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# Chemical characterization and antioxidant properties of fractions separated from extract of peanut skin derived from different industrial processes

Mariana Larrauri[a], Maria P. Zunino[b], Julio A. Zygadlo[b], Nelson R. Grosso[a], Valeria Nepote[b,*]

[a] Facultad de Ciencias Agropecuarias, Universidad Nacional de Córdoba (IMBIV—CONICET), CC 509, 5000 Cordoba, Argentina
[b] Facultad de Ciencias Exactas, Físicas y Naturales, Universidad Nacional de Córdoba (IMBIV—CONICET), Cordoba, Argentina

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ABSTRACT

Peanut skins are a natural source of phenolic compounds with antioxidant activity and potential utility as food preservatives. The purpose of this study was to determine the chemical composition and antioxidant activities of extracts and purified fractions obtained from peanut skins prepared by blanching and roasting processes. Peanut skins from blanching and roasting processes were used to obtain crude extracts. These crude extracts were purified by solvent partition with *n*-hexane, ethyl acetate, and water. The ethyl acetate fraction obtained from blanched peanut skins was separated in a column packed with Sephadex LH-20 and separated into three new fractions of different colors: yellow, purple, and brown. The extraction yield, total phenols and flavonoids, scavenging activity towards different radicals (DPPH, hydroxyl, and superoxide anion), ferrous ion chelating activity, and accelerated sunflower oil oxidation were evaluated in crude extracts and purified fractions. The peanut skin fraction compounds were analyzed by HPLC–ESI-MS/MS. The extracts obtained from blanched peanut skins displayed a higher phenolic content (672.40 mg GAE/g) than those prepared from roasted peanut skins (416.92 mg GAE/g). Purification using solvent partition with ethyl acetate and column chromatography increased total phenolic content and antioxidant activity of peanut skin extracts. Fractions with higher total phenolic contents were associated with higher scavenging activities towards DPPH and superoxide anion radicals, and higher ferrous ion chelating activity. The yellow fraction exhibited higher flavonoid content and showed higher hydroxyl radical scavenging activity. In the accelerated sunflower oil oxidation test, peroxide values were lower in the color fraction samples. The main compounds present in peanut skin color fractions were phenolic acids, flavonoids, and stilbenes. The purified fractions of peanut skins displayed antioxidant properties and reduced peroxide formation in sunflower oil. These fractions could be used as a natural antioxidant in food products.

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## 1. Introduction

During the preparation of some products, such as blanched peanuts or peanut butter, the peanut industry removes the skins from the kernels. Peanut skins are a form of industrial waste with a low value mainly used for livestock (Sarnoski et al., 2012). However, peanut skins are an excellent raw material for the production of phenolic compounds. These phenolic compounds have demonstrated high antioxidant activity and constitute a potential additive for food as a preserving agent (O'Keefe and Wang, 2006; Yu et al., 2010; Larrauri et al., 2013, 2016).

The antioxidant activity of phenolic compounds is given by their ability to scavenge free radicals, such as hydroxyl and superoxide anion, and to chelate metal ions (Wang et al., 2007; Su et al., 2007; Bazylko et al., 2014). In addition, there are many studies on grapes, teas, nuts, cereals, and vegetables that emphasize the potential benefits of phenolic compounds from natural sources to health (Meng et al., 2012; Chandrasekara et al., 2012; Bazylko et al., 2014; Bursal and Köksal, 2011). Particularly, natural phenolic compounds are often used to protect the organism from cardiovascular diseases and certain tumors (Oldoni et al., 2016; Roleira et al., 2015; Rangel-

* Corresponding author at: Facultad de Ciencias Exactas, Físicas y Naturales, Universidad Nacional de Córdoba (IMBIV—CONICET), Av. Velez Sarsfield 1611, 5000 Cordoba, Argentina.
*E-mail address:* valenepote@gmail.com (V. Nepote).

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Huerta et al., 2015). On the contrary, synthetic antioxidants have been demonstrated to be hazardous to health (Sun et al., 2011; Prakash et al., 2015); therefore, scientists are exploring natural ones as a safe alternative.

The industrial method used to process peanuts affects the amount of phenolic compounds in peanut skins (Davis et al., 2010; Yu et al., 2006). Davis et al. (2010) reported that total phenolic content decreases from 19.33 to 16.31 mg ferulic acid equivalents/100 g in peanut skins during 77 min of roasting at 166 °C.

Francisco and Resurreccion (2009a) and Sarnoski et al. (2012) have identified and quantified phenolic compounds in peanut skin extracts. They observed that peanut skins are rich in polyphenols, such as phenolic acids (chlorogenic acid, caffeic acid, and ferulic acid), flavonoids (epigallocatechin, epicatechin, catechin gallate, epicatechin gallate), and stilbenes (resveratrol). These compounds would be responsible for the antioxidant activity of peanut skin extract. There are few studies about the purification and separation of polyphenol fractions from peanut skins and their chemical composition and antioxidant properties (Nepote et al., 2002, 2004a, 2005). During the purification process, the antioxidant contents of some fractions are expected to increase relative to that of crude extracts.

The purpose of this work was to determinate the chemical composition and antioxidant activities of extracts and purified fractions obtained from the peanut skins separated by blanching and roasting processes.

## 2. Materials and methods

### 2.1. Materials

Peanuts type Runner from Argentina (crop 2012) were the raw material used to get peanut skins. These peanut skins were produced by two different industrial processes: blanching (90 °C during 10 min) and roasting (150 °C during 20 min). The peanut skins were provided by "Lorenzati, Ruetsch y Cia", Ticino, Cordoba, Argentina. This material was kept in a sealed plastic bag and stored at 4 °C until used.

