.09 ± 0.02^{iAB}	0.12 ± 0.03^{ijA}	n.d.	0.04 ± 0.06^{iAB}	0.12 ± 0.01^{jklA}
C18:0	0.82 ± 0.01^{fA}	0.71 ± 0.01^{fgB}	0.60 ± 0.03^{gC}	0.70 ± 0.02^{fgB}	0.78 ± 0.04^{fAB}	0.79 ± 0.02^{gAB}
C18:1c9	27.48 ± 0.07^{bC}	27.00 ± 0.13^{bD}	25.77 ± 0.05^{bE}	27.95 ± 0.07^{bB}	29.84 ± 0.13^{bA}	25.63 ± 0.03^{bE}
C18:1c11	0.75 ± 0.02^{fgB}	0.81 ± 0.02^{fAB}	0.97 ± 0.03^{fA}	0.82 ± 0.06^{fAB}	0.78 ± 0.08^{fB}	0.78 ± 0.03^{gB}
C18:2	50.16 ± 0.12^{aD}	50.89 ± 0.1^{aC}	53.94 ± 0.00^{aA}	49.66 ± 0.07^{aE}	48.76 ± 0.06^{aF}	52.44 ± 0.01^{aB}
C18:3	7.69 ± 0.00^{dB}	7.55 ± 0.02^{dC}	4.72 ± 0.00^{dE}	7.63 ± 0.05^{dBC}	6.52 ± 0.01^{dD}	7.83 ± 0.02^{dA}
C20:0	0.51 ± 0.01^{hA}	0.44 ± 0.00^{ghAB}	0.40 ± 0.03^{hB}	0.45 ± 0.02^{hAB}	0.44 ± 0.02^{ghB}	0.43 ± 0.00^{iB}
C20:1	1.35 ± 0.02^{eA}	1.33 ± 0.03^{eA}	1.41 ± 0.07^{eA}	1.38 ± 0.05^{eA}	1.35 ± 0.01^{eA}	1.26 ± 0.02^{eA}
C22:0	0.61 ± 0.04^{ghA}	0.56 ± 0.05^{fgAB}	0.49 ± 0.01^{ghB}	0.57 ± 0.02^{ghAB}	0.58 ± 0.00^{fgB}	0.52 ± 0.01^{hAB}
C22:1	1.27 ± 0.00^{eAB}	1.24 ± 0.06^{eABC}	1.33 ± 0.03^{eA}	1.22 ± 0.00^{eBC}	1.16 ± 0.01^{eC}	1.17 ± 0.02^{fBC}
C24:0	0.12 ± 0.02^{iA}	0.14 ± 0.03^{hiA}	0.16 ± 0.03^{ijA}	0.17 ± 0.04^{iA}	0.20 ± 0.01^{hiA}	0.17 ± 0.01^{jkA}
SFA	11.00 ± 0.17^{AB}	10.94 ± 0.28^{AB}	11.6 ± 0.07^{A}	11.14 ± 0.03^{AB}	11.44 ± 0.39^{AB}	10.66 ± 0.05^{B}
MUFA	31.16 ± 0.05^{BC}	30.61 ± 0.16^{C}	29.74 ± 0.07^{D}	31.56 ± 0.06^{B}	33.28 ± 0.32^{A}	29.07 ± 0.03^{E}
PUFA	57.85 ± 0.12^{C}	58.44 ± 0.12^{B}	58.66 ± 0.00^{B}	57.3 ± 0.02^{D}	55.28 ± 0.08^{E}	60.27 ± 0.02^{A}
Total (Ω3)	7.69 ± 0.00^{B}	7.55 ± 0.02^{C}	4.72 ± 0.00^{E}	7.63 ± 0.05^{BC}	6.52 ± 0.01^{D}	7.83 ± 0.02^{A}
Total (Ω6)	50.16 ± 0.12^{D}	50.89 ± 0.10^{C}	53.94 ± 0.00^{A}	49.66 ± 0.08^{E}	48.76 ± 0.06^{F}	52.44 ± 0.01^{B}
Ω6/Ω3	6.53 ± 0.01^{D}	6.74 ± 0.01^{C}	11.42 ± 0.01^{A}	6.51 ± 0.05^{D}	7.48 ± 0.00^{B}	6.7 ± 0.01^{C}
MCFA	0.23 ± 0.001^{AB}	0.23 ± 0.07^{AB}	0.22 ± 0.03^{AB}	0.27 ± 0.04^{A}	0.17 ± 0.01^{AB}	0.09 ± 0.04^{B}
LCFA	99.77 ± 0.01^{AB}	99.77 ± 0.07^{AB}	99.78 ± 0.03^{AB}	99.73 ± 0.04B	99.83 ± 0.01^{AB}	99.91 ± 0.04^{A}

The results are expressed as g/100 g. In the table: n.d. – not detected; WSQ – white Spanish quinoa obtained from organic farming; WBQI and WBQII – two different brand of white Bolivian Real quinoa obtained from organic farming; WPQ – white Peruvian quinoa; RBQ – red Bolivian Real quinoa obtained from organic farming; BBQ – black Bolivian Real quinoa obtained from organic farming. Lower-case letter refers to the comparison of the different compounds in the same samples while upper-case letter refers to the comparison of the same compound between the different quinoa flours samples; results followed by the same lower/upper-case letter are not significantly different according to Tukey's HSD post-hoc test ($p > 0.05$).

