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Nutritional value and the kaempferol and quercetin contents of quinoa (*Chenopodium quinoa* Willd.) from different regions

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Abstract This study compared the nutritional value of quinoa cultivated in different regions, i.e., Peru (PQ), United States (UQ), and Korea (KQ), focusing on their proximate and nutrient compositions and functional components. Moisture, protein, lipid, and ash contents were highest in KQ, and the carbohydrate content was the highest in UQ. KQ had the highest amount of total amino acids, especially lysine. KQ had the lowest levels of Na but the highest levels of K, P, Fe, Mg, Zn, and Mn. The antioxidant compounds, quercetin and kaempferol were not detected in KQ, which consequently had the lowest total phenolic and total flavonoid contents (TPC and TFC, respectively). These values were comparatively higher in UQ. Meanwhile, PQ had the highest TPC and TFC values as well as kaempferol content, but lacking quercetin. These results demonstrate that the nutritional value of quinoa varies according to the region in which it is cultivated.

Keywords: amino acids, kaempferol, nutrition value, quercetin, quinoa

Introduction

Quinoa (*Chenopodium quinoa* Willd) is an ancient crop that originated 3,000-5,000 years ago in Bolivia and Peru, in the Andes region of South America (Lee, 2007). Quinoa cultivation has recently expanded to other regions across the globe owing to its high resistance to the cold temperatures and dry climate found 4000 m above sea level where other crops fail to grow. There is a widespread interest in quinoa as an important food crop that can alleviate food shortages in developing countries (Carciochi et al., 2014). In particular, quinoa can potentially be cultivated in North India and the Himalayan plains, which are environmentally similar to the high mountains of South America (Carciochi et al., 2014; FAO, 2011). Japan has already succeeded in cultivating quinoa (Hirose et al., 2010). In Korea, cultivation of this crop was established in Gangwon Province on a farm in Wonju in 2013 and in Hongcheon in 2015; currently, 60 tons of quinoa are produced across 495,000 m^2 of agricultural land (Seoul Economy, 2017).

Quinoa seeds are rich in proteins, lipids, vitamins, minerals, and dietary fibers compared to other types of cereal crop (Lee, 2007). Their essential amino acids and protein compositions have recently attracted an attention for their potential use in various food products (Hirose et al., 2010; Lee, 2007). According to the Food and Agriculture Organization (FAO), the levels of essential amino acids in a serving of quinoa are higher than the recommended intake for children aged from 3 to 10 year old (FAO, 2013). In particular, the content of lysine, a limiting amino acid in many cereal crops, in rice is 6.6 g per 100 g protein, which is approximately 2 fold higher than that in wheat (3.2 g) and corn (3.4 g). Additionally, the content of methionine often scarce in legumes is 2.4 g per 100 g protein, which is 0.7 times higher than that in soybean (1.7 g). Thus, quinoa is a high-protein food (12-18 g/100 g dry weight) with a balanced amino acid composition (Carciochi et al., 2014).

Quinoa is an equally abundant source of minerals including K, Ca, Mg, P, Fe, and Zn, despite having less Na than other cereal crops (Kim, 2016; Konishi et al., 2004). It also contains vitamins A, E, B_1, B_2, and C (Ruales and Nair, 1994) as well as functional compounds such as saponins, phytosterols, phenolic acids, and flavonoids that are important for disease prevention (Carciochi et al., 2014; Kim, 2016; Konishi et al., 2004; Lee, 2007; Simone et al., 1990). Quinoa has high levels of phenolic compounds including kaempferol, quercetin, caffeic acid, ferulic acid, and vanillic acid (Carciochi et al., 2014) that have positive effects on human health (Chandrasekara and Shahidi, 2011), such as antioxidant, antimicrobial, anti-inflammatory, and antitumor activities. Especially, the flavonoids, kaempferol and quercetin, were reported to be rich in quinoa, and also are known to prevent such chronic diseases through antioxidant action (Carciochi et al., 2014; Chen and Chen, 2013). Indeed, phenolic compounds are known to prevent chronic diseases such as cardiovascular disorders, cancer, obesity, diabetes, and Alzheimer's disease (Shahidi and Chandrasekara, 2013). Previous studies on quinoa have investigated its antioxidant activity and phenolic and flavonoid compositions (Carciochi et al., 2014; Hirose et al., 2010); mineral content (Konishi et al., 2004); the effects of pounding the saponins in quinoa on phenolic composition (Gómez-Caravaca et al., 2014); phenol and betaine

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contents (Tang et al., 2015); and physico-chemical characteristics (Zuniga, 2016).