### 2.2. Crude extracts and purified fractions from peanut skins

The peanut skins crude extracts obtained for blanching (BCE) and roasting (RCE) processes were prepared according to Nepote et al. (2004b). Before to prepare the crude extract, peanut skins were defatted with *n*-hexane for 6 h using Soxhlet apparatus. Then, the polyphenols were extracted from defatted peanut skins using ethanol-water (70:30 v/v) by maceration at room temperature for 24 h.

Dried crude extracts (8 g) were suspended in distilled water (55 mL) and partitioned in a separating funnel with 90 mL *n*-hexane. This solvent was used to eliminate residual lipids in the extract to avoid antagonistic polarity in the fractions and to improve their drying-off procedure. Then, the aqueous phase was partitioned with 500 mL ethyl acetate. This solvent was chosen because phenol compounds have good solubility in it according to the reported by other researches (Nepote et al., 2004a; Larrauri et al., 2013, 2016). The ethyl acetate fractions from blanched skins (BEA) and roasted skins (REA) were dried in rotatory evaporator at 35 °C (Larrauri et al., 2016). The aqueous fractions from blanched skins (BW) and roasted skins (RW) were lyophilized to dryness (Pizzolitto et al., 2013).

The BEA fraction was separated in three new fractions using a column packed with Sephadex LH-20 (10 mm internal diameter, 33.5 cm length) and ethanol and acetone:distilled water (proportion 90:10) as running solvents. Two fractions were eluted with ethanol: Yellow (Y) and purple (P) fractions. The last fraction was brown color (B). Y and P fractions were dried in a rotatory evaporator (35 °C), and B fraction was lyophilized.

### 2.3. Extraction yield, total phenolic and flavonoid determinations

The extraction yield of peanut skin extracts and fractions was calculated according to the formula: Extraction yield = (g dry extracted matter)/(g dry peanut skins).

Total phenolic compounds in extracts and purified fractions were determined using the Folin-Ciocalteu method (Waterman and Mole 1994; Nepote et al., 2005). The absorbance of samples was measured in a spectrophotometer at 760 nm (Spectrum SP-2100, Zhejiang, China). Gallic acid (GAE, Sigma-Aldrich, St. Luois, USA) was used as standard. Total phenolic content was expressed as mg GAE/g sample.

Total flavonoids were determined according to the $AlCl_3$ method (Luximon-Ramma et al., 2005) measuring absorbance at 367 nm. The calibration curve was prepared using quercetin (QE, Sigma-Aldrich, St. Luois, USA). The results were expressed in mg QE/g sample.

### 2.4. DPPH radical scavenging activity

The radical-scavenging activity of peanut skin extracts and purified fractions was determined using diphenyl picryl hydrazyl radical (DPPH) according to Nepote et al. (2004a). Different aliquots of samples on methanol (300 μg/mL) were added to 1.5 mL DPPH methanolic solution (20 μg/mL). The absorbance of samples was measured at 517 nm. BHT (Fluka, Sigma-Aldrich. St. Luois, USA) was used as positive control. The radical-scavenging activity was calculated using the formula: % RSA = [1 − (absorbance of DPPH and sample − absorbance of sample)/absorbance of DPPH] × 100. The inhibitory concentration 50% ($IC_{50}$) was calculated from the curve obtained by plotting inhibition percentage of vs. final extracts concentrations (Quiroga et al., 2011).

### 2.5. Chelating activity on ferrous ion ($Fe^{2+}$)

The $Fe^{2+}$ chelating activity of extracts and fractions was determined according to Yamaguchi et al. (2000) and Bursal and Köksal (2011). Samples and $FeSO_4$ solutions were prepared and measured at 522 nm. EDTA (Biopack, Buenos Aires, Argentina) was used as positive control. The ability to chelate the ferrous iron was calculated using the formula: Chelating activity (%) = $(1 - A_{sample}/A_{control}) \times 100$. The inhibitory concentration 50% ($IC_{50}$) was calculated (Quiroga et al., 2011).

### 2.6. Hydroxyl radical scavenging activity

The hydroxyl radical-scavenging activity of peanut skin extracts and purified fractions was determined according to Gao et al. (2010) (modified). The sample solutions were measured at 532 nm. Ascorbic acid (Biopack, Buenos Aires, Argentina) was used as positive control. The scavenging effect of hydroxyl radical (%) was calculated using the following formula: Scavenging effect (%) = $(1 - A_{sample}/A_{control}) \times 100$. The inhibitory concentration 50% ($IC_{50}$) was calculated (Quiroga et al., 2011).

### 2.7. Superoxide anion radical-scavenging activity

The superoxide anion radical scavenging activity of peanut skin extracts and purified fractions was evaluated according to Okamura et al. (1993). The absorbance of the samples was measured at 560 nm. BHT (Fluka, Sigma-Aldrich. St. Luois, USA) was used as positive control. The scavenging effect of superoxide

anion (%) was calculated using the formula: Scavenging activity (%) = $(1 - A_{sample}/A_{control}) \times 100$. The inhibitory concentration 50% ($IC_{50}$) was calculated according to Quiroga et al. (2011).

### 2.8. Accelerated oxidation test

The antioxidant activity of peanut skin extracts and purified fractions was determined by accelerated oxidation test (Quiroga et al., 2011). In test tubes, 7 mL sunflower oil was mixed with 0.2% (w/w) of crude extracts or fractions (BCE, RCE, BEA, REA, BW, RW, Y, P, or B) or 0.02% (w/w) BHT, a synthetic antioxidant used as reference. Sunflower oil without additives was the control sample. The samples were stored at 60 ± 1 °C for 4 days and peroxide values ($meqO_2\ Kg^{-1}$ oil, AOAC, 2010) were analyzed on samples every 24 h.