Table 3
Physico-chemical and techno-functional properties of six quinoa flours (mean ± standard deviation).

Physico-chemical properties						
	WSQ	WBQI	WPQ	WBQII	RBQ	BBQ
pH	6.42 ± 0.06^{c}	6.55 ± 0.01^{b}	6.60 ± 0.03^{ab}	6.63 ± 0.01^{a}	6.59 ± 0.01^{ab}	6.56 ± 0.02^{b}
aw	0.483 ± 0.014^{b}	0.519 ± 0.010^{a}	0.380 ± 0.004^{cd}	0.400 ± 0.004^{c}	0.410 ± 0.003^{c}	0.354 ± 0.001^{d}
L*	86.24 ± 0.48^{a}	83.48 ± 0.61^{b}	86.29 ± 0.25^{a}	86.37 ± 0.33^{a}	69.32 ± 1.98^{c}	69.94 ± 0.97^{c}
a*	0.10 ± 0.03^{cd}	0.59 ± 0.22^{c}	0.31 ± 0.08^{cd}	0.11 ± 0.05^{d}	4.36 ± 0.72^{a}	1.38 ± 0.20^{b}
b*	14.35 ± 0.24^{cd}	16.68 ± 0.91^{a}	15.39 ± 0.33^{b}	15.00 ± 0.43^{bc}	13.77 ± 0.61^{d}	10.08 ± 0.73^{e}
h_{ab}	89.61 ± 0.13^{ab}	88.01 ± 0.69^{b}	88.86 ± 0.28^{ab}	89.59 ± 0.21^{a}	72.51 ± 2.27^{d}	82.29 ± 0.93^{c}
C_{ab}*	14.35 ± 0.24^{c}	16.69 ± 0.91^{a}	15.39 ± 0.33^{b}	15.00 ± 0.43^{bc}	14.45 ± 0.75^{bc}	10.22 ± 0.74^{d}
Techno-functional properties						
WHC (g/g)	1.50 ± 0.05^{a}	1.80 ± 0.05^{a}	1.60 ± 0.03^{a}	1.66 ± 0.05^{a}	1.44 ± 0.13^{a}	1.49 ± 0.06^{a}
OHC (g/g)	1.01 ± 0.02^{a}	1.04 ± 0.05^{a}	1.02 ± 0.03^{a}	0.96 ± 0.01^{a}	0.96 ± 0.03^{a}	0.89 ± 0.20^{a}
SWC (mL/g)	8.55 ± 0.05^{c}	8.88 ± 0.14^{bc}	9.21 ± 0.21^{ab}	8.58 ± 0.00^{c}	9.57 ± 0.27^{a}	8.98 ± 0.00^{abc}
EC (%)	33.00 ± 4.00^{bc}	15.00 ± 1.00^{d}	39.00 ± 1.00^{ab}	41.00 ± 1.00^{a}	36.00 ± 1.00^{ab}	26.00 ± 1.00^{c}
ES (%)	100.00 ± 0.00^{a}	69.00 ± 3.00^{b}	58.00 ± 11.00^{bc}	55.00 ± 7.00^{bc}	49.00 ± 9.00^{bc}	39.00 ± 2.00^{c}

For each assessment, results followed by same case letter are not significantly different according to Tukey's HSD post-hoc test ($p > 0.05$). In the table: WSQ – white Spanish quinoa obtained from organic farming; WBQI and WBQII – two different brand of white Bolivian Real quinoa obtained from organic farming; WPQ – white Peruvian quinoa; RBQ – red Bolivian Real quinoa obtained from organic farming; BBQ – black Bolivian Real quinoa obtained from organic farming; L* – lightness; a* – red-green coordinate; b* –yellow–blue coordinate, C_{ab}* – Chroma; h_{ab} – Hue; WHC – water holding capacity; OHC – oil holding capacity; BHC – bile holding capacity; SWC – swelling capacity; EC – emulsion capacity; ES – emulsion stability.

3.4. Physico-chemical properties

Table 3 showed the physico-chemical properties of quinoa flours analyzed. Regarding pH, the values ranged ($p < 0.05$) from 6.42 in WSQ to 6.63 in WBQII. These values were in agreement with Miranda et al. (2012) who reported pH values comprised between 6.18 and 6.40 from quinoa seeds cultivated in different regions of Chile. Concerning to water activity (Table 3), all quinoa seeds analyzed ($p < 0.05$) showed water activity values lower than 0.5 except WBQI (0.519). This parameter is widely related with product deterioration; these low valor obtained on six quinoa flours analyzed indicate that the risk of deterioration caused by microorganism, enzymes or non-enzymatic reactions is minimal.

