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Qualitative and quantitative analysis of characteristic free and bound phenolics in three colored quinoas

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Abstract Quinoa is a good source of phenolics, which both exist as free and bound forms. In order to mark clear the characteristic free and bound phenolics in different quinoa samples, in this study, characteristic free and bound phenolics in three colored quinoas including WQ (white quinoa), RQ (red quinoa) and BQ (black quinoa) were investigated. Result showed a total of 14 phenolics both acted as free and bound form were analyzed in three colored quinoas (WQ, RQ and BQ). Gallic acid, vanillic acid, epicatechin, p-coumaric acid and quercetin existed both as free and bound forms were common phenolics in quinoas. The highest total free phenolics (238.10 mg/kg) and bound phenolics (3 377.75 mg/kg) were presented in WQ and RQ, respectively. It indicated WQ and RQ were respectively good source of free and bound phenolics. Moreover, characteristic free and bound phenolics in three colored quinoas could be well analyzed by principal component analysis (PCA), indicating it was an effective and reliable method in distinguishing three colored quinoas based on their characteristic free and bound phenolics, respectively.

Keywords: quinoa; free phenolics; bound phenolics; PCA

1 Introduction

Quinoa (*Chenopodium quinoa Willd*) as a gluten-free pseudocereal, belongs to the Chenopodiaceae family with over 7 000 years' agricultural history [1]. Quinoa is considered as a "full nutrition food" or "superfood", because it has a balanced profile of amino acid and is rich in carbohydrate, dietary fiber and vitamin, polyphenols, and these nutritional qualities in quinoa are significantly higher than that of rice, wheat and corn [2-4]. Although quinoa originates from Andean region of South America, in recent years, it has been widely cultivated in the USA, Canada, China, Europe, Australia and India, regardless of extreme ecological conditions of air temperature, humidity, sea level and soil [5, 6]. Recently, more and more commercial and scientific attentions have been paid on quinoa [4, 7].

Among varieties of nutritional compositions in quinoa, phenolic acids are the primary substances that contribute the outstanding antioxidant capacity, anti-inflammatory property and antimicrobial activity [8, 9]. Phenolic compounds are the important secondary metabolites with the total content of 1.67−3.08 g/kg DW in quinoa [10]. Up to now, over 50 phenolics have been found in quinoas, and ferulic acid, rutin, coumarin, vanillic acid and caffeic acid are

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common [11-13]. Indeed, phenolic acids exist both as free and bound forms in quinoas. Free phenolic acids can be directly utilized by the human body, while bound phenolics are covalently conjugated to sugar moieties or cell wall structural substances that can survive in the stomach, intestinal and colon, and difficult to digest [14]. Moreover, only a few amounts of phenolics present as free form in quinoa while a large number exist as bond form [15]. Bound phenolics in quinoa can be release by acid hydrolysis, alkaline hydrolysis and enzymatic hydrolysis [13] as well as extrusion [11] and germination [2]. Based on the different appearances, the quinoas are mainly classified as white quinoa, red quinoa, and black quinoa [16, 17], and significant sensory and quality characteristics are presented in different colored quinoas [4, 12].

The aims of this study were to make clear both of the free and bound characteristic phenolics and their content in three colored quinoas, and distinguish the characteristic individual phenolic of three colored quinoas by PCA.

2 Material and method

2.1 Quinoa material

Three colored quinoas of white quinoa (WQ), red quinoa (RQ) and black quinoa (BQ) respectively come from Chaoyang of Liaoning Province (119.4 E, 41.25 N), Golmud of Qinghai Province (94.9 E, 36.41 N) and Linxi of Shandong Province (117.63 E, 35.50 N) in China. About 5.0 kg of each variety of quinoa samples were collected, and transported to laboratory in three days with vacuum packing and kept in (4 ± 0.5) ℃ cold storage.

2.2 Reagent

Standard phenolics of quercetin, dihydroactinidiolide, p-coumaric acid, protocatechuic acid, sinapic acid, epicatechin, resveratrol, (+)–catechin, isorhamnetin, apigenin glycoside, vanillic acid, syringic acid, gallic acid and catechol were purchased from Sigma-Aldrich (St. Louis, MO, USA). Methanol, ethanol, sodium hydroxide, hydrochloric acid and ethyl acetate of HPLC grade were obtained from Tianjin Baiaotai technology development company (Tianjin, China).