### 2.9. HPLC–ESI-MS/MS analysis on purified fractions (Y, P, and B)

An Agilent Series 1200 LC System (Agilent, USA) coupled to a MicrOTOF Q II (Bruker Daltonics, USA) was used for HPLC–ESI-MS/MS analysis. The HPLC system consisted in a micro vacuum degasser, binary pumps, autosampler (40 μL sample loop), thermostated column compartment, and diode array detector. The mass spectrometer equipped with electrospray ion source and qTOF analyzer was used in MS and MS/MS mode for the structural analysis of peanut skin extract compounds. HPLC analyses were performed using a thermostated (40 °C) Phenomenex Luna C18 250 × 4.6 mm (5 μm) column and a solvent system formed 0.5% (v/v) formic acid (solvent A) and methanol (solvent B) and 0.4 mL/min flow rate. The solvent gradient program was started with 20% B changing to 50% in 3 min, kept for 5 min, followed by a second ramp until reaching 80% B in 5 min. The injection volume was 40 μL. ESI-MS detection was performed in negative ion mode with mass acquisition between 100 and 1500 Da. Nitrogen was used as drying and nebulizer gas (7 L/min and 3.5 bar, respectively). For MS/MS analysis, the fragmentation was carried out using Auto MS2 option. DAD analyses were gotten in the range between 200 and 700 nm. The peanut skin extract components were indentified by co-analysis of pure compound showing identical retention time and mass data; and by comparison with spectral properties (UV, ESI-MS, and MS/MS) of compounds available in literature data. The results were expressed in relative percentage (%).

### 2.10. Statistical analysis

All experiments were carried out in three repetitions. Data were analyzed with the InfoStat software version 2013p (Facultad de Ciencias Agropecuarias, Universidad Nacional de Cordoba, Cordoba, Argentina). Means and standard deviations were calculated for each variable. Analysis of variance (ANOVA) and DGC multiple range test were used to figure out significant differences among means ($\alpha = 0.05$). Pearson coefficients were estimated to stablish correlations between dependent variables. Principal component analysis (PCA) was carried out on the correlation matrix of normalized data from all measured variables. The purpose of the PCA was to explore associations between variables and peanut skin extracts/fractions. Cluster analysis (CA) was made to get groups of peanut skin extracts/fractions with similar characteristics. Sample similarities were based on the Euclidean distance; and groups of extracts/fractions with similar characteristics were obtained using the average linkage of unweighted pair-group method with arithmetic mean (UPGMA). Means, standard deviations, ANOVA, and DGC multiple range test were also performed in extracts/fractions groups obtained from the cluster analysis (Nepote et al., 2009).

## 3. Results and discussion

### 3.1. Extraction yield, total phenolic and flavonoid determinations

The extraction yield and total phenolic and flavonoid determinations are shown in Table 1. The extraction yield of dry matter in the extract of blanched peanut skins (BCE, 179.93 mg/g) was greater than in roasted peanuts skins (RCE, 167.27 mg/g). In addition, the

**Table 1**
Extraction yield, total phenolic content, total flavonoid content, and $IC_{50}$ of DPPH radical scavenging, ferrous ion chelating, hydroxyl radical scavenging, and superoxide anion scavenging activities of peanut skin extracts and purified fractions.

| Samples[a] | Extraction Yield (mg/g)[b] | Total phenolic content (mg GAE/g)[c] | Total flavonoids content (mg QE/g)[d] | $IC_{50}$ (μg/mL)[e] | | | |
|---|---|---|---|---|---|---|---|
| | | | | DPPH radical scavenging activity | Chelating activity on ferrous ions (Fe2 + ) | Hydroxyl radical scavenging activity | Superoxide anion radical scavenging activity |
| RCE | 167.27 ± 2.05**b** | 416.92 ± 7.08**f** | 20.64 ± 0.20**c** | 2.33 ± 0.38**d** | 73.00 ± 0.52**c** | 15.37 ± 0.38**a** | 29.01 ± 0.46**d** |
| BCE | 179.93 ± 1.54**a** | 672.40 ± 5.42**d** | 19.97 ± 2.65**d** | 2.01 ± 0.08**d** | 54.59 ± 1.69**d** | 9.58 ± 1.24**c** | 20.75 ± 2.90**e** |
| RW | 148.31 ± 1.82**c** | 295.06 ± 0.83**g** | 16.65 ± 0.16**d** | 5.62 ± 0.17**a** | 108.54 ± 6.76**a** | 10.47 ± 1.36**c** | 41.25 ± 7.23**c** |
| BW | 97.76 ± 2.48**d** | 558.96 ± 4.99**e** | 21.56 ± 0.18**b** | 3.03 ± 0.08**c** | 74.67 ± 2.11**c** | 16.40 ± 0.89**a** | 49.62 ± 6.08**c** |
| REA | 18.96 ± 0.23**g** | 673.84 ± 5.42**d** | 19.97 ± 0.39**c** | 2.09 ± 0.16**d** | 30.12 ± 1.74**f** | 12.53 ± 0.46**b** | 18.01 ± 2.51**e** |
| BEA | 82.17 ± 2.48**e** | 716.14 ± 5.06**c** | 13.07 ± 0.04**e** | 1.51 ± 0.02**e** | 54.69 ± 0.83**d** | 8.97 ± 0.54**c** | 70.31 ± 1.41**b** |
| Y | 6.23 ± 0.74**h** | 179.70 ± 0.83**h** | 36.22 ± 1.09**a** | 2.54 ± 0.20**c** | 104.78 ± 2.66**b** | 4.13 ± 0.28**d** | 158.68 ± 5.29**a** |
| P | 8.69 ± 0.30**h** | 866.12 ± 5.83**a** | 10.74 ± 0.14**f** | 0.98 ± 0.03**f** | 47.48 ± 0.96**d** | 13.01 ± 0.64**b** | 51.04 ± 0.59**c** |
| B | 67.26 ± 0.44**f** | 763.73 ± 6.00**b** | 12.40 ± 0.34**e** | 1.04 ± 0.06**f** | 25.75 ± 3.18**f** | 1.79 ± 0.92**d** | 34.41 ± 3.22**d** |
| BHT[f] | | | | 3.68 ± 0.03**b** | | | |
| EDTA[g] | | | | | 104.38 ± 4.57**a**–**b** | | |
| Ascorbic acid | | | | | | 9.61 ± 0.54**c** | 47.03 ± 0.07**c** |