The nutrient composition of quinoa varies according to the soil and other characteristics of the region in which it is cultivated (FAO, 2011). Additionally, protein content is affected by application of nitrogen-based fertilizers (Lee, 2007). It is therefore important to compare the nutrient composition of quinoa grown in different parts of the world so that its nutritional value can be more accurately represented. Most previous studies examined quinoa cultivated in its original habitat of South America. One study comparing quinoa grown in Japan, Bolivia, and Peru reported similar levels of bioactive compounds among these varieties (Hirose et al., 2010). The recent surge in consumer demand for quinoa in Korea has led to its cultivation in the high-altitude regions of Gangwon Province in an environment that is similar to the original habitat. However, neither of the two studies on Korean quinoa cultivated in Hongseong (Chungcheong Province) and Wonju (Gangwon Province) (Kim, 2016; Lee, 2015) analyzed their nutrient composition in relation to that of quinoa varieties grown in other countries.

Quinoa is now mass produced in Korea and is used by contracted food services (Seoul Economy, 2017). It is necessary to establish the nutritional value of quinoa to assure a consistent standard of quality. To this end, the present study compared the nutrient composition and functional components of quinoa from Peru (the original habitat), the United States (with a high probability of use in food products), and Korea (recently cultivated successfully in Asia), henceforth referred to as PQ, UQ, and KQ, respectively. We analyzed the proximate and nutrient compositions of amino acids and minerals that are known to be more abundant in quinoa than in other cereal crops, as well as the levels of phenolic compounds such as the flavonoids kaempferol and quercetin. Particularly, quinoa produced in Japan was reported to be richer in kaempferol and quercetin than that produced in South America, the original home of quinoa (Hirose et al., 2010). Since Korea is an Asian country which is similar to Japan in natural environments, the kaempferol and quercetin contents of quinoa produced in Korea were analysed to be compared with those of quinoa produced in Japan.

Materials and Methods

Plant materials

To compare the nutrient compositions and functional components of quinoa seeds cultivated in different regions, seeds produced in Peru and United States were purchased through an online store in September 2014, and Korean quinoa seeds produced in Wonju were purchased directly from the farm in August 2014. The samples were stored at −20°C until use.

Preparation of quinoa seed extracts

Samples of dried quinoa seed were ground with a domestic blender and 100 g of material was extracted by reflux for 3 h at 80°C with 1 L of 70% ethanol. Samples were cooled and filtered under vacuum using Whatman No. 2 filter paper (Whatman, Kent, UK). The residue was re-extracted with 70% ethanol and the solvent of the combined extracts was evaporated with a rotary vacuum evaporator (N-1000, EYELA, Tokyo, Japan) at 60°C; the remaining water was removed by freeze-drying (Bondiro MCFD 8508 Freeze Dryer, Ilsin Co., Seoul, Korea). Freeze-dried extracts were ground to fine powder (0.15 mm particle size) and stored in screw cap bottles at −20 °C until analysis.

Analysis of proximate composition of quinoa seeds

The proximate composition of quinoa seeds including moisture, total ash, crude protein, and crude lipid contents was analyzed according to the guidelines of the Association of Official Analytical Chemists (AOAC, 2000). Moisture analysis was carried out using an infrared moisture analyzer (MB45, Ohaus, Zurich, Switzerland). Crude lipid content was determined by the etherextraction method using a Soxtec Avanti 2050 system (Foss Tecator AB, Hoganas, Sweden). Crude protein content was evaluated by the Kjeldahl method using a Kjeltec 2200 auto distillation unit (FOSS, Hillerod, Denmark). Ash content was determined using the ash oven method (AOAC, 2000). All tests and analysis were conducted in triplicate, and results are presented as the mean of three measurements. Carbohydrate content was calculated by subtracting the values of moisture, crude protein, crude lipid, and crude ash contents from 100%.

Analysis of amino acid composition of quinoa seeds

Amino acid content was determined according to the guidelines of the Korea Food and Drug Administration (KFDA, 2009) using an L-8900 high speed amino acid analyzer (Hitachi, Tokyo, Japan). A 0.3 g sample was hydrolyzed with 15 mL of 6 N HCl; the mixture was shaken for 1 min using a vortex mixer (G-560, Scientific Industries, Bohemia, NY, USA) and sealed in a glass ampoule filled with nitrogen gas and heated in an oven at 105°C for 24 h. After cooling to room temperature, the hydrolysate was filtered through a membrane filter (0.2 μm pore size) using a disposable syringe. The ampoule was rinsed twice with distilled water, was filtered, and added to the sample. Amino acid analysis was carried out using an automatic analyzer with a Nova-Pak C_{18} column (3.9×50 mm, Waters Co., Milford, MA, USA) with 10 μL of sample at a column temperature of 30°C. A fluorescence detector (excitation/emission, 250/395 nm) was used, and the mobile phase was analyzed by the gradient method using 0.14 M sodium acetate (A) and 60% acetonitrile (B). Reagents used for the amino acid analysis were purchased from Sigma-Aldrich (St. Louis, MO, USA).

Analysis of mineral content of quinoa seeds

Mineral content was determined according to AOAC guidelines (1995) using a microwave (C900, Ctrl-M Scientific, Cerritos, CA, USA) for wet combustion of the samples. The sample (0.1 g) was placed in a microwave digestion tube and then 2% nitric acid solution and 3 mL distilled water was added to it.