2.3 Phenolic analysis

2.3.1 Free and bound phenolic extractions

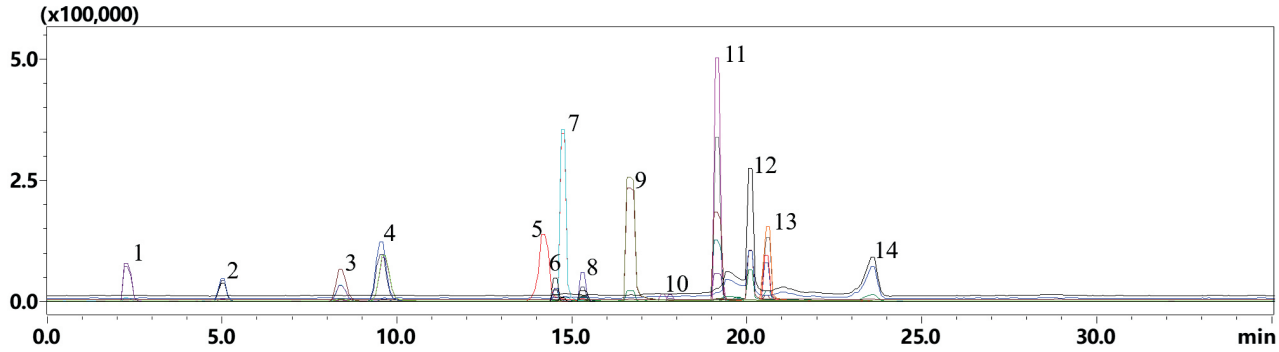
Free and bound phenolics in three colored quinoas were extracted according to the methods of Song, et al. (2022) [11] and Tang, et al. (2016) [13]. Briefly, about 100 g of each variety of quinoa samples were crushed into powder by a pulverizer (JYL-CO20, Joyoung, Jinan, China) and the quinoa powders were passed through 80 meshes sieve (Baijie, Shanghai, China), then accurate 2.0 g of each quinoa flour sample was extracted twice with ethanol/water (80/20, *V*/*V*) solution under the assist of the ultrasound for 10 min to obtained the free phenolics. Next, the extract was centrifugated at 8 500 g for 5 min and the supernatants were collected, and then the sample was evaporated and reconstituted with 2 mL of ethanol/water (1/1, *V*/*V*). The extracts were marked and stored in refrigerator (−18 °C) with stopper test tubes.

The bound phenolics of three colored quinoas were obtained using the residues after free phenolic extraction above. The residues were digested with 200 mL NaOH (2 mol/L), and the extraction was kept for 4 h with flowing nitrogen gas and shaking. Then, under cooling ice bath condition, the solution was acified to pH 2−3 with 10 mol/L HCl. Accurate 500 mL of hexane was used to remove the lipids from solution, and the solution was centrifugated at 12 000 g for 5 min. The residues were extracted with 100 mL of 1/1 diethyl ether/ethyl acetate (*V*/*V*) five times. The supernatants were combined and evaporated to dryness, and then dissolved with 2 ml of methanol/water (1:1, *V*/*V*). Next, the extracts were marked and stored at −18 °C refrigerator with stopper test tubes.

2.3.2 Qualitative and quantitative analysis of phenolics

Both of free and bound phenolics of three

colored quinoas were determined by based on the method of Song, et al. (2022) [11]. Accordingly, the liquid chromatography system (Agilent, 1290 series) of LC-ESI-QTOF-MS equipped with a Kinetex C^{18} column (2.6 µm, 150 mm * 4.6 mm) was applied to the separation of the phenolics. Milli-Q water and acetonitrile was respectively used as mobile phase A and B. The gradient elution procedure was as follows, 0−5 min (95% A, 5% B), 6−40 min (0% A, 100% B), and 41−45 min (95% A, 5% B), and the flow rate was 0.5 mL/min. The column temperature and the injection volume was 30 °C and 20 µL, respectively. The identification of individual phenolic in quinoas was based on the standard (Fig. 1) and previous studies [11, 12]. The quantitative determination of the phenolics was carried out by external standard method, and standard solution (200 ppb−100 ppm) was used for the establishment of the calibration curves of individual phenolics. The result of the phenolics in three colored quinoas were presented as mg/kg of dry basis.



