

PHENOLIC COMPOSITION AND ANTIOXIDANT CAPACITY OF AQUEOUS AND ETHANOLIC EXTRACTS OF BLACKBERRIES¹

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ABSTRACT - The objective of this study was to evaluate the content of phenolic compounds, anthocyanins and flavonoids extracted with 80% ethanol and water, and antioxidant capacity (DPPH and ABTS) of five blackberry cultivars produced in Western Paraná, Brazil. Brazos, Tupy, Arapaho, Choctaw and Guarani blackberries were studied. Soluble solids, titratable acidity and ascorbic acid of fruits were also characterized. Total phenolic compounds ranged from 8.23 to 14.98 mg GAE g⁻¹ (f.w.) and Arapaho cultivar exhibited the highest contents in both solvents. Anthocyanins ranged from 2.57 to 9.42 mg ECy3glu g⁻¹ (f.w.), being the solvent ethanol 80% more efficient than the water, and Choctaw cultivar showing the highest content. Flavonoids ranged from 0.46 to 1.14 mg EQ g⁻¹ (f.w.) and Guarani cultivar showed the highest content. High linear correlations were found between total phenolics and antioxidant capacity in both extraction solvents. However, linear correlations between anthocyanins and antioxidant capacity were observed only for the aqueous solvent. Ascorbic acid ranged from 87.87 to 134.09 mg 100 g⁻¹, with emphasis on Brazos cultivar. The aqueous extract showed greater ability to scavenge ABTS radical, but the ethanolic extract was more efficient for the DPPH radical. Blackberries produced under Western Paraná conditions showed high levels of antioxidants with emphasis on Arapaho cultivar. This study showed that water and ethanol solvents influence different results on phenolic composition and antioxidant activity of blackberries.

Index terms: *Rubus* spp., total phenolic, flavonoids, anthocyanins.

COMPOSIÇÃO FENÓLICA E ATIVIDADE ANTIOXIDANTE DOS EXTRATOS AQUOSO E ETANÓLICO DE AMORA-PRETA

RESUMO - O objetivo deste trabalho foi avaliar o teor de compostos fenólicos, antocianinas e flavonoides, extraídos com etanol a 80% e água, e a capacidade antioxidante (DPPH e ABTS) de cinco cultivares de amora-preta produzidas na região oeste do Paraná, Brasil. As amoras-pretas 'Brazos', 'Tupy', 'Arapaho', 'Choctaw' e 'Guarani' foram estudadas. Sólidos solúveis, acidez titulável e ácido ascórbico também foram caracterizados. Compostos fenólicos totais variaram de 8,23 a 14,98 mg EAG g⁻¹ (p.f.) e 'Arapaho' exibiu os maiores conteúdos em ambos os solventes. Antocianinas variaram de 2,57 a 9,42 mg ECy3glu g⁻¹ (p.f.), sendo etanol 80% o extrator mais eficiente, com o maior conteúdo encontrado em 'Choctaw'. Flavonoides variaram de 0,46 a 1,14 EQ g⁻¹ (p.f.) e 'Guarani' mostrou o maior conteúdo. Correlações lineares elevadas foram verificadas entre compostos fenólicos totais e atividade antioxidante em ambos os solventes de extração. O conteúdo de antocianinas totais se correlacionou linearmente com atividade antioxidante apenas quando extraída com solvente aquoso. Ácido ascórbico variou de 87,87 a 134,09 mg 100 g⁻¹ (p.f.), com destaque para 'Brazos'. O extrato aquoso apresentou maior capacidade de sequestrar o radical ABTS, mas o etanólico foi mais eficiente para o radical DPPH. As amoras-pretas produzidas nas condições do oeste do Paraná mostraram elevados níveis de compostos antioxidantes, com destaque para a cultivar Arapaho. Este estudo mostrou que os solventes água e etanol influenciam diferentes resultados na composição fenólica e na atividade antioxidante de amoras-pretas.

Termos para indexação: *Rubus* spp., fenólicos totais, flavonoides, antocianinas.

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INTRODUCTION

Fruits are excellent sources of phenolic compounds, considered effective agents for protection against degenerative diseases, such as cardiovascular diseases and cancer (KAUME et al., 2012). Blackberry (*Rubus* spp.) has been reported as a powerful source of phenolic compounds, with antioxidant properties (PANTELIDIS et al., 2007; ACOSTA-MONTOYA et al., 2010). Several studies have reported the high antioxidant capacity of blackberries based on their oxygen radical absorbance capacity in comparison to other fruits (WANG; LIN, 2000).