In Table 3 were also showed the color parameters (L*, a*, b*, h_{ab} and C_{ab}*). The difference in lightness (L*) was statistically significant ($p < 0.05$) among white flours and red and black ones, for the latest in fact were recorded the lowest values ($p < 0.05$). The red-green coordinate (a*) were significantly higher ($p < 0.05$) in RBQ and lower ($p < 0.05$) in WBQII, while the yellow-blue coordinate (b*), were higher ($p < 0.05$) in WBQI and lower ($p < 0.05$) in BBQ. Consequentially, the same statistically differences were showed in Chroma (C_{ab}*), for which WBQI and BBQ recorded values of 16.69 and 10.22, respectively; concerning hue values (h_{ab}), higher degrees ($p < 0.05$) were recorded for WSQ (89.61) while lower ones for RBQ (72.51). The obtained results suggest therefore, that the incorporation of a certain quantity of these flours may change appearance of target systems, thus quantities and target products should be chosen considering consumer preferences and product marketability.

3.5. Techno-functional properties

To establish the techno-functional properties of quinoa flours, water-holding capacity (WHC), oil holding capacity (OHC), swelling capacity (SWC) as well as emulsion capacity and emulsion stability (EC and ES respectively) were assessed, results were showed in Table 3. WHC allow assessing the flour ability to retain water under a centrifugal gravity force, considering physically entrapped, capillary, bound and hydrodynamic water. The results obtained showed that there no were statistical differences ($p > 0.05$) among the samples. The values ranged between 1.44 for RBQ and 1.80 for WBQI. The WHC results were lower than reported Ogungbenle, (2003) and Ogungbenle et al. (2009), who mentioned that quinoa flours were capable of retaining 147% of its weight in water. In the same way, Abugoch et al. (2009) found that the WHC of quinoa flour was 4.5 g of water/g flour. OHC, like WHC is the flour ability to retain oil under a centrifugal gravity force, in addition, this property affects the flavor and mouth feel of the product. As occur with WHC, for OHC (Table 3) there were no statistical differences ($p > 0.05$) among the samples. These results were lower than those obtained for wheat (1.82), fine-grained maize (1.94), buckwheat (1.57) and teff (1.73) by Mancebo et al. (2015). Swelling capacity (SWC), allowed establishing the enlargement rate of the flours particles as a result of a water absorption and accumulation. Among the samples, the highest values ($p < 0.05$) were obtained for RBQ while WBQII had lowest ($p < 0.05$). These results were in accordance with those presented by Aluwi et al. (2017) who recorded SWC values from different quinoa flours ranging from 6.27 mL/g to 8.37 mL/g.

Emulsion capacity and emulsion stability of flours are two emulsifying properties related to proteins and other amphoteric molecules (Tiwari and Singh, 2012). Emulsion capacity of quinoa flours (Table 3) was in the range of 15.00 mL/100 mL (WBQI) and 41.00 mL/100 mL (WBQII) with statistical differences ($p < 0.05$) between them. The EC values obtained were lower than those reported by Ogungbenle et al. (2009) who found an EC of quinoa flours of 104%. As regards the ES quinoa flours were in the range of 39.00 mL/100 mL (BBQ) and 100.00 mL/100 mL (WSQ) again with statistical differences ($p < 0.05$) between samples. The high protein content of quinoa flours could explain its high EA due to most proteins are strong emulsifying agents.

3.6. Total phenolic and total flavonoid content

The total phenol content (TPC) and total flavonoids content (TFC) of quinoa flours were given in Fig. 2.

As regard the TPC, the samples RBQ, BBQ, WSQ and WPQ flours in this order showed highest TPC content with no statistical differences between them ($p < 0.05$). The results agreed with those presented by Tang et al. (2015b), who found a higher TPC in black quinoa (5.18 mg GA eq./g). However, Dini et al. (2010) found a TPC for two varieties of quinoa, sweet and bitter of 7.70 and 8.60 mg GA eq./g respectively. The difference could be attributed to the different extraction procedures involved but also to the reactivity of Folin-Ciolcateu reagent with other non-phenolic compounds (e.g. vitamins, aminoacids and proteins) as reported Everette et al. (2010). Regarding TFC, again the flours RBQ and BBQ had the highest ($p < 0.05$) content with no statistical

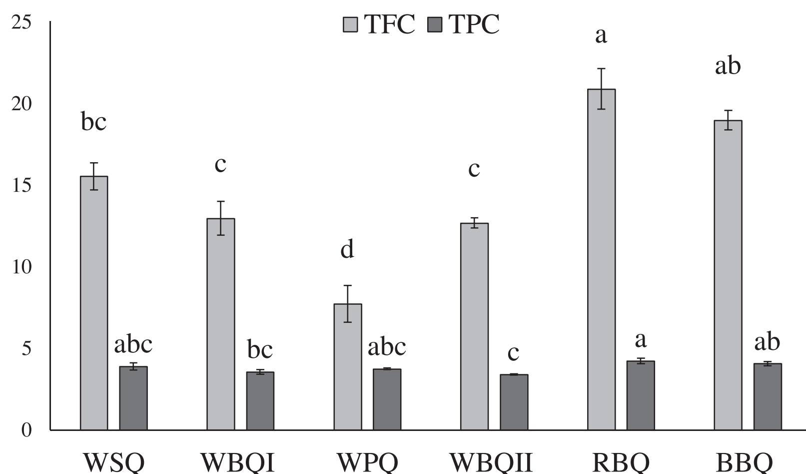

Fig. 2. Total flavonoid and total phenolic content (TFC and TPC respectively) assessed on the different quinoa. TPC results were expressed as mg Gallic Equivalents/g fresh weight, while TFC results were expressed as mg Rutin Equivaents/g fresh weight. In the figure: WSQ – white Spanish quinoa obtained from organic farming; WBQI and WBQII – two different brand of white Bolivian Real quinoa obtained from organic farming; WPQ – white Peruvian quinoa; RBQ – red Bolivian Real quinoa obtained from organic farming; BBQ – black Bolivian Real quinoa obtained from organic farming. For each assay, bars with same case letter are not significantly different according to Tukey's HSD post-hoc test ($p > 0.05$).