Data expressed as mean ± SE (n = 3). Values with the same letter within a column are not significantly different (ANOVA and DGC test, $p = 0.05$).

[a] Samples abbreviations. RCE = roasting crude extracts; BCE = blanching crude extracts; RW = roasting water fraction; B = blanching water fraction; REA = roasting ethyl acetate fraction; BEA = blanching ethyl acetate fraction; Y = yellow fraction; P = purple fraction; B = brown fraction.

[b] Expressed as mg of dry matter/g of dry peanut skins.

[c] GAE = gallic acid equivalent/g of extract.

[d] QE = quercetin equivalent/g of extract.

[e] $IC_{50}$ is a measured of scavenging/chelating activity of sample concentration required to inhibit 50% radical/ion.

[f] BHT = butylated hydroxytoluene.

[g] EDTA = ethylenediaminetetraacetic.

BCE were higher in phenolic content (672.40 mg GAE/g) but lower in flavonoid content (19.97 mg QE/g) than the RCE (416.92 mg GAE/g and 20.64 mg QE/g, respectively). Francisco and Resurreccion (2009b) reported phenolic contents between 101.43-280.42 mg GAE/g in Runner peanut skins of American peanuts. Also, Yu et al. (2005) studied American peanut skins and found similar results to those of Francisco and Resurreccion (2009b), reporting total phenolics between 90 and 125 mg GAE/g using ethanol as the extraction solvent. The total phenolic content found in this study was greater than those reported by the above-mentioned authors, but similar to those reported by Nepote et al. (2004a,b, 2005) in Argentinean peanut skins. The difference between the total phenolic content of American and Argentinean peanut skins could be explained by genetic and environmental effects (Young et al., 2005).

The four fractions purified by solvent partition from BCE and RCE were aqueous fractions (BW and RW) and ethyl acetate fractions (BEA and REA). They exhibited significant differences in their extraction yields and phenolic and flavonoid contents. Water fractions contained more dry matter (97.76 and 148.31 mg/g in BW and RW, respectively) than ethyl acetate fractions (82.17 and 18.96 mg/g in BEA and REA, respectively). On the contrary, ethyl acetate fractions BEA and REA displayed a higher total phenolic content (716.14 mg GAE/g and 673.84 mg GAE/g, respectively) than their corresponding water fractions (558.96 mg GAE/g in BW and 295.06 mg GAE/g in RW) and crude extracts (672.40 mg GAE/g in BCE and 416.92 mg GAE/g in RCE). Polyphenols due to their chemical structure presents good solubility in ethyl acetate solvent. For that reason, the ethyl acetate fractions showed greater proportion of these this kind of compounds during the partition procedure. This greater proportion of polyphenol could explain a higher antioxidant activity in the ethyl acetate fractions. In addition, ethyl acetate extracted a greater proportion of flavonoids from roasted skin samples (19.97 mg QE/g in REA) than water (16.65 mg QE/g in RW). However, the water fractions obtained from blanched skin samples showed a higher flavonoid content (21.56 mg QE/g in BW) than the ethyl acetate fractions (13.07 mg QE/g in BEA). These results suggest that the industrial processes of blanching and roasting have different effects on the resulting peanut skins, which in turn affect the yields of dry matter and phenolic and flavonoid contents in the extracts.

The three colored fractions: yellow (Y), purple (P), and brown (B), separated by column chromatography from the BEA fraction, showed significant differences in dry matter yield and phenolic and flavonoid contents. Fraction B (67.26 mg/g) presented a higher dry matter yield in comparison with Y (6.23 mg/g) and P (8.69 mg/g). Fraction P (866.12 mg GAE/g) had a higher phenolic content than B (763.73 mg GAE/g) and Y (179.70 mgGAE/g). Fraction Y (36.22 mgQE/g) was the fraction with the highest flavonoid content. In some fractions, it was observed that the concentration of phenolics and/or flavonoids increased with each subsequent purification step. For example, the phenolic concentration was increasing from the BEA to the P and B fractions (672.40 mg GAE/g in BCE < 716.14 mg GAE/g in BEA < 763.73 mg GAE/g in B and 866.12 mg GAE/g in P) and the flavonoid concentration was increasing from the BCE to the Y fraction (19.97 mgQE/g in BCE < 36.22 mgQE/g in Y).

The total flavonoid contents reported in the present research were lower than those found by Wang et al. (2007) in Chinese peanut skins. The authors reported 65 mg QE/g in an extract obtained by aqueous ethanol (50:50) extraction. The solvent composition used to obtain crude extract differed between this study (ethanol:water, 70:30) and that of Wang et al. (2007). The amount of flavonoids found depends on the dissolution of each compound at the cellular level in the plant material matrix (Xiaodi et al., 2015). Therefore, flavonoid content could be affected by different extraction conditions and different origin, variety, and type of peanuts.