1 – Quercetin; 2 – Dihydroactinidiolide; 3 – *p*-Coumaric acid; 4 – Protocatechuic acid; 5 – Sinapic acid; 6 – Epicatechin; 7 – Resveratrol; 8 – (+) – Catechin; 9 – Isorhamnetin; 10 – Apigenin glycoside; 11 – Vanillic acid; 12 – Syringic acid; 13 – Gallic acid; 14 – Catechol.

Fig. 1 Standard spectrograms of 14 polyphenols

2.4 Statistical analysis

SPSS software of 20.0 version (SPSS Inc., Chicago, IL) was applied to the phenolic data treatment of three colored quinoas. Phenolic contents of three colored quinoa samples were presented as mean ± SD (standard deviation) of three repetitions. The verify differences of the phenolics in different quinoas were analyzed by Duncan's multiple analysis at the level of $P < 0.05$. Principal component analysis (PCA) was used to analysis the characteristic phenolics of three colored quinoas.

3 Results and discussion

3.1 Basic information of quinoa samples

In Table 1, the moisture content, weight, color and appearance of WQ, RQ and BQ were presented. The water content of RQ and BQ was 10.76% and 10.69, respectively, which was significant ($P < 0.05$) higher than that of WQ (7.88%). Color value of L^* (the lightness), a^* (the redness) and b^* (the yellowness) were applied to characterize the color sense of different quinoa samples [18]. The highest color value of L^*, a^* and b^* was respectively showed in WQ (48.77), BQ (3.03) and WQ (5.57), and significant differences ($P > 0.05$) of the color value of a^* (1.27 of RQ − 3.03 of BQ) and b^* (0.22 of BQ − 5.57 of WQ) was presented among three colored quinoas. Clearly, the three colored quinoas can be easily distinguished according to their color values. No significant difference ($P > 0.05$) was found in the weight of thousand seeds ≈ 0.35 g, which was higher than that of BQ (0.27 g).

Table 1 Weight, water content, color and picture of three colored quinoas

Sample	Water content (%)	The weight of thousand seeds (g)	Color			Picture
			*L**	*a**	*b**	
WQ	7.88 ± 0.07a	0.35 ± 0.03b	48.77 ± 1.06b	2.39 ± 0.03b	5.57 ± 0.33c	
RQ	10.76 ± 0.12b	0.38 ± 0.03b	39.69 ± 1.10a	1.27 ± 0.04a	1.17 ± 0.08b	
BQ	10.69 ± 0.16b	0.27 ± 0.01a	38.74 ± 1.08a	3.03 ± 0.15c	0.22 ± 0.01a	

Note: WQ – White quinoa; RQ – Red quinoa; BQ – Black quinoa.
Mean values with different lower-case letters in the same column correspond to significant differences at $P < 0.05$. Data are represented as the mean ± SD (standard deviation).

3.2 Free phenolics in quinoa samples

Free phenolics in plants are usually easy to be dissolved in various solvents [19], and will be absorbed in the stomach and small intestine [20]. Hence, free phenolics in the grains were close with their antioxidant ability and biological values [21].

A total of 14 characteristic free phenolics were analyzed in three colored quinoas and the result was shown in Table 2. Gallic acid (38.90 mg/kg of BQ − 161.26 mg/kg of WQ), quercetin (45.11 mg/kg of WQ − 62.00 mg/kg of BQ), vanillic acid (9.87 mg/kg of BQ − 16.60 mg/kg of WQ), protocatechuic (2.31 mg/kg of WQ − 9.76 mg/kg of BQ), epicatechin (3.43 mg/kg of BQ − 4.76 mg/kg of WQ) and (+) – catechin (4.15 mg/kg of BQ − 5.39 mg/kg of RQ) were common in three colored quinoas, and similar results were also reported in quinoas in previous studies [1, 11-13, 22]. As shown in Table 2, the total content of free phenolic in WQ was 238.10 mg/kg, which was significantly ($P < 0.05$) higher than that of RQ (171.41 mg/kg) and BQ (133.67 mg/kg). It indicated WQ was a good source of free phenolics. Moreover, the highest content of individual phenolic of gallic acid, quercetin, *p*-coumaric acid, protocatechuic acid, epicatechin, and vanillic acid was respectively presented in WQ, BQ, BQ, BQ, RQ, and WQ (Table 2), indicating phenolic resources can also be selected based on the free-formed phenolic composition of three colored quinoas.