differences ($p > 0.05$) between them. In general terms, the values obtained were higher than those presented by Chacaliaza-Rodríguez et al. (2016) who found a total flavonoid content of 8.69 and 9.14 mg RE/g for quinoas of two varieties Salcedo and Altiplano.

The differences observed between these values for both TPC and TFC could be explained, at least in part, by the use of different solvents and extraction methods employed. In addition, it is important to mention that the amount of polyphenolic compounds, *i.e.* phenolic acids and flavonoids, are strongly influenced by the genotype (variety and cultivar), soil, environmental conditions, plant maturity, harvest and post-harvest conditions, among others (Skrovankova et al., 2015).

3.7. LC-ESI–MS/MS phenolic profile identification

Table 4 shown the results of phenolic profile characterization obtained for the different flours. The average of total phenolic compounds detected was comprised between 752.97 μg/g (WBQII) and 875.84 μg/g (WBQI) with no statistical differences ($p > 0.05$) among the samples.

In all samples analyzed the main component ($p < 0.05$) was 4-hydroxibenzoic acid, except for WSQ which presented also higher concentrations ($p < 0.05$) of Neohesperidin. For all the samples, the compound which was found in minor concentrations ($p < 0.05$) was quercetin.

Among the samples the results showed no significantly differences ($p < 0.05$) in the analytes concentrations except for: syringic acid, for which WPQ showed higher concentrations ($p < 0.05$) and BBQ lower ($p < 0.05$); quercetin, for which WSQ and WBQI registered higher concentrations ($p < 0.05$) while lower were detected for BBQ and WBQII; and Neohesperidin, for which WSQ recorded higher values ($p < 0.05$) and WPQ lower ones ($p < 0.05$). The obtained results were in accordance with concentrations ranges founded in scientific literature by Repo-Carrasco-Valencia et al. (2010) and Tang et al. (2015b).

3.8. Antioxidant activity

Table 5 shows the results for the antioxidant properties of quinoa flours. To characterize the different mechanisms naturally involved in the antioxidant activity, four antioxidant assay methods (ABTS, DPPH, FRAP and FIC) were applied. However, it should be born in mind that to compare the antioxidant activity reported by other authors is important consider that the samples should be analyzed with a similar protocol, for example the type of solvent, time of the reaction, and form to express the values because these parameters affect the values obtained for other authors. The comparison of the different flours results showed that the best antioxidant activities in all assays were obtained for RBQ and BBQ ($p < 0.05$), while lowest antioxidant capacity was obtained, in all assays, for WPQ ($p < 0.05$). The results obtained were higher

Table 4
Polyphenolic profile by UHPLC-ES-MS/MS of six quinoa flours (mean ± standard deviation).