### 3.2. Radical scavenging and ion ferrous chelating activities

The results of ferrous ion chelating and DPPH, hydroxyl, and superoxide anion radical scavenging activities of peanut skin extracts and fractions are shown as $IC_{50}$ in Table 1. These techniques are commonly used as a measure of the antioxidant activity of extracts (Costa de Camargo et al., 2015; Wang et al., 2007). In general, a high $IC_{50}$ indicates a low activity towards the respective compound (ion or radical).

The BCE showed higher activities (lower $IC_{50}$) towards ferrous ion (59.59 μg/mL), hydroxyl radical (9.58 μg/mL), and superoxide anion (20.75 μg/mL) than the RCE (73.00, 15.37, and 29.01 μg/mL, respectively) (Table 1). Both crude extracts (BCE and RCE) showed similar DPPH radical- scavenging activities.

The ethyl acetate fractions (BEA and REA) had higher activities towards DPPH radical and ferrous ion than aqueous fractions (BW and RW). On the contrary, the RW showed greater hydroxyl radical-scavenging activity than REA. However, the BEA exhibited higher hydroxyl radical-scavenging activity than the BW. The REA had higher superoxide anion radical-scavenging activity than the RW but the BW showed higher superoxide anion radical-scavenging activity than the BEA.

With respect to column chromatography fractions, the P and B fractions showed higher activities towards DPPH radical, ferrous ion, and superoxide anion than the Y fraction. Fraction B had higher hydroxyl radical-scavenging activity than Y and P.

In general, the peanut skin extracts and fractions showed higher DPPH radical-scavenging activity than the BHT, with the exception of the RW fraction, and higher ion ferrous chelating activity than EDTA, with exception of the RW and Y fractions. For the hydroxyl radical scavenging activity, Y and B were the fractions with greater activities than ascorbic acid. In relation to superoxide anion radical-scavenging activity, the RCE, BCE, REA, and B fractions showed higher activities than ascorbic acid. According to the results, those extracts and fractions could have protective effects against peroxidation.

In previous works, Nepote et al. (2002, 2004a, 2005) reported similar DPPH results in crude peanut skin extract and its ethyl acetate fraction. Wang et al. (2007) reported an $IC_{50}$ for DPPH of 30.8 μg/mL in ethanolic peanut skin extract. Some authors studied the metal-chelating and scavenging activities towards hydroxyl and superoxide anion radicals of different peanut skin extracts. Gaafar et al. (2015) reported 76.71% metal chelating capacity in ethanolic extract of peanut skins (concentration 100 μg/mL). Costa de Camargo et al. (2015) found 884.2 μmol of catechin equivalents per dry weight of hydroxyl radical scavenging activity in irradiated peanut skin extracts (diethyl ether:ethyl acetate, 1:1). In addition, Wang et al. (2007) reported an $IC_{50}$ of 25.4 μg/mL for the superoxide anion radical in skin extracts (ethanol:water, 50:50) of American peanuts.

### 3.3. Accelerated oxidation test

The efficiency of peanut skin extracts and purified fractions as antioxidants was determined by an accelerated oxidation test in sunflower oil. The peroxide value (PV) is used as an indicator of the initial stages of lipid oxidation and constitutes a useful parameter that indicates the quality of fat and oil (Hasiewicz-Derkacz et al., 2015). Initially (day 0), all sunflower samples had low PV (1.88 meq$O_2$/kg). The peroxide values in sunflower samples during storage are shown in Table 2. The PV increased during storage in all samples. After four days, control and RW samples had higher PV than all other samples followed by BW fraction. The BCE extract and all other fractions displayed lower peroxide value at day 4 of storage. Larrauri et al. (2013) also reported a protective effect of crude peanut skin extract against lipid oxidation in a food prod-

**Table 2**
Peroxide values (means and DE, n = 3) of sunflower oil samples during storage at 60 °C.

| Sample[a] | Day 1[*] | Day 2[*] | Day 3[*] | Day 4[*] |
|---|---|---|---|---|
| Control | 2.66 ± 0.10**a** | 7.25 ± 3.00**b** | 21.02 ± 2.30**b** | 62.04 ± 11.00**c** |
| RCE | 3.46 ± 0.40**b** | 4.94 ± 0.40**a** | 20.05 ± 0.50**b** | 34.33 ± 5.90**a** |
| BCE | 3.04 ± 0.10**b** | 3.89 ± 0.30**a** | 15.95 ± 0.70**a** | 39.68 ± 0.30**a** |
| RW | 3.79 ± 0.30**c** | 5.04 ± 0.10**a** | 25.87 ± 1.30**c** | 62.45 ± 2.40**c** |
| BW | 4.01 ± 0.30**c** | 6.2 ± 0.10**b** | 24.34 ± 1.80**c** | 47.63 ± 3.30**b** |
| REA | 3.37 ± 0.60**b** | 3.21 ± 0.70**a** | 23.6 ± 1.80**c** | 36.43 ± 1.60**a** |
| BEA | 2.57 ± 0.10**a** | 4.05 ± 0.30**a** | 20.13 ± 2.40**b** | 30.2 ± 1.50**a** |
| Y | 3.14 ± 0.10**b** | 4.49 ± 0.20**a** | 20.07 ± 0.60**b** | 30.62 ± 1.00**a** |
| P | 2.4 ± 0.10**a** | 4.5 ± 0.00**a** | 21.86 ± 1.50**b** | 29.8 ± 0.00**a** |
| B | 2.4 ± 0.10**a** | 4.53 ± 0.10**a** | 21.82 ± 0.60**b** | 37.23 ± 4.00**a** |
| BHT | 2.59 ± 0.20**a** | 3.82 ± 0.40**a** | 24.88 ± 2.20**c** | 37.99 ± 4.20**a** |

[a] Samples abbreviations. RCE = roasting crude extracts; BCE = blanching crude extracts; RW = roasting water fraction; B = blanching water fraction; REA = roasting ethyl acetate fraction; BEA = blanching ethyl acetate fraction; Y = yellow fraction; P = purple fraction; B = brown fraction.
[*] Different letters in each column indicate significant differences between samples (ANOVA and test DGC, $p = 0.05$).