Blackberry is a fruit that contains high levels of anthocyanins and ellagitannins (KOPONEN et al., 2007), in addition to other phenolic compounds such as flavan-3-ols, procyanidins and lignans that contribute to their high antioxidant capacity (MAZUR et al., 2007). Anthocyanins (anthocyanin glycoside and alkyl glycoside) are important in food industry because they are potential substitutes for synthetic food colorants, and in human nutrition they act as protective agents against disease (KAUME et al., 2012).

Different solvent systems have been used for the extraction of phenols from plant material, and the extraction efficiency is dependent on the solvent and method of extraction (IGNAT et al., 2011). In addition, the polarities of phenolic compounds vary significantly and it is difficult to develop a single method for optimum extraction of all phenolic compounds (GARCIA-SALAS et al., 2010). The most common extraction solvents used are water, and aqueous mixtures of ethanol, methanol and acetone (HAYOUNI et al., 2007). It has been reported that the extraction of phenolic compounds in some fruits such as *Ribes nigrum* L. (KAPASAKALIDIS et al., 2006) and grape pulp (CASTAÑEDA-OVANDO et al., 2009) is more efficient with methanol. However, in another studies, water and aqueous ethanol were superior to methanol for extracting phenols in other fruits such as teas (ROBY et al., 2013).

North America, Europe, Asia, South America, Central America, Oceania and Africa (in decreasing order of production) are the main blackberry production regions in the world (STRIK et al., 2008). However, research has been focused on commercial varieties grown in temperate climates, with little attention given to the varieties grown in tropical or subtropical regions. The production of blackberries in Brazil is growing mainly in the south and southeast, and is estimated at 150 tons in total area of 450 hectares (GONÇALVES et al., 2011). There are

reports that the State of Paraná, Brazil, presents good climatic conditions to blackberries production (CAMPAGNOLO; PIO, 2012). The objective of this study was to evaluate the content of phenolic compounds, anthocyanins, flavonoids extracted with ethanol and water, and antioxidant capacity (DPPH and ABTS) in five blackberry cultivars produced in Western Paraná, Brazil.

MATERIALS AND METHODS

Samples and extraction

The fruits of blackberry Brazos, Tupy, Arapaho, Choctaw and Guarani cultivars were produced in Marechal Cândido Rondon, Paraná, Brazil, between the coordinates 24° 26' S and 53° 57' W, at 420 m altitude and humid subtropical climate. The lyophilized samples were ground in mill (AIKA, A11) and then the extraction was performed in aqueous solvent (100% distilled water) and ethanolic solvent (80% ethanol in distilled water, v/v). Extractions occurred through adding 10 mL of solvent in 1 g of ground sample and homogenization in Vortex for 1 minute. The extracts were then centrifuged at 2500 g for 10 minutes and subsequently filtered in qualitative filter paper (15 µm) and stored at -24°C. The procedure was in the dark and in triplicate.

Total phenolic compounds

Total phenolic compounds were determined by the Folin-Ciocalteu spectrophotometric method described by Cheng et al. (2013). The results were expressed in mg g⁻¹ of fresh weight in gallic acid equivalent (GAE), and calculated by means of the gallic acid calibration curve. Analyses were performed in triplicate.

Total flavonoids

This was determined according to Shivanna et al. (2013). Results were expressed in mg g⁻¹ of fresh weight in quercetin equivalent (QE), and calculated by means of the quercetin calibration curve. Analyses were performed in triplicate.

Total anthocyanins

Total anthocyanin content was determined by the differential pH method proposed by Khoddami et al. (2013) through the potassium chloride buffer solution (pH 1.0) and another buffer solution of sodium acetate (pH 4.5). Final absorbance (Abs) was calculated by the equation:

$$Abs = (A_{510nm} - A_{700nm})_{pH1.0} - (A_{510nm} - A_{700nm})_{pH4.5}$$

Total anthocyanin content (TA) was expressed as cyanidin-3-glucoside equivalent (Cy3gluE), and was obtained by the equation:

$$TA(\text{mg}100\text{g}^{-1}) = Abs \times PM \times FD \times 100 / (\epsilon \times l)$$

Molecular weight (MW) and molar absorptivity (ϵ) used in the equation correspond to cyanidin-3-glucoside (MW=449.2 and ϵ =26900). The dilution factor (DF) was used for the result in fresh weight. Analyses were performed in triplicate.