The tube was left to stand for 30 min and then transferred to the microwave for gradual decomposition under the following conditions: 5 min at 100°C under 1300 W; 10 min at 140°C under 1200 W; 10 min at 160°C under 1200 W; and 20 min at 200°C under, 1200 W. The sample was slowly cooled to 50°C and then transferred to a 50 mL volumetric flask, and mixed with distilled water to obtain a standard mixture solution, which was separated and used for analysis. Ca, K, P, Fe, Mg, Zn, Mn, and Na contents were determined by inductively coupled plasma optical emission spectrometry (Optima 8300, PerkinElmer Inc., Waltham, MA, USA) at the following wavelengths: Ca, 317.933 nm; K, 766.490 nm; P, 213.618 nm; Fe, 238.204 nm; Mg, 285.213 nm; Zn, 213.857 nm; Mn, 259.373 nm; Na, 589.592 nm.

Analysis of quercetin and kaempferol levels in quinoa seed extract

Quercetin and kaempferol levels in quinoa seed extracts were determined by liquid chromatography-tandem mass spectrometry (LC-MS/MS). Quercetin and kaempferol reference substances were diluted in methanol to produce 500 mg/100 g, 200 mg/100 g, 100 mg/100 g, 50 mg/100 g, and 10 mg/100 g solutions for analysis. Extracts were prepared by adding 1 mL methanol to 10 mg sample; the mixture was allowed to stand for 7 h at room temperature, and the supernatant was analyzed with a quadrupole time-of-flight mass spectrometer (6530 Series, Agilent Technologies, Santa Clara, CA, USA) connected to a 1260 Infinity high-performance liquid chromatography system (Agilent Technologies, Santa Clara, CA, USA). The mobile phases were 0.1% formic acid (solvent A) diluted in distilled water and 0.1% formic acid (solvent B) diluted in acetonitrile. The flow rate was 0.5 mL/min and the injection volume was 3 μL. An Extend-C18 column (2.1×50 mm, particle size 1.8 μm, Agilent Technologies, Santa Clara, CA, USA) was used. LC-MS/MS conditions were as follows: positive mode of electrospray ionization (ESI), mass range=100-500 m/z, gas temperature=300°C, gas flow=10 L/min, nebulizer pressure=45 psig, sheath temperature=350°C, sheath gas flow=11 L/min, capillary voltage energy=2000 V, and fragmentor =120 V. Data were analyzed using MassHunter v.B.06.00 software (Agilent Technologies, Santa Clara, CA, USA).

Determination of total phenolic content (TPC) and total flavonoid content (TFC) of quinoa seed extracts

TPC of quinoa seed extracts was determined with the Folin-Ciocalteu method (Yu et al., 2002), with some modifications. Extracts (200 μL) were mixed with 400 μL of 2 N Folin-Ciocalteu reagent and 800 μL of 10% sodium carbonate. After shaking, the mixtures were allowed to stand for 1 h before measuring absorbance at 750 nm (V-530, Jasco, Tokyo, Japan). TPC values were determined from a standard curve generated using various concentrations of gallic acid (Sigma Chemical Co., St, Louis, Mo, USA). Results are expressed as mg gallic acid equivalents (GAE)/100 g extract.

TFC of quinoa seed extracts was determined as previously described (Um and Kim, 2007), with some modifications. Extracts (1.0 mL) were mixed with 10 mL of diethylene glycol and 1 mL of 1 N NaOH. After shaking, the mixtures were allowed to stand for 1 h at 37°C before measuring absorbance at 420 nm. Quercetin (Sigma Chemical Co., St, Louis, Mo, USA) was used to establish a standard curve. Results are expressed as mg quercetin equivalents (QUE)/100 g extract.

Statistical analysis

Results are expressed as mean ± standard deviation of three parallel measurements. Data were analyzed by two-way analysis of variance using SPSS v.23.0 software (SPSS Inc., Chicago, IL, USA), and significant differences between groups were determined with Duncan's multiple range test ($p<0.05$).

Results and Discussion

Proximate composition of quinoa seeds cultivated in different regions

Proximate compositions of quinoa seeds cultivated in different regions are presented in Table 1. In general, quinoa contained 9.88-10.13% moisture, 10.82-12.31% crude protein, 4.65-12.93% crude lipid, 2.08-3.66% crude ash, and 60.97-74.10% carbohydrate, but proximate composition varied according to the region in which the plants were cultivated.