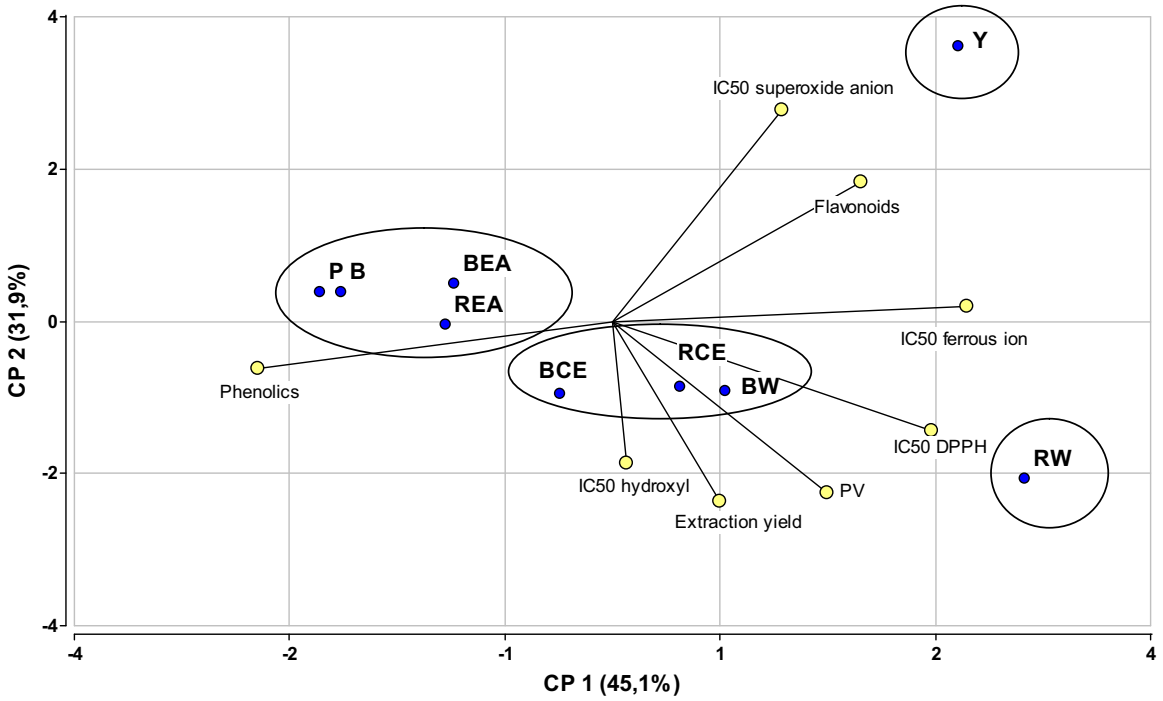


**Fig. 1.** Biplot of first and second component from principal component analysis. Variables: extraction yield, total phenolics, total flavonoids, peroxide value (PV), and activity (IC50) on DPPH, ferrous ion, hydroxyl radical, and superoxide anion radical. Treatments: peanut skin extracts (BCE and RCE) and purified fractions (REA, BEA, RW, BW, Y, P, and B). Grouped samples in each circle have similarity by cluster analysis.
Samples abbreviations. RCE = roasting crude extracts; BCE = blanching crude extracts; RW = roasting water fraction; B = blanching water fraction; REA = roasting ethyl acetate fraction; BEA = blanching ethyl acetate fraction; Y = yellow fraction; P = purple fraction; B = brown fraction.

uct like salami after 42 days of storage. The results observed in this study indicate that the extracts (RCE and BCE) and purified fractions (REA, BEA, Y, P, and B) showed similar antioxidant activities in sunflower oil with respect to BHT treatment. In previous study, Nepote et al. (2002) found antioxidant activity in sunflower oil of crude peanut skin extracts prepared with methanol, ethanol, acetone, and water. In that research, 0.05% crude extract and 0.02% BHT were added into sunflower oil samples. Those authors reported that crude peanut skin extracts have similar PV between them, but they present lower PV than control samples and higher PV than BHT samples. In the present study, crude extracts and purified fractions obtained from peanut skins were added at higher concentration (0.2%), which could explain a higher antioxidant activity observed in this experiment. For that reason, some extracts (RCE, BCE, REA, BEA, Y, P, and B) showed similar antioxidant activity compared with BHT samples.

### 3.4. Principal component and cluster analysis

The biplot obtained from the first two principal components (PC) of PCA is presented in Fig. 1. The variables were represented by vectors and treatments by points. The first two PCs of the PCA explained 77% of the total variability. This percentage was considered acceptable to establish correlations between variables. In a PCA, a high dispersion point indicates high variability among samples: angles between vectors lower than 90° indicate positive associations and angles near 180° indicate negative associations between variables. In the present PCA, the total phenolic content was found on the left side of the biplot, and it was associated with the P, B, BEA, and REA fractions. These fractions were grouped by the cluster analysis because of their similarity considering all studied variables. The other variables and treatments were placed on right side of the biplot. Variables such as flavonoid content, DPPH, and ferrous ion

**Table 3**
Means and SE of extraction yield, total phenolics, total flavonoids, peroxide value (PV), and $IC_{50}$ on DPPH, ferrous ion, hydroxyl, and superoxide anion in groups of peanut skin extracts and fractions from cluster analysis.