Table 2 Content of free phenolic compositions in WQ, RQ and BQ quinoas

Peak	Phenolic compounds	Free phenolic content (mg/kg)		
		WQ	RQ	BQ
1	Quercetin	45.11 ± 2.37a	53.70 ± 1.84b	62.00 ± 3.05c
2	Dihydroactinidiolide	0.13 ± 0.01a	0.34 ± 0.02c	0.24 ± 0.00b
3	*p*-Coumaric acid	0.40 ± 0.01a	0.70 ± 0.03b	3.55 ± 0.41c

(to be continued)

Continued Table 2

Peak	Phenolic compounds	Free phenolic content (mg/kg)		
		WQ	RQ	BQ
4	Protocatechuic acid	2.31 ± 0.17a	4.95 ± 0.50b	9.76 ± 0.39c
5	Sinapic acid	2.01 ± 0.11c	0.94 ± 0.10b	0.74 ± 0.04a
6	Epicatechin	4.76 ± 0.24b	5.58 ± 0.29c	3.42 ± 0.08a
7	Resveratrol	–	0.32 ± 0.01a	0.31 ± 0.02a
8	(+)-Catechin	4.87 ± 0.30b	5.39 ± 0.35c	4.15 ± 0.27a
9	Isorhamnetin	0.08 ± 0.01a	0.07 ± 0.00a	0.06 ± 0.01a
10	Apigenin glycoside	0.05 ± 0.00a	0.15 ± 0.01b	0.19 ± 0.01c
11	Vanillic acid	16.60 ± 0.87b	10.17 ± 0.51a	9.87 ± 0.60a
12	Syringic acid	0.40 ± 0.02b	0.48 ± 0.02c	0.04 ± 0.00a
13	Gallic acid	161.26 ± 7.72c	88.38 ± 4.18b	38.90 ± 2.99a
14	Catechol	0.12 ± 0.01a	0.24 ± 0.01b	0.44 ± 0.01c
Total		238.10	171.41	133.67

Note: WQ – White quinoa; RQ – Red quinoa; BQ – Black quinoa.
Mean values with different lower-case letters in the same row correspond to significant differences at $P < 0.05$. Data are represented as the mean ± SD (standard deviation). "–", not detected.

3.3 Bound phenolics in quinoa samples

Bound phenolics are linked with the insoluble macromolecules of food matrixes by chemically covalent bonds, hydrogen bonding and hydrophobic interactions or physically entrapped in food matrixes and intact cells [23, 24]. Quinoa is rich in bound phenolics (> 1.0 mg/g) [13], and the release of bound phenolics can significantly increase the abilities of antioxidant, antiinflammation, anticancer, antiobesity and antidiabetic [25].

Table 3 showed a total of 14 bound phenolics were identified in three colored quinoas, and the highest total bound phenolic was presented in RQ (3 377.75 mg/kg), followed by BQ (2 315.91 mg/kg) which was significantly ($P < 0.05$) higher than that of WQ (238.22 mg/kg). It indicated bound phenolics showed great potential in RQ and BQ, and the result was agreed with Tang, et al. (2016) [13]. Among these bound phenolics, gallic acid (143.92 mg/kg in WQ – 2 894.96 mg/kg in RQ), (+)-catechin (13.46 mg/kg in WQ – 182.87 mg/kg in RQ), epicatechin (18.20 mg/kg – 195.42 mg/kg in RQ), quercetin (11.82 mg/kg in WQ – 36.10 mg/kg in RQ), *p*-coumaric acid (6.44 mg/kg – 17.30 mg/kg in RQ) vanillic acid, (9.19 mg/kg in BQ – 35.77 mg/kg in WQ) and sinapic acid (1.17 mg/kg in BQ – 6.06 mg/kg in WQ) were common in three colored quinoas with relative high content. Similar results were also reported in quinoas in previous studies [26, 27]. Other bound phenolics of dihydroactinidiolide, protocatechuic acid, resveratrol, isorhamnetin, syringic and catechin in three colored quinoas showed the highest content in BQ (0.44 mg/kg), RQ (24.70 mg/kg), RQ (0.32 mg/kg), WQ (0.08 mg/kg), RQ (4.46 mg/kg) and RQ (5.41 mg/kg), respectively (Table 3).