KQ and PQ had similar moisture contents (10.13% and 9.88%, respectively) and UQ had the lowest moisture content (8.34%; $p<0.01$). KQ had the highest crude protein content (12.31%), followed by PQ (12.18%) and UQ (10.82%; $p<0.01$ in the descending order). Crude lipid content was highest in KQ (12.93%), followed by PQ (5.07%) and UQ (4.65%; $p<0.001$). KQ also had the highest content of crude ash

Table 1. Proximate composition of quinoa cultivated in different regions

Composition	Treatments	Contents (%)	F (p)
Moisture	PQ[1)]	9.88±0.53[b]	18.169 (0.003)**
	UQ	8.34±0.08[a]	
	KQ	10.13±0.42[b]	
Crude protein	PQ	12.18±0.31[b]	13.048 (0.007)**
	UQ	10.82±0.33[a]	
	KQ	12.31±0.51[b]	
Crude lipid	PQ	5.07±0.88[b]	1815.092 (0.000)***
	UQ	4.65±0.07[a]	
	KQ	12.93±0.31[c]	
Crude ash	PQ	2.57±0.43[a]	30.471 (0.001)**
	UQ	2.08±0.06[a]	
	KQ	3.66±0.08[b]	
Carbohydrate	PQ	70.30±1.01[b]	155.499 (0.000)***
	UQ	74.10±0.51[c]	
	KQ	60.97±1.17[a]	

[1)]PQ: Peruvian quinoa, UQ: United States quinoa, KQ: Korean quinoa. Each value represents mean±SD (n=3). Values with different letters (a-c) within the same column differ significantly ($p<0.05$) through one-way ANOVA followed by Duncan's multiple range test.
**$p<0.01$, ***$p<0.001$

(3.66%; $p<0.01$), which was between that of PQ (2.57%) and UQ (2.08%). Carbohydrate content was the highest in UQ (74.10%), followed by PQ (70.30%) and KQ (60.97%) ($p<0.001$). Thus, KQ had the highest moisture, protein, lipid, and ash contents but had the lowest carbohydrate content; UQ had the lowest moisture, protein, lipid, and ash contents but had the highest carbohydrate content; and the proximate composition of PQ was between those of UQ and KQ, with moisture and protein contents similar to those of KQ and an ash content comparable to that of UQ.

The proximate composition of quinoa seeds per 100 g was as follows: carbohydrates, 56.54-74.30%; proteins, 11.13-16.50%; lipids, 3.95-9.30%; ash, 2.34-5.46%; and moisture, 7.74-15.18%. These values varied according to region, plant variety, and extent of nitrogen fertilizer application (Koziol, 1992; Miranda et al., 2011; Miranda et al., 2012a; Zuniga, 2016). Differences were observed among KQ seeds according to region of cultivation: quinoa cultivated in Wonju (Gangwon Province) was 60.97% carbohydrates, 12.31% proteins, 12.93% lipids, 3.66% ash, and 10.13% moisture, whereas quinoa cultivated in Hongseong (Chungcheong Province) was 79.19% carbohydrates, 5.40% proteins, 4.77% lipids, 2.61% ash, and 4.50% moisture. That is, plants grown in Wonju had lower carbohydrate but higher protein, lipid, ash, and moisture contents (Kim, 2016). A study on the proximate composition of quinoa cultivated in different regions of Chile also reported differences in the protein content between plants grown in Southern Chile (11.32-11.41%) and those grown in the Northern or Central regions (14.66-16.10%) (Miranda et al., 2011). Thus, even in the same country, the nutrient composition of quinoa seeds can vary depending on the region in which they are cultivated due to differences in soil quality or other environmental factors (Koziol, 1992; FAO, 2011). In particular, differences in protein content have been attributed to variations in the application of nitrogen fertilizers (Koziol, 1992; Lee, 2007).

Amino acid content of quinoa seeds cultivated in different regions

Amino acid contents of quinoa seeds cultivated in different regions are shown in Table 2. Total amino acid contents were highest in KQ (98.39 g/100 g; $p<0.001$) with no significant difference between UQ (89.73 g/100 g) and PQ (90.25 g/100 g). Thus, KQ has not only the highest protein content but also the highest total amino acid contents.

The most abundant amino acid in quinoa seeds from different regions was glutamic acid; the level was highest in KQ (17.92 g/100 g), followed by UQ (15.66 g/100 g) and PQ (15.04 g/100 g) ($p<0.001$). The next most abundant amino acid was arginine, with the highest content observed in KQ (10.94 g/100 g) followed by PQ (9.66 g/100 g) and UQ (9.32 g/100 g), although the difference between the latter two was not statistically significant. Aspartic acid was the most abundant in KQ (9.66 g/100 g) and was present in the lowest amount in UQ (9.06 g/100 g) ($p<0.01$). Glutamic acid was the most abundant amino acid in quinoa from Hongseong with a reported value of 1.12 mg/g (Kim, 2016). However, this is 10 times lower than the value found in other studies including the present investigation. One study reported that the most abundant amino acids in quinoa was glutamic acid (11.60-14.70 g/100 g) (Koziol, 1992), although the content was lower than that observed in the present study (15.04-17.92 g/100 g). This difference is not surprising given that the seeds were cultivated in different regions. Additionally, the