Antioxidant capacity - ABTS Method

ABTS antioxidant capacity estimates the capacity of the sample for scavenging the ABTS^{•+} radical [2,2'-azino-bis-(3-ethylbenz-thiazoline-6-sulfonic acid)] and was performed according to Re et al. (1999), with modifications. 30 μ L of the extract was added to 3.0 mL of the ABTS^{•+} radical and left for 6 minutes in the dark. Reading was made at 734 nm and the ethanol was used as a blank. The standard curve was fitted to Trolox [(+/-)-6-hydroxy-2,5,7,8-tetramethyl-chroman-2-carboxylic acid] and the results were calculated according to the equation fitted to the standard curve and expressed in μ g g⁻¹ of fresh weight in Trolox equivalent (TE). Analyses were performed in triplicate.

Antioxidant capacity - DPPH Method

The antioxidant capacity of the extracts, measured through their DPPH (2,2-diphenyl-1-picrylhydrazyl) radical scavenging capacity, was determined according to Rotili et al. (2013). 0.5 mL of the extract and 0.3 mL of the DPPH solution (0.5 mMol L⁻¹) were added to 3.0 mL of ethanol and left to rest for 60 minutes in the dark. Absorbance was then read at 517 nm. The control, containing 3.5 mL of ethanol and 0.3 mL of DPPH solution was used. Results were expressed in μ g g⁻¹ of fresh weight in Trolox equivalent (TE), calculated by means of the calibration curve for Trolox. The % of antioxidant capacity was also calculated by the formula:

$$\%AAT = (\text{control reading} - \text{sample reading} / \text{control reading}) \times 100$$

In addition, the antioxidant capacity of the ascorbic acid, gallic acid and pyrocatechin standards was also determined in aqueous solvent. Analyses were performed in triplicate.

Soluble solids, titratable acidity, pH and ascorbic acid

Total soluble solids content was determined in a benchtop refractometer (Quimis QI-107.1),

and expressed in °Brix, and total titratable acidity was determined by titration with sodium hydroxide (NaOH 0.1 mol L⁻¹) and phenolphthalein 1% as an indicator, with results expressed in g 100 g⁻¹ of fresh weight in citric acid equivalent (MUÑOZ-ROBREDO et al., 2011). Ascorbic acid content was determined by titration with 2,6-dichlorophenol-indophenol and the results expressed in mg 100 g⁻¹ of fresh weight. All analyses were performed in triplicate (ROTILI et al., 2013).

Statistical analysis

Analysis of variance was applied and the mean values were compared by the Tukey test to the significant parameters by the F test. *Pearson* linear correlation analysis was applied. The p<0.05 level of significance was used in all the analyses. The SAEG (2007) statistical package was used.

RESULTS AND DISCUSSION

Antioxidant compounds

The total content of phenolic compounds, anthocyanins and flavonoids of blackberry cultivars extracted with ethanol 80% and water are presented in Table 1. Total phenolic compounds ranged from 8.47 to 11.66 mg GAE g⁻¹ (f.w.) in water solvent and from 8.23 to 14.98 mg GAE g⁻¹ (f.w.) in ethanol 80%. Ethanol 80% was better than the water in the total phenolics extraction for Arapaho and Guarani cultivars, but the water solvent was more efficient for Brazos and Tupy, and there were no significant differences between the solvents for Choctaw. Regardless of the solvent used in the extraction, Arapaho cultivar exhibited the highest content of total phenolic compounds. These results show that the efficiency of water and ethanol 80% for total phenolics extraction is dependent on the blackberry cultivar, suggesting that there are different concentrations of phenolic groups with different polarities among the samples. It was reported that the extraction efficiency depends on the affinity between the solvent and the phenolic groups (HAYOUNI et al., 2007; IGNAT et al., 2011).

Hassimoto et al. (2008) evaluated the Guarani, Brazos and Tupy cultivars produced in the south of Minas Gerais (Brazil) and found lower contents for total phenolic compounds of 3.41, 4.27 and 3.73 mg GAE g⁻¹ (f.w.), respectively, and are lower than those found in this study (Table 1). The phenolics content in blackberries can vary due to different production factors, including genetics and environmental conditions (FAN-CHIANG;

WROLSTAD, 2005).