Table 3 Content of bound phenolic compositions in WQ, RQ and BQ quinoas

Peak	Phenolic compounds	Bound phenolic content (mg/kg)		
		WQ	RQ	BQ
1	Quercetin	11.82 ± 0.77a	36.10 ± 2.38c	18.47 ± 1.52b
2	Dihydroactinidiolide	0.20 ± 0.01a	0.34 ± 0.01b	0.44 ± 0.01c
3	*p*-Coumaric acid	6.44 ± 0.29a	17.30 ± 1.44c	9.25 ± 1.06b
4	Protocatechuic acid	1.20 ± 0.06a	24.70 ± 1.31c	16.03 ± 0.95b
5	Sinapic acid	6.06 ± 0.41c	2.40 ± 0.17b	1.17 ± 0.04a
6	Epicatechin	18.20 ± 1.45a	195.42 ± 8.82c	84.93 ± 3.04b
7	Resveratrol	0.26 ± 0.01a	0.32 ± 0.02b	0.26 ± 0.02a
8	(+)-Catechin	13.46 ± 1.10a	182.87 ± 9.24c	84.05 ± 4.29b
9	Isorhamnetin	0.08 ± 0.01b	0.06 ± 0.00a	0.06 ± 0.00a
10	Apigenin glycoside	0.05 ± 0.00a	0.05 ± 0.01a	0.04 ± 0.01a
11	Vanillic acid	35.77 ± 1.63c	13.36 ± 1.05b	9.19 ± 1.11a
12	Syringic acid	0.56 ± 0.03a	4.46 ± 0.19c	2.93 ± 0.22b
13	Gallic acid	143.92 ± 7.16a	2 894.96 ± 86.52c	2 085.82 ± 90.16b
14	Catechol	0.20 ± 0.00a	5.41 ± 0.31c	3.27 ± 0.24b
Total		238.22	3 377.75	2 315.91

Note: WQ – White quinoa; RQ – Red quinoa; BQ – Black quinoa.
Mean values with different lower-case letters in the same row correspond to significant differences at $P < 0.05$. Data are represented as the mean ± SD (standard deviation).

3.4 PCA analysis

PCA is a multivariate data statistical tool with the advantage of representing a group of factors by a small number of key factors, and examine the correlation between multiple variables shown as a 2D or 3D dataset [28]. In PCA visualization, observations overlapped or close to each other indicating they are similar, otherwise are dissimilar [29, 30]. In order to well analysis the characteristic free and bound phenolics in three colored quinoas, PCA was performed.

Based on the characteristic free phenolics, as shown in Fig. 2, three colored quinoas of WQ, RQ and BQ were well distinguished. It indicated the free phenolics in WQ, RQ and BQ was significantly different. Fig. 2 showed free phenolics of gallic acid, isorhamnetin, sinapic acid, and vanillic acid were closed to WQ, indicating WQ could be characterized by these free phenolics. Agreed with the result of Table 2, the highest content of gallic acid (161.26 mg/kg), isorhamnetin (0.08 mg/kg), sinapic acid (2.01 mg/kg), and vanillic acid (16.60 mg/kg) were presented in WQ. While, for the highest content among three colored quinoas, BQ was characterized by the free phenolics of quercetin (62.00 mg/kg), catechin (0.44 mg/kg), protocatechuic acid (9.76 mg/kg), and apigenin glycoside (0.19 mg/kg) (Fig. 2, Table 2).