Compound	WSQ	WBQI	WPQ	WBQII	RBQ	BBQ
Gallic acid	76.65 ± 6.75^{abcdA}	65.95 ± 6.48^{abcdeA}	89.64 ± 7.26^{abcA}	85.93 ± 17.21^{abcA}	84.72 ± 20.57^{abcA}	97.42 ± 24.28^{abA}
p-coumaric acid	41.36 ± 0.29^{efgA}	53.94 ± 3.07^{bcdeA}	48.92 ± 2.56^{cdefA}	44.67 ± 1.03^{efgA}	43.83 ± 4.33^{cdefA}	51.36 ± 6.77^{cdefA}
Syringic acid	87.73 ± 2.90^{abAB}	113.12 ± 0.37^{abAB}	132.37 ± 23.77^{aA}	93.08 ± 12.37^{abAB}	97.39 ± 9.42^{abAB}	83.01 ± 6.93^{abcB}
Ferulic acid	58.56 ± 8.57^{bcdeA}	70.47 ± 3.52^{abcdA}	62.52 ± 3.10^{cdeA}	63.37 ± 3.67^{cdeA}	63.03 ± 1.43^{bcdA}	66.49 ± 1.40^{bcdA}
Vanillic acid	84.22 ± 17.68^{abcA}	99.55 ± 2.96^{abA}	76.34 ± 5.03^{bcdA}	76.76 ± 4.09^{bcdA}	84.54 ± 23.14^{abcA}	88.11 ± 4.98^{abcA}
4-hydroxybenzoic	97.40 ± 8.04^{aA}	128.90 ± 11.25^{aA}	115.38 ± 34.38^{abA}	109.01 ± 8.72^{aA}	124.23 ± 22.44^{aA}	110.88 ± 27.55^{aA}
Rutin	37.28 ± 13.41^{efgA}	28.51 ± 5.91^{cdeA}	27.06 ± 4.56^{efgA}	26.36 ± 1.49^{fghiA}	29.40 ± 4.02^{defA}	26.61 ± 0.02^{defgA}
Rosmarinic	12.27 ± 0.63^{ghA}	13.73 ± 1.03^{deA}	13.70 ± 1.02^{fgA}	13.21 ± 3.04^{hiA}	13.59 ± 0.53^{efA}	12.63 ± 2.21^{fgA}
Quercetin	4.32 ± 0.49^{hA}	4.15 ± 0.66^{eA}	2.59 ± 1.71^{gAB}	1.26 ± 0.02^{iB}	2.38 ± 0.60^{fAB}	1.88 ± 0.15^{gB}
Chlorogenic acid	19.16 ± 3.66^{fghA}	18.29 ± 1.50^{deA}	17.24 ± 3.42^{efgA}	17.90 ± 0.04^{ghiA}	14.07 ± 1.69^{efA}	16.76 ± 2.74^{efgA}
Isoquercetin	50.06 ± 5.54^{deA}	47.90 ± 0.80^{bcdeA}	43.91 ± 5.91^{defgA}	49.10 ± 5.18^{defA}	48.39 ± 4.19^{cdefA}	54.23 ± 8.92^{cdeA}
Kaempferol	57.25 ± 1.77^{cdeA}	61.80 ± 59.82^{bcdeA}	49.26 ± 5.30^{cdefA}	33.83 ± 0.56^{fghA}	59.01 ± 0.71^{bcdeA}	22.76 ± 4.59^{efgA}
Neohesperidin	103.40 ± 7.33^{aA}	85.14 ± 7.78^{abcAB}	39.08 ± 3.50^{defgC}	65.38 ± 3.95^{bcdeBC}	95.20 ± 19.21^{abAB}	82.66 ± 4.28^{abcAB}
Hesperidin	34.08 ± 6.07^{efgA}	33.49 ± 11.77^{cdeA}	31.06 ± 2.49^{defgA}	26.83 ± 5.15^{fghiA}	41.28 ± 2.13^{cdefA}	27.95 ± 3.25^{defgA}
o-coumaric acid	47.13 ± 1.94^{defA}	50.91 ± 0.94^{bcdeA}	54.12 ± 0.83^{cdefA}	46.32 ± 11.93^{efgA}	52.48 ± 2.81^{bcdeA}	48.23 ± 0.02^{cdefA}
Tot	810.87 ± 48.76^{A}	875.84 ± 77.89^{A}	803.20 ± 17.23^{A}	752.97 ± 5.04^{A}	853.53 ± 12.00^{A}	790.97 ± 5.85^{A}

Results are expressed as μg/g FW (fresh weight) ± standard deviation calculated on 2 sample replicates extracted twice (n = 4). In the table: WSQ – white Spanish quinoa obtained from organic farming; WBQI and WBQII – two different brand of white Bolivian Real quinoa obtained from organic farming; WPQ – white Peruvian quinoa; RBQ – red Bolivian Real quinoa obtained from organic farming; BBQ – black Bolivian Real quinoa obtained from organic farming. Lower-case letter refers to the comparison of the different compounds in the same samples while upper-case letter refers to the comparison of the same compound between the different quinoa flours samples; results followed by the same lower/upper-case letter are not significantly different according to Tukey's HSD post-hoc test ($p > 0.05$).

Table 5
Antioxidant properties of six quinoa flours using four different methodologies DPPH, ABTS, FRAP and FIC assays (mean ± standard deviation).

Sample	WSQ	WBQI	WPQ	WBQII	RBQ	BBQ
DPPH	4.56 ± 0.03^{b}	3.43 ± 0.14^{c}	1.94 ± 0.11^{d}	3.39 ± 0.08^{c}	5.01 ± 0.04^{a}	4.77 ± 0.02^{ab}
ABTS	4.57 ± 0.28^{cd}	4.01 ± 0.25^{d}	3.88 ± 0.19^{d}	5.19 ± 0.18^{bc}	7.76 ± 0.17^{a}	5.72 ± 0.34^{b}
FRAP	3.65 ± 0.30^{bc}	3.36 ± 0.11^{c}	2.37 ± 0.28^{d}	2.95 ± 0.02^{cd}	4.57 ± 0.17^{a}	4.22 ± 0.00^{ab}
FIC	0.91 ± 0.00^{b}	0.77 ± 0.02^{c}	0.59 ± 0.01^{d}	0.77 ± 0.01^{c}	0.97 ± 0.00^{a}	0.94 ± 0.00^{ab}

DPPH, ABTS and FRAP results were expressed as mg TE/g FW, while FIC results as μg EDTA/g FW. The values showed represent the means ± standard deviation calculated on the assessment of 2 sample replicates extracted twice ($n = 4$). For each assay, results followed by same case letter are not significantly different according to Tukey's HSD post-hoc test ($p > 0.05$). In the table: WSQ – white Spanish quinoa obtained from organic farming; WBQI and WBQII – two different brand of white Bolivian Real quinoa obtained from organic farming; WPQ – white Peruvian quinoa; RBQ – red Bolivian Real quinoa obtained from organic farming; BBQ – black Bolivian Real quinoa obtained from organic farming.