Table 2. Amino acid content of quinoa cultivated in different regions

Amino acid (g/100 g)	PQ[1)]	UQ	KQ	F (p)
Asp[2)]	9.31±0.08^{b}	9.06±0.12^{a}	9.66±0.12^{c}	24.380(0.001)**
Thr	4.21±0.03^{a}	4.27±0.02^{b}	4.39±0.03^{c}	38.153(0.000)***
Ser	4.93±0.04^{a}	4.98±0.06^{a}	5.22±0.06^{b}	26.263(0.001)**
Glu	15.04±0.27^{a}	15.66±0.28^{b}	17.92±0.19^{c}	110.891(0.000)***
Gly	5.88±0.04^{b}	5.68±0.04^{a}	6.93±0.11^{c}	252.926(0.000)***
Ala	4.94±0.06^{a}	4.80±0.12^{a}	5.15±0.06^{b}	13.367(0.006)**
Val	4.78±0.07^{ab}	4.65±0.07^{a}	4.86±0.06^{b}	7.436(0.024)*
Ile	3.74±0.08^{a}	3.86±0.03^{b}	3.86±0.20^{b}	5.538(0.043)*
Leu	7.23±0.06^{ab}	7.01±0.19^{a}	7.44±0.09^{b}	8.968(0.016)*
Tyr	3.12±0.03^{b}	2.93±0.07^{a}	3.47±0.12^{c}	32.556(0.001)**
Phe	4.32±0.04^{a}	4.30±0.05^{a}	4.57±0.07^{b}	23.686(0.001)**
Lys	6.18±0.05^{a}	6.28±0.06^{a}	6.59±0.06^{b}	45.830(0.000)***
His	2.87±0.08	2.98±0.08	3.02±0.04	4.321(0.069)
Arg	9.66±0.40^{a}	9.32±0.29^{a}	10.94±0.16^{b}	24.849(0.001)**
Pro	4.05±0.07^{b}	3.93±0.02^{a}	4.36±0.06^{c}	57.332(0.000)***
Total	90.25±0.27^{a}	89.73±0.61^{a}	98.39±0.23^{b}	422.425(0.000)***

[1)]PQ: Peruvian quinoa, UQ: United States quinoa, KQ: Korean quinoa.
[2)]Ala: alanine, Arg: arginine, Asp: aspartic acid, Glu: glutamic acid, Gly: glycine, His: histidine, Ile: isoleucine, Leu: leucine, Lys: lysine, Phe: phenylalanine, Pro: proline, Ser: serine, Thr: threonine, Tyr: Tyrosine, Val: valine.
Each value represents mean±SD (n=3). Values with different letters (a-c) within the same column differ significantly ($p<0.05$) through one-way ANOVA followed by Duncan's multiple range test.
*$p<0.05$, **$p<0.01$, ***$p<0.001$

second most abundant essential amino acid reported in the earlier study was arginine with a content of 7.30-9.70 g/100 g (Koziol, 1992), which is lower than our measured value of 9.32-10.94 g/100 g. However, another group reported a value of 8.69 mg/g in KQ cultivated in Hongseong (Kim, 2016), indicating that significant variations in amino acid content exist based on the region of cultivation. This was substantiated by an analysis of amino acid content of quinoa grown in different regions of Chile (Miranda et al., 2012a). These authors found that the most abundant essential amino acid in quinoa was arginine, which varied from 10.70-10.90 g/100 g in Northern Chile to 10.90-12.00 g/100 g in Central Chile to 11.90 g/100 g in Southern Chile (p<0.05). The amino acid profile of quinoa is affected by the production region of the quinoa plant: the south Chilean quinoa has the highest content of amino acids (histidine, leucine, lysine, methionine, phenylalanine, tyrosine, taurine, glycine, and serine), whereas the Central Chilean quinoa has the lowest amino acid content (Miranda et al., 2012a).

Quinoa contains high levels of lysine, which is a limiting amino acid in rice, the major grain consumed by Koreans (Caballero et al., 2003; FAO, 2011; Koziol, 1992; Miranda et al., 2012a). We found that lysine content was higher in KQ (6.59 g/100 g) than in PQ (6.18 g/100 g) or UQ (6.28 g/100 g) (p<0.001). This is consistent with studies comparing quinoa to other cereal crops, which reported a lysine content of quinoa (5.69-8.84 g/100 g) that was around two times higher than that of rice (3.80 g/100 g), wheat (2.90 g/100 g), or corn (2.60 g/100 g) (Jancurová et al., 2009; Miranda et al., 2012a). Quinoa also contains high levels of methionine and cysteine which are typically scarce in legumes (Caballero et al., 2003) as well as all 10 essential amino acids (including two that cannot be synthesized in infants) (Kim, 2016). The protein efficiency ratio (PER) in raw debittered quinoa is 78.00-93.00%, which is higher than that in casein; this value increases to 102.00-105.00% in cooked quinoa (Caballero et al., 2003). Preliminary protein fractionation studies have shown that the major proteins in quinoa are albumin and globulin, with prolamin present at a low level (Jancurová et al., 2009). The digestibility of quinoa proteins is comparable to that of other high-quality food proteins (Comai et al., 2007). The solubility of extracted quinoa proteins can be improved by enzymatic hydrolysis (Instituto et al., 1986). Thus, adding quinoa to the meal in which rice, wheat, corn, or beans is the major ingredient is expected to provide a source of amino acids lacking in these grains, this promoting protein synthesis, due to high protein content and PER.