Choctaw cultivar exhibited the highest contents of total anthocyanins (9.42 mg Cy3gluE g⁻¹, f.w.) in ethanol 80% extraction (Table 1), and Tupy exhibited the lowest (6.76 mg Cy3gluE g⁻¹, f.w.). Compared with our results, Hassimotto et al. (2008) found lower contents of total anthocyanins in Guarani, Brazos and Tupy blackberries (1.94, 1.33 and 1.16 mg Cy3gluE g⁻¹, f.w., respectively). Also, lower content of total anthocyanins extracted in ethanol was found by Koca and Karadeniz (2009) on Arapaho blackberry (1.15 mg Cy3gluE g⁻¹, f.w.) produced in the Black Sea region, Turkey, and by Pantelidis et al. (2007) on Choctaw blackberry (1.26 mg Cy3gluE g⁻¹, f.w.) produced in Northern Greece. In tropical or subtropical climatic conditions (typical of the Brazilian regions) prolonged periods of drought or too much rain, high radiation levels and extreme temperatures cause environmental stresses. These stresses can increase the production of phenolic antioxidants as a plant mechanism to detoxify the cells against the high levels of free radicals (reactive oxygen species) produced due to oxidative stresses (ATKINSON et al., 2005).

Ethanol 80% was significantly more efficient to extract total anthocyanins than water in all the analyzed Blackberry cultivars (Table 1). The greater efficiency of ethanol for extracting anthocyanins, compared to water, was also demonstrated by other authors (VATAI et al., 2009). Ethanol has been the most recommended extraction solvent due to its low toxicity, compared, for example, to methanol (IGNAT et al., 2011).

Total flavonoids extracted with water are not presented, because of errors in the absorbance reading. However, in ethanol 80% extraction (Table 1), Guarani cultivar presented the highest contents of total flavonoids (1.14 mg QE g⁻¹, f.w.) and Brazos presented the lowest content (0.46 mg QE g⁻¹, f.w.). In similar research, Hassimotto et al. (2008) also found higher total flavonoids content in Guarani blackberry, compared to Brazos and Tupy. Several studies have suggested the potential benefit to the health related to consumption of flavonoids (HE; GIUSTI, 2010). Flavonoids act as free radical scanners, by chelation of metal ions or by suppression of the reactions of reactive oxygen species formation, and may also regulate endogenous antioxidant defenses (PIETTA, 2000).

Antioxidant capacity

For all blackberry cultivars tested, extraction with water exhibited greater ability to scavenge ABTS radical than the ethanol 80% (Table 2). However, the opposite result was found for the DPPH assays

(Table 3). These results suggest that compounds extracted with high polarity solvent (water) have greater ability to scavenge ABTS radical, but are less effective to scavenge DPPH radical. In contrast, low polarity solvent (ethanol) extracts compounds with greater efficiency to scavenge DPPH radical, but less effective to scavenge ABTS radical. In addition, antioxidant phytochemicals of different polarities can be present in extracts with high antioxidant capacity. It has been reported that changes in solvent polarity change its ability to dissolve certain group of antioxidant compounds, and this interferes with its antioxidant capacity estimation (HAYOUNI et al., 2007).

Statistical differences in antioxidant capacity were found among blackberry cultivars (Table 2 and 3), agreeing with Scalzo et al. (2005) in similar research. Independent of the solvent used in this study, Arapaho blackberry had the highest antioxidant capacity for both ABTS and DPPH assays. Among the antioxidant standards (ascorbic acid, gallic acid and pyrocatechin), gallic acid presented the greater efficiency to scavenge DPPH radical, but was significantly less efficient than the Arapaho blackberry extract. This suggests that Arapaho is the genetic material with greater biological activity between the samples tested. Ascorbic acid does not showed ability to scavenge DPPH radical, and was much lower than the other samples tested. Hassimotto et al. (2008) found that the efficiencies of DPPH radical inhibition of Brazos, Tupy and Guarani blackberries (ethanolic extracts) were 66, 71 and 76%, respectively, and this trend was similar to the results in our study.

DPPH and ABTS antioxidant capacity values of blackberry cultivars were correlated positively with total phenolics for both extractions with water (0.89 and 0.81, respectively) and ethanol 80% (0.88 and 0.75, respectively) (Table 4), suggesting that between 75 and 89% of the antioxidant capacity of extracts is due to the presence of phenolic compounds. Positive linear correlation between total phenolics and antioxidant capacity of blackberries has been reported by other authors (WANG; LIN, 2000; HAYOUNI et al., 2007; KOCA; KARADENIZ, 2009).