| Variable | Group 1 (BEA, REA, B, P)[a] n = 3 × 4 | Group 2 (BCE, RCE, BW)[a] n = 3 × 3 | Group 3 (RW)[a] n = 3 × 1 | Group 4 (Y)[a] n = 3 × 1 |
|---|---|---|---|---|
| Extraction yield | 44.27 ± 9.40**a** | 148.32 ± 12.81**b** | 148.31 ± 1.82**b** | 6.22 ± 0.74**a** |
| Total phenolics | 754.96 ± 21.73**d** | 549.43 ± 37.07**c** | 295.06 ± 0.83**b** | 179.7 ± 0.83**a** |
| Total flavonoids | 14.05 ± 1.07**a** | 20.73 ± 0.80**b** | 16.65 ± 0.16**a** | 36.22 ± 1.09**c** |
| IC50 DPPH | 1.40 ± 0.14**a** | 2.46 ± 0.19**b** | 5.62 ± 0.17**c** | 2.54 ± 0.20**b** |
| IC50 ferrous ion | 39.51 ± 3.70**a** | 67.42 ± 3.31**b** | 41.25 ± 7.23**c** | 104.77 ± 2.66**c** |
| IC50 hydroxyl | 9.08 ± 1.38**b** | 13.79 ± 1.15**b** | 10.47 ± 1.36**b** | 4.12 ± 0.28**a** |
| IC50 superoxide anion | 43.44 ± 5.93**a** | 33.13 ± 4.71**a** | 41.25 ± 7.23**a** | 158.68 ± 5.29**b** |
| PV (day 4) | 33.42 ± 1.42**a** | 40.55 ± 2.75**b** | 62.45 ± 2.38**c** | 30.62 ± 1.02**a** |

Different letters in each column indicate significant differences between samples (ANOVA and test DGC, $p = 0.05$).
[a] Samples abbreviations. RCE = roasting crude extracts; BCE = blanching crude extracts; RW = roasting water fraction; B = blanching water fraction; REA = roasting ethyl acetate fraction; BEA = blanching ethyl acetate fraction; Y = yellow fraction; P = purple fraction; B = brown fraction.

**Table 4**
Relative percentage of peanut skin compounds from purified fractions (yellow, purple, and brown) analyzed by HPLC-ESI–MS/MS.

| Retention Time (min) | Compound | [M−H]- | $MS^2$[M−H]- | Fraction | | |
|---|---|---|---|---|---|---|
| | | | | Yellow | Purple | Brown |
| 6.7 | Quinic acid[a] | 191 | 0 | 0.32 | 0.17 | nd |
| 10.7 | Procyanidin dimer type B[b] | 577 | 289 | 14.15 | 1.51 | nd |
| 11.3 | Catechin[a] | 289 | 245 | nc | 23.73 | nc |
| 11.4 | Gallic acid[a] | 169 | 0 | nc | nd | nd |
| 11.5 | Procyanidin dimer A[b] | 575 | 449. 289. 285 | 4.81 | 3.28 | 20.31 |
| 11.6 | Epicatechin[a] | 289 | 245 | nc | 20.28 | 3.88 |
| 12.3 | Proanthocyanidin dimer[b] | 573 | 289 | 12.34 | 1.64 | nd |
| 12.6 | Proanthocyanidin dimer[b] | 573 | 447. 289. 285 | nc | 1.99 | nd |
| 12.8 | Procyanidin dimer A[b] | 575 | 449. 285. 289 | nc | nc | 52.70 |
| 13.0 | Proanthocyanidin dimer[b] | 573 | 289. 447. 283 | 24.33 | nd | nd |
| 13.7 | Procyanidin dimer type A[b] | 575 | 289. 449. 245 | 31.49 | nc | nc |
| 14.0 | Resveratrol hexoside[b] | 389 | 227 | 0.37 | 4.50 | nd |
| 17.2 | Isorhamnetin hexoside[b] | 477 | 315 | nc | nd | nd |
| 18.1 | Isoquercetin[a] | 463 | 301 | 0.26 | 2.38 | nd |
| 18.4 | Cumaric acid[a] | 163 | | nc | nd | nd |
| 19.2 | Resveratrol[a] | 227 | 185 | 1.14 | 3.28 | nd |
| 19.6 | Isorhamnetin hexoside[b] | 477 | 315 | 0.18 | 1.56 | nd |
| 19.8 | Quercetin hexoside[b] | 463 | 301 | 0.63 | 2.89 | nd |
| 20.3 | Isorhamnetin rutinoside[b] | 623 | 315 | 0.45 | 1.14 | nd |
| 20.4 | Isorhamnetin hexoside[b] | 477 | 315 | 1.04 | 3.03 | nd |
| 23.4 | Quercetin[a] | 301 | 179 | 6.68 | 22.45 | 23.09 |
| 27.2 | Isorhamnetin[b] | 315 | 300 | 1.74 | 6.09 | nd |
| 28.1 | Apigenina[a] | 269 | 225 | nc | nd | nd |
| 33.6 | Chrysina[a] | 253 | 209 | nc | nd | nd |

Procedures used for identification.
Abreviation: nd = not detected; nc = not quantified.
[a] Co-analysis relative to a pure compound showing identical retention and mass data.
[b] Comparison of MS. MS/MS and UV data with the literature.

$IC_{50}$ formed angles near 180° with phenolic content, indicating a negative association. The P, B, BEA, and REA treatments were also negatively associated with flavonoid content, but positively associated with DPPH and ferrous ion ($IC_{50}$). The Y fraction was mainly associated with high flavonoid content and high superoxide anion radical $IC_{50}$ (low scavenging activity towards this radical). The RW fraction was associated with high PV and $IC_{50}$ for DPPH. The BCE, RCE, and BW extracts were grouped by the CA and were associated with high values of extraction yield, $IC_{50}$ for hydroxyl, and PV.