Mineral content of quinoa seeds cultivated in different regions

The levels of eight types of mineral in quinoa seeds cultivated in different regions were measured (Table 3). The mineral content of quinoa was 439.82-665.81 mg/kg of Ca, 3872.81-12610.01 mg/kg of K, 5926.08-7261.41 mg/kg of P, 47.99-85.73 mg/kg of Fe, 1936.19-2284.76 mg/kg of Mg, 31.87-75.31 mg/kg of Zn, 18.43-65.28 mg/kg of Mn, and 83.05-808.54 mg/kg of Na, with significant differences observed among seeds cultivated in different regions (p<0.001).

Ca content was the highest in PQ (665.81 mg/kg), followed by KQ (609.53 mg/kg) and UQ (439.82 mg/kg) (p<0.001). Na content was highest in PQ (808.54 mg/kg) and lowest in KQ (83.05 mg/kg) (p<0.001). K and Fe contents were highest in KQ (12610.01 and 85.73 mg/kg, respectively) and lowest in UQ (3872.81 and 47.99 mg/kg, respectively) (p<0.001). Zn and Mn contents were also highest in KQ (75.31 and 65.28 mg/kg, respectively) and lowest in UQ (31.87 and 18.43 mg/kg, respectively) (p<0.001). Although KQ had the lowest Na content, it had the highest K, P, Fe, Mg, Zn, and Mn contents among the three varieties of quinoa examined, indicating a superior mineral content. Thus, consuming quinoa as an alternative to rice, barley, wheat, or corn can provide valuable minerals to the human body, since quinoa has 3-26 times higher contents of minerals such as Ca, K, Fe, Mg, and Cu than the above-mentioned staple foods (Jancurová et al., 2009; Konishi et al., 2004; Koziol, 1992). It has been reported that minerals are lost from quinoa upon washing or drying; indeed, the Instituto Nacional Autónomo de Investigaciones Agropecuarias demonstrated reductions in Ca (29.00%), Mg (20.00%), Na (48.00%), K (49.00%), Cu (38.00%), Fe (52.00%), and Mn (27.00%) upon washing quinoa seeds (Instituto et al., 1986). However, most quinoa seeds currently available on the market have been coated with glazers, which likely minimize the loss of minerals even when the seeds absorb water during cooking. Although the specific amount may differ according to age and sex and excluding pregnant or breast-feeding mothers, it is expected that 100 g of quinoa would satisfy the recommended dietary intake

Table 3. Mineral content of quinoa cultivated in different regions

Treatments	Minerals (mg/kg)							
	Ca	K	P	Fe	Mg	Zn	Mn	Na
PQ[1)]	665.81±3.66^{c}	5084.56±48.82^{b}	5926.08±104.81^{a}	59.54±1.25^{b}	1936.19±10.34^{a}	33.69±0.69^{b}	29.18±0.47^{b}	808.54±22.46^{c}
UQ	439.82±0.98^{a}	3872.81±16.63^{a}	5994.33±116.15^{a}	47.99±1.37^{a}	1950.74±2.81^{a}	31.87±0.45^{a}	18.43±0.31^{a}	161.78±9.80^{b}
KQ	609.53±8.61^{b}	12610.01±49.90^{c}	7261.41±26.52^{b}	85.73±0.52^{c}	2284.76±30.27^{b}	75.31±0.35^{c}	65.28±0.23^{c}	83.05±2.81^{a}
F (p)	1407.895 (0.000)***	39158.449 (0.000)***	202.138 (0.000)***	905.428 (0.000)***	399.275 (0.000)***	6751.921 (0.000)***	14413.708 (0.000)***	2345.151 (0.000)***

[1)]PQ: Peruvian quinoa, UQ: United States quinoa, KQ: Korean quinoa.
Each value represents mean±SD (n=3). Values with different letters (a-c) within the same column differ significantly (p<0.05) through one-way ANOVA followed by Duncan's multiple range test.
***p<0.001

of minerals by providing Na (1-2%), Ca (4-6%), Zn (10-15%), P (11-16%), K (15-19%), Fe (27-40%), Mn (23-76%), and Cu (47-200%) (Koziol, 1992).