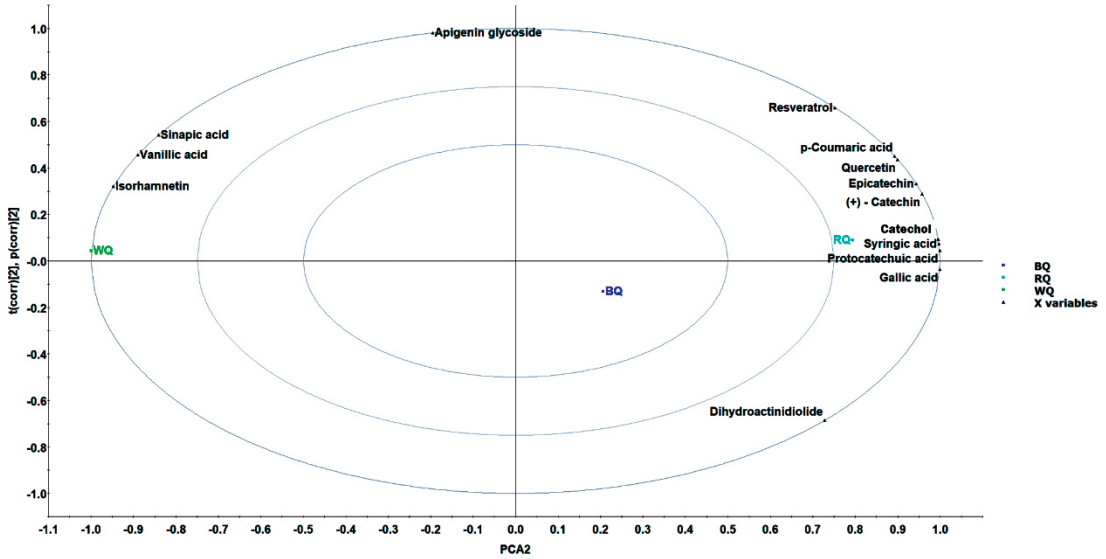


Fig. 2 PCA analysis of three colored quinoas (WQ, RQ and BQ) based on their free phenolics

PCA was also used to analyzed three colored quinoas (WQ, RQ and BQ) based on their characteristic bound phenolic profiles (Fig. 3). Clearly, quinoa samples (WQ, RQ and BQ) were well separated in the PCA visualization, it indicated bound phenolics in three colored quinoas were significantly different. Bound phenolics of isorhamnetin, vanillic acid, and sinapic acid were closed to WQ, indicating these bound phenolics could characterized WQ. Noteworthy, RQ was surrounded by bound phenolics of catechin, syringic acid, protocatechuic acid, (+)-catechin, epicatechin, quercetin, and *p*-coumaric acid, because of their highest content in RQ (Fig. 3, Table 3). It indicated RQ was great potential source of bound phenolic. In general, three colored

quinoas of WQ, RQ and BQ could be well distinguished by PCA according to their characteristic free and bound phenolics, respectively.

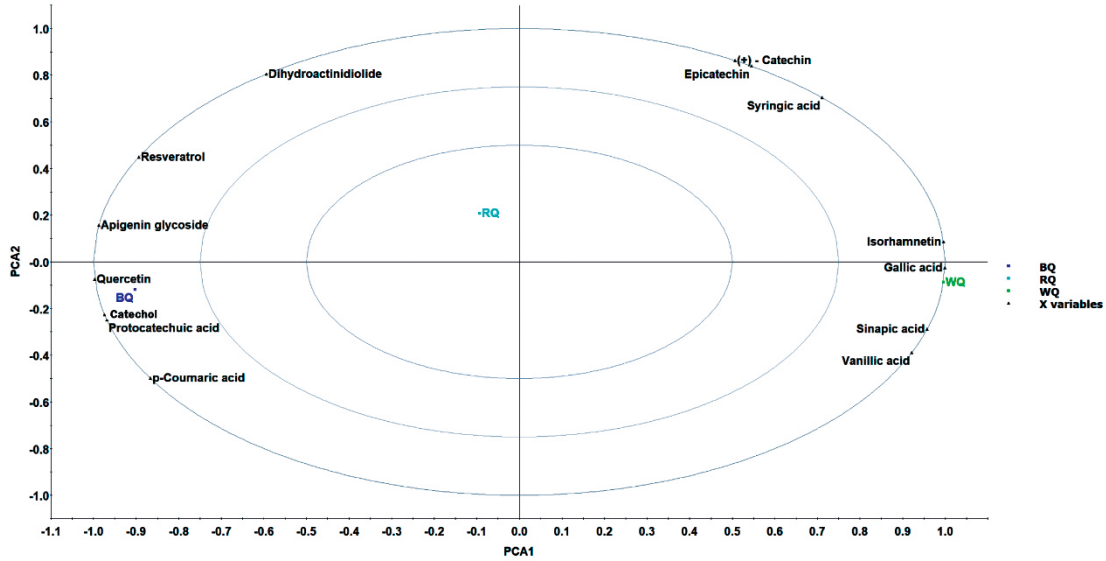


Fig. 3 PCA analysis of three colored quinoas (WQ, RQ and BQ) based on their bound phenolics

4 Conclusion

A total of 14 phenolics both acted as free and bound form were analyzed in three colored quinoas (WQ, RQ and BQ). Gallic acid, vanillic acid, epicatechin, *p*-coumaric acid and quercetin existed both as free and bound forms were common phenolics in quinoas. The highest total free phenolic (238.10 mg/kg) and bound phenolic (3 377.75 mg/kg) was presented in WQ and RQ, respectively. PCA was an effective and reliable method in distinguishing three colored quinoas based on their characteristic free and bound phenolics, respectively.

Acknowledgments

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