than those presented by Alvarez-Jubete et al. (2010) which recorded only 0.577 and 0.921 mg TE/g for DPPH and FRAP assays respectively. Regarding ABTS values, the obtained values are in slightly higher than those obtained by Repo-Carrasco-Valencia and Serna (2011), who reported an ABTS values for raw quinoa ranging from 2.35 to 3.68 mg TE/g sample. Regarding the FIC results were in accordance with the range assessed by Hemalatha et al. (2016) who obtained a FIC values for quinoa whole grain and its milled fractions a range from 1.32 to 9.25 μmol EDTA/g samples (that correspond to a range from 0.38 to 2.70 mg EDTA/g sample). The correlation coefficients (r) between the antioxidant activity assays and total phenolic and flavonoids contents were also calculated (Table 3, supplementary data). Among the assays there was a positive correlation between the assays results. In particular, DPPH-ABTS-FRAP-FIC-TF and TPC-FRAP-TFC presented a strong correlation ($r > 0.7$), while among TPC and DPPH, ABTS and FIC assays there was a moderate correlation ($0.7 < r > 0.3$). Thus, the detected antioxidant activity could be ascribed to phenols and flavonoids.

4. Conclusions

Quinoa seeds could be processed to obtain flours rich in sugars, organic acids and bioactive compounds such as: dietary fibre, Ω3 fatty acids and polyphenolic compounds mainly phenolic acids and flavonoids indicating the way for their use as functional ingredient (in terms of antioxidant activity and control diseases) in different food products. The investigated flours showed also interesting techno-functional mainly swelling capacity. In addition, the antioxidant activity assessed allowed to establish their antioxidant power of this food and the good correlations with total phenolic and flavonoid contents. In general, coloured seed flours presented higher potentiality of applications while the lower ones were obtained from white Peruvian quinoa.

Thus, the results of this study suggest that quinoa flour can be employed as ingredient to enrich food systems. However, further investigations should be undertaken in respect of target product, anyhow the present study allowed to increase the knowledge about this Andean region species.

Acknowledgements

This research was supported by the grant of Ministerio de Economía, de Industria y Competitividad for the project: GL2016-75687-C2-2-R (AEI/FEDER, UE). We thank Manuel Sergi, Faculty of Bioscience and Technologies for Food, University of Teramo, Italy; for LC–MS analysis support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.indcrop.2017.10.006.

References

AOAC, 2000. 17th edition. Official Methods of Analysis of AOAC International, vol. 1 AOAC International, Gaithersburg A. International, Ed.

Abugoch, L.E., Romero, N., Tapia, C.A., Silva, J., Rivera, M., 2008. Study of some physicochemical and functional properties of quinoa (*Chenopodium quinoa* willd) protein isolates. J. Agric. Food Chem. 56 (12), 4745–4750.

Abugoch, L.E., Castro, E., Tapia, C.A., Añón, M.C., Gajardo, P., Villarroel, A., 2009. Stability of quinoa flour proteins (*Chenopodium quinoa* Willd.) during storage. Int. J. Food Sci. Technol. 44, 2013–2020.

Ahamed, N.T., Singhal, R.S., Kulkarni, P.R., Pal, M., 1996. Physicochemical and functional properties of *Chenopodium quinoa* starch. Carb. Pol. 31 (1-2), 9–103.

Aluwi, N.A., Murphy, K.M., Ganjyal, G.M., 2017. Physicochemical characterization of different varieties of quinoa. Cereal Chem. J. http://dx.doi.org/10.1094/cchem-10-16-0251-r.

Alvarez-Jubete, L., Holse, M., Hansen, Å., Arendt, E.K., Gallagher, E., 2009. Impact of baking on vitamin E content of pseudocereals amaranth, quinoa, and buckwheat. Cereal Chem. J. 86, 511–515.

Alvarez-Jubete, L., Wijngaard, H., Arendt, E.K., Gallagher, E., 2010. Polyphenol composition and in vitro antioxidant activity of amaranth, quinoa buckwheat and wheat as affected by sprouting and baking. Food Chem. 119 (2), 770–778.

Blasa, M., Candiracci, M., Accorsi, A., Piacentini, M.P., Albertini, M.C., Piatti, E., 2006. Raw Millefiori honey is packed full of antioxidants. Food Chem. 97 (2), 217–222.

Borderias, A.J., Sanchez, I., Pérez-Mateos, M., 2005. New applications of fibres in foods: addition to fishery products new applications of fibres in foods: addition to fishery products. Trends Food Sci. Technol. 16 (10), 458–465.

Brand-Williams, W., Cuvelier, M.E., Berset, C., 1995. Use of a free radical method to evaluate antioxidant activity. LWT-Food Sci. Technol. 28 (1), 25–30.

Carter, P., 1971. Spectrophotometric determination of serum iron at the submicrogram level with a new reagent (ferrozine). Anal. Biochem. 40 (2), 450–458.

Chacaliaza-Rodríguez, L., Espinoza-Begazo, G., Ramos-Escudero, F., Servan, K., 2016. Proximate chemical composition and content of biologically active components in leaves of two quinoa cultivars (Salcedo and Altiplano) produced in Peru. Res. J. Med Plants. 10 (8), 450–456.