There were clear differences in mineral content of quinoa cultivated in different regions. For example, although quinoa is known to have 20 times higher Ca content than other cereal crops, studies on the Ca content in Chilean quinoa has reported values ranging from 77.10 to 221.29 mg/100 g hydrolysis (Instituto et al., 1986). Specifically, North Chilean quinoa was found to contain 77.10 mg Ca/100 g, whereas South Chilean quinoa contained 221.29 mg/100 g, which is around three times higher (Miranda et al., 2012b). Other studies comparing the mineral content of quinoa cultivated in different regions reported a high degree of variation in Ca (275.00-1487.00 mg/kg), P (1400.00-5300.00 mg/kg), Mg (0.00-5020.00 mg/kg), Fe (14.00-168.00 mg/kg), Zn (0.00-48.00 mg/kg), K (0.00-12000.00 mg/kg), and Cu (0.00-51.00 mg/kg) (Koziol, 1992). We found here that quinoa cultivated in Wonju contained 609.52 mg/kg Ca showed 49-fold higher than quinoa cultivated in Hongseong with 1.25 mg/100 g Ca (Kim, 2016). Taken together, these findings indicate that quinoa seeds cultivated in different regions even within a single country differ in terms of nutritional value since their variety is influenced by environmental conditions (Koziol, 1992; Miranda et al., 2012b).

Quercetin and kaempferol contents in quinoa seed extracts

The ESI Ion Trap M analysis of quercetin and kaempferol standard substances in positive mode produced $[M+H]^+$ and ionized state fragment MS/MS values (Table 4). The LC-MS/MS analysis revealed high correlation coefficients (R^2) in the standard curves of quercetin and kaempferol (0.9979 and 0.9982, respectively).

In the quantification of quercetin from extracts of quinoa cultivated in different regions, mass values for UQ indicated the presence of the H^+ attached form with the molecular ion peak of $[M+H]^+$ at *m/z* 303.0537. The retention time was 2.467 min for UQ. Quercetin was present in UQ extract at a concentration of 18.66 mg/100 g, but was not detected in KQ or PQ. Mass values of the H^+ attached form were present in both PQ and UQ, with the molecular ion peak of $[M+H]^+$ at *m/z* 287.0584 and 257.1386, respectively. The retention times were similar i.e., 2.656 min for PQ and 2.649 min for UQ. Kaempferol content was higher in PQ than in UQ (78.40 vs. 45.12 mg/100 g). Neither quercetin nor kaempferol was detected in KQ, likely because their concentrations were below the detection limit (Ko, 2015). The mass values of quercetin and kaempferol were *m/z* 303.0537 and *m/z* 285.0583, respectively, which are consistent with a previous report (Yao et al., 2015). We found that while UQ contained both quercetin (18.66 mg/100 g) and kaempferol (45.12 mg/100 g). However PQ lacked quercetin but had a 1.74 fold higher kaempferol content than UQ.

Previous studies showed the quercetin and kaempferol contents of quinoa varies depending on cultivated regions and processing methods. Quercetin was not detected Ecuadorian quinoa (Zuniga, 2016); meanwhile, quercetin content was three times higher in Japanese as compared to Bolivian quinoa, whereas kaempferol content in Japanese quinoa was around three times lower than in Bolivian or Peruvian quinoa (Hirose et al., 2010). These authors also showed that on 3 days after germination, quercetin content increased 5.91 folds from 0.23 to 1.36 mg/100 g, whereas kaempferol content increased 1.80 folds from 0.15 to 0.27 mg/100 g (Carciochi et al., 2014). With longer germination times, TPC and TFC also increased 4.40-7.84 folds, enhancing the overall antioxidant activity of quinoa. Possible reasons for the variable quercetin and kaempferol contents of quinoa reported in previous studies are differences in geographical parameters or processing methods. Germination of quinoa seeds has been shown to increase quercetin and kaempferol contents (Carciochi et al., 2014). The observed increase in the phenolic content of quinoa suggests that processing quinoa seeds by germination or dehydration is an effective approach for increasing antioxidant activity. As such, future studies should investigate whether processing can increase the content of phenolic compounds such as flavonoids in KQ, which contains lower amounts of quercetin and kaempferol than quinoa cultivated in other regions.

TPC and TFC of quinoa seeds from different regions

TPC and TFC of quinoa extracts are shown in Table 5. TPC was the highest in PQ (5.00 mg GAE/g), followed by UQ (4.70 mg GAE/g) and KQ (3.84 mg GAE/g) ($p<0.001$). TFC was the highest in PQ (2.18 mg QUE/g), followed by UQ (1.76 mg QUE/g) and KQ (1.60 mg QUE/g) ($p<0.001$). Although TPC differed significantly among quinoa cultivated in different regions, TFC values for PQ and UQ were similar, while

Table 4. Quercetin and kaempferol contents of quinoa cultivated in different regions

Vitamin		Retention time (min)	Abundance (area)	Mass (m/z)	Calibration concentration (mg/100 g)	Molecular formula
Quercetin	PQ[1)]	N.D.[2)]	N.D.	N.D.	N.D.	N.D.
	UQ	2.467	109474	303.0537	18.66	$C_{15}H_{10}O_7H$
	KQ	N.D.	N.D.	N.D.	N.D.	$C_{15}H_{10}O_7H$
Kaempferol	PQ	2.656	384937	287.0583	78.40	$C_{15}H_{10}O_6H$
	UQ	2.649	238889	257.1386	45.12	$C_{15}H_{10}O_6H$
	KQ	N.D.	N.D.	N.D.	N.D.	$C_{15}H_{10}O_6H$

[1)]PQ: Peruvian quinoa, UQ: United States quinoa, KQ: Korean quinoa
[2)]N.D.: not detected.