For aqueous extraction, positive linear correlations were observed between total anthocyanins and antioxidant capabilities (0.87 and 0.84, respectively to DPPH and TEAC) (table 4). However, for extraction with ethanol 80% there was no correlation between total anthocyanins and antioxidant capacity, suggesting that anthocyanins when extracted with ethanol have less influence on

the antioxidant capacity of blackberries than other phenolic groups. Similar results were also reported by other researchers (WANG; LIN, 2000; PANTELIDIS et al., 2007; KOCA; KARADENIZ, 2009). Similarly, there was no correlation between antioxidant capacity and total flavonoids of blackberries extracted with ethanol 80%. Several explanations for relationship between antioxidant capacity and phenolic compounds show that not all phenolic groups incorporate significant antioxidant capacity, but when they have this property, act as reducing agents, hydrogen donors or singlet and triplet oxygen suppressors (PIETTA, 2000), and may also display metal chelation properties (SAITO et al., 2008).

Chemical characteristics

According to Table 5, Brazos blackberry showed the highest content of ascorbic acid (134.09 mg 100 g⁻¹, f.w.), and Choctaw the lowest (87.87 mg 100 g⁻¹, f.w.). Barcia et al. (2010) evaluated different blackberry cultivars and found ascorbic acid content of 75.7 mg 100 g⁻¹ (f.w.) for Tupy cultivar. Pantelidis et al. (2007) evaluated blackberry cultivars grown in the north of Greece and found that ascorbic acid content ranged from 14.3 to 17.5 mg 100 g⁻¹ (f.w.),

with Choctaw exhibiting 14.6 mg 100 g⁻¹ (f.w.), being much lower than this results. Deighton et al. (2000) found in wild and domesticated blackberry cultivars produced in Corvallis, Oregon, USA, ascorbic acid content that varied from 12.3 to 16.4 mg 100 g⁻¹ (f.w.).

Soluble solids ranged from 6.78 °Brix (Choctaw) to 9.70 °Brix (Tupy) and the titratable acidity ranged from 1.11 g CAE 100 g⁻¹ (Tupy) to 1.37 g CAE 100 g⁻¹ (Guarani) (table 5). Tupy cultivar presented the biggest soluble solids/titratable acidity ratio (8.74) and that indicates its best flavor, compared to other varieties. Besides have had the highest antioxidant activity, Arapaho showed good soluble solids/titratable acidity ratio (7.08) that was near to Tupy. Guarani cultivar presented the least soluble solids/titratable acidity ratio (5.24), indicating more acid flavor and, consequently, less tasty. Acidity and soluble sugars are important parameters for blackberries market and can serve as a reference to classify fruit pulp for juice production. The ratio between sugars and organic acids has been linked as a parameter of flavor quality between cultivars, and can also be used as a harvest parameter (MUÑOZ-ROBREDO et al., (2011).

TABLE 1-Total contents of phenolics, anthocyanins and flavonoids of blackberry cultivars extracted with aqueous and ethanolic solvent.

Cultivar	Total phenolic compounds mg GAE g ⁻¹ (f.w.)		Total anthocyanins mg Cy3gluE g ⁻¹ (f.w.)		Total flavonoids mg QE g ⁻¹ (f.w.)
	H ₂ O	EtOH 80%	H ₂ O	EtOH 80%	EtOH 80%
	Brazos	8.77 ± 0.07 cA	8.23 ± 0.16 eB	3.86 ± 0.01 bB	7.02 ± 0.02 dA
Tupy	9.51 ± 0.11 bA	8.88 ± 0.06 dB	3.18 ± 0.01 cB	6.76 ± 0.03 eA	0.86 ± 0.02 c
Arapaho	11.66 ± 0.05 aB	14.98 ± 0.54 aA	4.36 ± 0.02 aB	8.36 ± 0.02 cA	0.85 ± 0.01 c
Choctaw	9.81 ± 0.09 bA	9.67 ± 0.25 cA	3.21 ± 0.02 cB	9.42 ± 0.03 aA	0.92 ± 0.01 b
Guarani	8.47 ± 0.16 cB	12.55 ± 0.38 bA	2.57 ± 0.01 dB	8.45 ± 0.03 bA	1.14 ± 0.01 a

Mean values followed by the same capital letter in the line and small letter in the column do not differ at $p < 0.05$ by the Tukey test. Mean values ± standard deviation (n=3).

GAE: gallic acid equivalent.

Cy3gluE: cyaniding-3-glucoside equivalent.

QE: quercetin equivalent.

f.w.: fresh weight.