Dini, I., Tenore, G.C., Dini, A., 2010. Antioxidant compound contents and antioxidant activity before and after cooking in sweet and bitter *Chenopodium quinoa* seeds. LWT-Food Sci. Technol. 43 (3), 447–451.

Doughty, E., 1995. Separation of acids, carbohydrates and fermentation products by HPLC. Lebensmittel-Und Biotechnol. 12, 100–101.

Everette, J.D., Bryant, Q.M., Green, A.M., Abbey, Y.A., Wangila, G.W., Walker, R.B., 2010. Thorough study of reactivity of various compound classes toward the Folin-Ciocalteu reagent. J. Agric. Food Chem. 58 (14), 8139–8144.

Fabio, A.D., Parraga, G., 2017. Origin, production and utilization of pseudocereals. In: Haros, C.M., Schoenlechner, R. (Eds.), Pseudocereals. Wiley & Sons, New York, pp. 1–27.

Fischer, S., Wilckens, R., Jara, J., Aranda, M., Valdivia, W., Bustamante, L., Grafa, F., Obala, I., 2017. Protein and antioxidant composition of quinoa (*Chenopodium quinoa* Willd.) sprout from seeds submitted to water stress, salinity and light condition. Ind. Crops Prod. 107, 558–564.

Gómez-Caravaca, A.M., Iafelice, G., Lavini, A., Pulvento, C., Caboni, M.F., Marconi, E., 2012. Phenolic compounds and saponins in quinoa samples (*Chenopodium quinoa* Willd.) grown under different saline and nonsaline irrigation regimens. J. Agric. Food Chem. 60 (18), 4620–4627.

Gawlik-Dziki, U., Świeca, M., Sułkowski, M., Dziki, D., Baraniak, B., Czyz, J., 2013. Antioxidant and anticancer activities of *Chenopodium quinoa* leaves extracts – *In vitro* study. Food Chem. Toxicol. 57, 154–160.

Golay, P.A., Moulin, J., 2016. Determination of labeled fatty acids content in milk products, infant formula, and adult/pediatric nutritional formula by capillary gas chromatography: collaborative study, Final Action 2012.13. J. AOAC Int. 99 (1), 210–222.

Gordillo-Bastidas, E., Díaz-Rizzolo, D.A., Roura, E., Massanés, T., Gomis, R., 2016. Quinoa (*Chenopodium quinoa* Willd), from nutritional value to potential health benefits: an integrative review. J. Nutr. Food Sci. 63 (3), 1–10.

Graf, B.L., Rojas-Silva, P., Rojo, L.E., Delatorre-Herrera, J., Baldeón, M.E., Raskin, I., 2015. Innovations in health value and functional food development of quinoa (*Chenopodium quinoa* Willd.). Comp. Rev. Food Sci. Food Saf. 14 (4), 431–445.

Gullón, B., Pintado, M.E., Fernández-López, J., Pérez-Álvarez, J.A., Viuda-Martos, M., 2015. *In vitro* gastrointestinal digestion of pomegranate peel (*Punica granatum*) flour