The correlation (Pearson) coefficient between variables showed a similar result to the association observed in the biplot (Fig. 1). Significant and positive correlations were found between flavonoids and superoxide anion $IC_{50}$ ($r = 0.66$), $IC_{50}$ of DPPH and $IC_{50}$ of ferrous ion ($r = 0.74$), and $IC_{50}$ of DPPH and PV ($r = 0.76$). Negative correlations were detected between phenolic content and other variables, such as flavonoid content ($r = -0.76$), $IC_{50}$ of ferrous ion ($r = -0.88$), and $IC_{50}$ of DPPH ($r = -0.70$).

Table 3 shows the averages of the studied variables in groups of samples formed by cluster analysis (circles in Fig. 1). Higher extraction yields were found in Groups 2 (BCE, RCE, and BW) and 3 (RW). The extracts (BEA, REA, P, and B) in Group 1 had higher phenolic content and lower $IC_{50}$ of DPPH, and $IC_{50}$ of ferrous ion. Group 4 (Y fraction) exhibited lower phenolic content and higher flavonoid content and $IC_{50}$ of superoxide anion. Groups 1 and 4 showed lower PV from the accelerated oxidation test. According to the result of CA, the extracts/fractions of Group 1 formed by ethyl acetate fractions (BEA and REA) and the purified fractions (P and B) showed, for one side, the highest total phenolic content and for other side, a lower $IC_{50}$ for DPPH, ferrous ion, and superoxide anion, and PV from the accelerated oxidation test. Therefore, it can be considered that the Group 1 samples are the peanut skin extracts/fractions with better antioxidant properties.

### 3.5. *Identification of purified peanut skin fractions by HPLC–ESI-MS/MS*

The compounds identified by HPLC–ESI-MS/MS on purified peanut skin fractions (Y, P, and B) are shown in Table 4. In frac-

tions Y, P, and B, 24, 18, and 6 different compounds were found, respectively. Three types of phenolic compounds were detected in all fractions: phenolic acids, flavonoids, and stilbenes. The Y fraction was characterized by the presence of three organic acids (quinic, gallic, and cumaric acids), sixteen flavonoids (catechin, epicatechin, quercetin, isoquercetin, genistein, isorhamnetin, apigenin, chrysin, procyanidins, and proanthocyanidins) and one stilbene (resveratrol). The major components in this fractions were procyanidin dimer type A (31.49%), proanthocyanidin dimer (24.33%), and procyanidin dimer type B (14.15%).

The P fraction exhibited two organic acids (quinic and cumaric acids), seven flavonoids (catechin, epicatechin, quercetin, isoquercetin, isorhamnetin, procyanidins, and proanthocyanidins) and one stilbene (resveratrol). The major components detected in this fraction were catechin (23.73%), quercetin (22.45%), and epicatechin (20.28%).

Four flavonoids were identified in the B fraction (procyanidin dimer A, catechin, epicatechin, and quercetin). The major components in this fraction were procyanidin dimer A $MS^2$[M−H]- 449.285.289 (52.70%), quercetin (23.09%), and procyanidin dimer A $MS^2$[M−H]- 449.289.285 (20.31%).

On one hand, the Y and P fractions had a greater variety of phenolic compounds and both had resveratrol. The P fraction exhibited the greatest relative percentage of resveratrol (3.28%). On the other hand, the P and B fractions displayed a greater content of procyanidins. The highest content of procyanidin dimer A $MS^2$[M−H]- 449.285.289 (52.70%) was only detected in fraction B. Also, the P and B fractions displayed a higher content of epicatechin (20.28% and 3.88%, respectively) and quercetin (22.45% and 23.09%, respectively). Both of these fractions (P and B) showed greater scavenging and chelating activities, indicating a possible association between the above-mentioned compounds and the greater antioxidant property of those peanut skin extracts.

Yu et al. (2005) working with raw peanut skins identified phenolic acid-like phenolic compounds, such as chlorogenic acid, caffeic acid and ferulic acid; flavonoids including epigallocatechin, epicatechin, catechin gallate, epicatechin gallate; and stilbenes (resveratrol). Francisco and Resurreccion (2009a) reported quinic and cumaric acids and resvertarol in Virginia, Spanish, and Runner peanut skin extracts. Catechin, procyanidins, and proanthocyanidins were identified by Ma et al. (2014) in dry-blanched peanut skins.

Ballard et al. (2010) found resveratrol in peanut skin extract using microwave-assisted extraction. In this study, resveratrol was detected in the Y and P fractions. This stilbenic compound was extensively studied in grapes and wine because of its antioxidant properties and health benefits. Grapes are rich in polyphenols, such as flavonoids (anthocyanins, flavonols, and flavanols), stibenes and phenolic acids. It has been reported that the resveratrol present in wine helps to prevent cardiovascular diseases, according to a number of epidemiological findings (Renaud et al., 2004; Anastasiadi et al., 2012).

## 4. Conclusion

In general, peanut skin extracts show a high polyphenol content with antioxidant activity. Those peanut skins processed by blanching process exhibit a greater total phenolic content than those derived from a roasting process. Solvent partition using ethyl acetate and column purification are methods that allow the total phenolic content and antioxidant activity of peanut skin extracts to increase. Fractions with higher total phenolic contents are associated with higher scavenging activities towards DPPH and superoxide anion radicals, and higher chelating activity towards ferrous ion. The Yellow fraction presents greater total flavonoid content and hydroxyl radical-scavenging activity. Different antioxidant properties displayed among fractions are probably associated with differences in phenolic composition.

Purified peanut skin fractions could constitute a natural preserving compound to reduce the lipid oxidative deterioration and to prolong the shelf-life of foods.

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