TABLE 2-ABTS antioxidant capacity of blackberry cultivars extracted with aqueous and ethanolic solvent.

Cultivar	ABTS antioxidant capacity µg TE g ⁻¹ (f.w.)	
	H ₂ O	EtOH 80%
Brazos	25.84 ± 0.05 bA	15.15 ± 0.03 cB
Tupy	21.10 ± 0.30 eA	15.47 ± 0.06 cB
Arapaho	35.15 ± 0.16 aA	21.99 ± 0.25 aB
Choctaw	23.82 ± 0.10 cA	17.26 ± 0.36 bB
Guarani	22.91 ± 0.08 dA	15.16 ± 0.67 cB

Mean values followed by the same capital letter in the line and small letter in the column do not differ at $p < 0.05$ by the Tukey test. Mean values ± standard deviation (n=3).

TE: trolox equivalent.

f.w.: fresh weight.

TABLE 3- DPPH antioxidant capacity of blackberry cultivars extracted with aqueous and ethanolic solvent.

Cultivar	DPPH antioxidant capacity			
	mg TE g ⁻¹ (f.w.)		%	
	H ₂ O	EtOH 80%	H ₂ O	EtOH 80%
Brazos	78.15 ± 0.79 dB	91.52 ± 0.53 dA	48.83 ± 0.31 dB	53.13 ± 0.21 dA
Tupy	65.80 ± 2.03 fB	96.81 ± 0.31 cA	43.18 ± 0.81 fB	55.60 ± 0.12 cA
Arapaho	125.72 ± 0.55 aB	137.69 ± 0.82 aA	70.62 ± 0.22 aB	74.68 ± 0.33 aA
Choctaw	74.81 ± 2.17 eB	100.85 ± 0.94 bA	47.30 ± 0.86 eB	57.48 ± 0.38 bA
Guarani	63.10 ± 0.57 fB	101.35 ± 1.18 bA	41.94 ± 0.22 fB	57.72 ± 0.48 bA
<i>Antioxidant Standards</i>				
Gallic acid	118.57 ± 0.59 b		67.77 ± 0.26 b	
Pyrocatechin	83.13 ± 0.53 c		52.21 ± 0.23 c	
Ascorbic acid	3.35 ± 1.15 g		17.17 ± 0.50 g	

Mean values followed by the same capital letter in the line and small letter in the column do not differ at $p < 0.05$ by the Tukey test.

Mean values ± standard deviation (n=3).

TE: trolox equivalent.

f.w.: fresh weight.

TABLE 4- Coefficients of *Pearson* linear correlation to antioxidant capacity and phenolic composition of blackberry cultivars extracted with aqueous and ethanolic solvent.

Variables	Total phenolics	Anthocyanins	Flavonoids
Water extract			
DPPH	0.89**	0.87**	-
TEAC	0.81**	0.84**	-
Ethanolic extract			
DPPH	0.88**	0.34ns	0.21ns
TEAC	0.75**	0.39*	0.06ns

* $p < 0.05$; ** $p < 0.01$; ns not significant at $p < 0.05$.

TABLE 5- Chemical characterization of fresh fruits of blackberry cultivars (f.w.).

Cultivar	Ascorbic acid mg 100 g ⁻¹	Soluble solids °Brix	Titrateable acidity g CAE 100 g ⁻¹	Soluble solids / acidity
Brazos	134.09 ± 1.31 a	7.51 ± 0.06 c	1.28 ± 0.02 b	5.85 ± 0.08 c
Tupy	114.39 ± 3.30 b	9.70 ± 0.05 a	1.11 ± 0.03 c	8.74 ± 0.23 a
Arapaho	96.96 ± 3.03 cd	8.92 ± 0.04 b	1.26 ± 0.02 b	7.08 ± 0.10 b
Choctaw	87.87 ± 2.14 d	6.78 ± 0.05 e	1.23 ± 0.02 b	5.49 ± 0.14 d
Guarani	100.00 ± 6.44 c	7.17 ± 0.02 d	1.37 ± 0.02 a	5.24 ± 0.08 d

Mean values followed by the same letter in the column do not differ at $p < 0.05$ by the Tukey test. Mean values ± standard deviation (n=3).

CAE: citric acid equivalent.

CONCLUSIONS

Blackberries produced under the conditions of Western Paraná contain high levels of antioxidants, with emphasis on Arapaho cultivar. This study showed that the water and ethanol solvents influence different results on phenolic composition and antioxidant activity of blackberries.

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