obtained from co-products: changes in the antioxidant potential and bioactive compounds stability. J. Funct. Foods 19, 617–628.
Hemalatha, P., Bomzan, D.P., Rao, B.V.S., Sreerama, Y.N., 2016. Distribution of phenolic antioxidants in whole and milled fractions of quinoa and their inhibitory effects on α-amylase and α-glucosidase activities. Food Chem. 199, 330–338.
Lamothe, L.M., Srichuwong, S., Reuhs, B.L., Hamaker, B.R., 2015. Quinoa (*Chenopodium quinoa* W.) and amaranth (*Amaranthus caudatus* L.) provide dietary fibres high in pectic substances and xyloglucans. Food Chem. 167, 490–496.
Li, G., Zhu, F., 2017. Physicochemical properties of quinoa flour as affected by starch interactions. Food Chem. 221, 1560–1568.
Mancebo, C.M., Picón, J., Gómez, M., 2015. Effect of flour properties on the quality characteristics of gluten free sugar-snap cookies. LWT-Food Sci. Technol. 64 (1), 264–269.
Marchyshyn, S.M., Shanayda, M.I., Kernychna, I.Z., Demydiak, O.L., 2016. Qualitative composition and organic acids content in the above ground part of plants from families. Int. J. Medc. Med. Res. 2 (1), 19–22.
Miranda, M., Vega-Gálvez, A., Uribe, E., López, J., Martínez, E., Rodríguez, M.J., Di Scala, K., 2011. Physico-chemical analysis, antioxidant capacity and vitamins of six ecotypes of Chilean quinoa (*Chenopodium quinoa* Willd). Proced. Food Sci. 1, 1439–1446.
Miranda, M., Vega-Gálvez, A., Quispe-Fuentes, I., Rodríguez, M.J., Maureira, H., Martínez, E.A., 2012. Nutritional aspects of six quinoa (*Chenopodium quinoa* willd.) ecotypes from three geographical areas of Chile. Chile J. Agric. Res. 72 (2), 175–181.
Nowak, V., Du, J., Charrondiere, U.R., 2016. Assessment of the nutritional composition of quinoa (*Chenopodium quinoa* Willd.). Food Chem. 193, 47–54.
Ogungbenle, H.N., Oshodi, A.A., Oladimeji, M.O., 2009. The proximate and effect of salt applications on some functional properties of quinoa (*Chenopodium quinoa*) flour. Pak. J. Nutr. 8 (1), 49–52.
Ogungbenle, H.N., 2003. Nutritional evaluation and functional properties of quinoa (*Chenopodium quinoa*) flour. Int. J. Food Sci. Nutr. 54 (2), 153–158.
Oyaizu, M., 1986. Studies on products of browning reaction: antioxidative activity of products of browning reaction prepared from glucosamine. Jap. J. Nutr. 44 (6), 307–315.
Peiretti, P.G., Gai, F., Tassone, S., 2013. Fatty acid profile and nutritive value of quinoa (*Chenopodium quinoa* Willd.) seeds and plants at different growth stages. An. Feed Sci. Technol. 183, 56–61.
Pellegrini, N., Agostoni, C., 2015. Nutritional aspects of gluten-free products. J. Sci. Food Agric. 95 (12), 2380–2385.
Repo-Carrasco-Valencia, R., Arana, J.V., 2017. Carbohydrates of kernels. Pseudocereals. John Wiley & Sons Ltd., pp. 49–70.
Repo-Carrasco-Valencia, R.A., Serna, L.A., 2011. Quinoa (*Chenopodium quinoa*, willd.) as a source of dietary fiber and other functional components. Ciência e Tecnologia de Alimentos Campinas 31, 225–230.
Repo-Carrasco-Valencia, R., Hellström, J.K., Pihlava, J.M., Mattila, P.H., 2010. Flavonoids and other phenolic compounds in Andean indigenous grains: quinoa (*Chenopodium quinoa*), kañiwa (*Chenopodium pallidicaule*) and kiwicha (*Amaranthus caudatus*). Food Chem. 120 (1), 128–133.
Ridout, C.L., Price, K.R., Dupont, M.S., Parker, M.L., Fenwick, G.R., 1991. Quinoa saponins-analysis and preliminary investigations into the effects of reduction by processing. J. Sci. Food Agric. 54 (2), 165–176.
Ruiz, K.B., Biondi, S., Oses, R., Acuña-Rodríguez, I.S., Antognoni, F., et al., 2014. Quinoa biodiversity and sustainability for food security under climate change. Review. Agro. Sust. Develop. 34 (2), 349–359.
Simopoulos, A.P., 2008. The importance of the omega-6/omega-3 fatty acid ratio in cardiovascular disease and other chronic diseases. Exp. Biol. Med. 233, 674–688.
Singleton, V.L., Rossi, J.A., 1965. Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. Am. J. Enol. Vitic. 16 (3), 144–158.
Skrovankova, S., Sumczynski, D., Mlcek, J., Jurikova, T., Sochor, J., 2015. Bioactive compounds and antioxidant activity in different types of berries. Int. J. Mol. Sci. 16 (10), 24673–24706. http://dx.doi.org/10.3390/ijms161024673.
Tang, Y., Li, X., Chen, P.X., Zhang, B., et al., 2015a. Characterisation of fatty acid, carotenoid, tocopherol/tocotrienol compositions and antioxidant activities in seeds of three *Chenopodium quinoa* Willd genotypes. Food Chem. 174, 502–508.
Tang, Y., Li, X., Zhang, B., Chen, P.X., Liu, R., Tsao, R., 2015b. Characterisation of phenolics: betanins and antioxidant activities in seeds of three *Chenopodium quinoa* Willd genotypes. Food Chem. 166, 380–388.
Tiwari, B., Singh, N., 2012. Pulse Chemistry and Technology. The Royal Society of Chemistry.
Vázquez-Ovando, A., Rosado-Rubio, G., Chel-Guerrero, L., Betancur-Ancona, D., 2009. Physicochemical properties of a fibrous fraction from chia (*Salvia hispanica*). LWT-Food Sci. Technol. 42, 168–173.
Veberic, R., Jakopic, J., Stampar, F., 2008. Internal fruit quality of figs (*Ficus carica* L.) in the northern Mediterranean region. Ita. J. Food Sci. 2, 1–8.
Vega-Gálvez, A., Miranda, M., Vergara, J., Uribe, E., Puente, L., Martínez, E.A., 2010. Nutrition facts and functional potential of quinoa (*Chenopodium quinoa* willd.), an ancient Andean grain: a review. J. Sci. Food Agric. 90 (15), 2541–2547.
Viuda-Martos, M., López-Marcos, M.C., Fernández-López, J., Sendra, E., López-Vargas, J.H., Pérez-Alvarez, J.A., 2010. Role of fibre in cardiovascular diseases: a review. Comp. Rev. Food Sci. Food Saf. 9, 240–258.
Wang, S., Zhu, F., 2016. Formulation and quality attributes of quinoa food products. Food Bioproc. Technol. 91, 49–68.
Wright, K.H., Pike, O.A., Fairbanks, D.J., Huber, C.S., 2002. Composition of *Atriplex hortensis*, sweet and bitter *Chenopodium quinoa* seeds. J. Food Sci. 67 (4), 1383–1385.
Wu, G., 2015. Nutritional properties of quinoa. Quinoa: Improvement and Sustainable Production. pp. 193–210. http://dx.doi.org/10.1002/9781118628041. ch 11.