Table 5. Total polyphenol and flavonoid contents of extracts from quinoa cultivated in different regions

Treatments	TPC (mg GAE[2])/g)	TFC (mg QUE[3])/g)
PQ[1]	5.00±0.10[c]	2.18±0.08[b]
UQ	4.70±0.10[b]	1.76±0.05[b]
KQ	3.84±0.05[a]	1.60±0.08[a]
F (*p*)	152.306(0.000)***	56.603(0.000)***

[1]PQ: Peruvian quinoa, UQ: United States quinoa, KQ: Korean quinoa.
[2]TPC is expressed as mg gallic acid equivalents (GAE)/g extract).
[3]TFC is expressed as mg quercetin equivalents (QUE)/g extract).
Each value represents mean±SD (n=3). Values with different letters (a-c) within the same column differ significantly (p<0.05) through one-way ANOVA followed by Duncan's multiple range test.
***p<0.001

deviating significantly from the TFC of KQ.

Quinoa is a pseudocereal grain with a composition similar to that of other grains. The polyphenol content of quinoa depends on the variety and growth conditions as well as on environmental factors such as soil pH, precipitation, and temperature. All these factors can influence the genes related to TPC, which can differ even among seeds grown in the same region (Miranda et al., 2010). TPC and TFC values were 3.72-16.55 and 7.77-14.37 mg QUE/100 g, respectively, in Chilean quinoa (Miranda et al., 2014) and 43.20 and 11.40 mg QUE/100 g, respectively, in Indian quinoa (Kaur et al., 2014); these values were lower than those obtained in the present study. Aside from minor differences in TPC and TFC of specific varieties, Chilean quinoa had lower TPC but higher TFC than Indian quinoa did. In addition, other studies have reported 0.40-8.64 mg/g of TPC and 0.10-1.80 mg/g of TFC (FAO, 2011), which are consistent with the results of the present study except for the TFC of PQ. The TPC and TFC values obtained here were in agreement with the results of the flavonoid content analysis. Neither quercetin nor kaempferol was detected in KQ, but quercetin and kaempferol contents in UQ were 18.66 and 45.12 mg/100 g, respectively, suggesting a relationship between a balanced flavonoid content and high TPC and TFC. However, PQ had the highest TPC and TFC despite lacking quercetin, which was probably due to the high kaempferol content (78.40 mg/100 g). Although quercetin and kaempferol were not detected in KQ, other types of phenolic compound may be present that contribute to the unexpectedly high TPC and TFC values.

Most plants produce phenolic compounds including flavonoids, which can combine with macromolecules like as proteins and act as a reducing agent, singlet oxygen quencher, and hydrogen donor. We and others have confirmed that phenolic compounds with antioxidant activity such as quercetin and kaempferol are found in quinoa. However, the type and amount of phenolic compounds vary according to the region in which the quinoa seeds are cultivated, resulting in different TPC and TFC values. Further research is necessary to assess the correlation between these compounds and the antioxidant activities of quinoa, so that these properties can be exploited.

Conclusions

This study compared the nutrient composition and functional components of quinoa cultivated in different regions, including Peru, United States, and Korea (PQ, UQ, and KQ, respectively). KQ had the highest moisture, protein, lipid, and ash contents but the lowest carbohydrate content. UQ had the highest carbohydrate content and the lowest moisture, protein, lipid, and ash contents. Total amino acid content was highest in KQ, which also had the highest protein content. KQ had the highest level of lysine, which is a limiting amino acid in rice, the major grain in the Korean diet. Despite having the lowest Na content, KQ had the highest levels of K, P, Fe, Mg, Zn, and Mn and therefore showed superior mineral content to quinoa from other regions. The flavonoids, quercetin and kaempferol, were not detected in KQ, which consequently had the lowest TPC and TFC. In contrast, UQ had balanced contents of both flavonoids and relatively high TPC and TFC. PQ showed the highest TPC and TFC values despite lacking quercetin, since it contained the highest amount of kaempferol. In summary, the results of this study demonstrate that KQ has superior nutritional value as compared to quinoa cultivated in other regions in terms of protein, amino acid, and mineral contents. These results indicate that KQ can have health benefits if consumed as an alternative to traditional staple foods such as rice.

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