Bioactive compounds, bromatological and mineral characterization of blackberries in a subtropical region[1]

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ABSTRACT

Given the above, the objective of this study was to evaluate the bromatological, mineral and bioactive compounds of blackberry grown in a subtropical region. Blackberries fruits (*Rubus* sp.), Grown in an orchard of Unioeste, *Campus* Marechal Cândido Rondon (Paraná, Brazil), were used. Immediately after harvest, the fruits were taken to the Food Technology Laboratory for chemical analysis and bioactive compounds. The fruit samples for the analysis of reducing, bromatological and mineral sugars were frozen and sent to private laboratories. Hybrids are more perishable than cultivars. There is variation in color among the cultivars and hybrids studied. Hybrids and cultivars of black mulberry have a high content of ascorbic acid and fibers, with emphasis on the cultivar Tupy (75.0 mg 100 mL^{-1} and 7.23, respectively). Higher pH is verified in the cultivars Tupy and Arapaho (3.22 and 3.24, respectively). The Arapaho cultivar has fewer acid fruits (0.25 g 100 g^{-1}), SS/total acidity ratio (36.88) and reducing sugar content (8.28 g 100g^{-1}). Blackberry fruits are a rich source of bioactive compounds, such as cv. Chickasaw obtaining a higher content of total phenolic compounds (1368.84 mg EAG100mL^{-1}) and the Boysenberry hybrid a greater amount of anthocyanin (5.11mg Ci-3-Gly g^{-1}). The Chickasaw cultivar has a higher lipid content (4.59). There is no difference in moisture content, dry biomass and fruit firmness.

Keywords: *Rubus* sp.; small fruits; post-harvest; nutritional value.

INTRODUCTION

The blackberry (*Rubus* sp.) is a fruit specie of shrub growth, upright or creeping, and produces fruits known as mini drupe, weigh about 4 to 7g (depends on the cultivar or hybrid), black color when ripe and acid to sweet acid flavor (Rotili *et al.*, 2019).

The fruits have 85% of water, 10% of carbohydrates and vitamins A and B (Souza *et al.*, 2015). It is considered a functional food, with basic functional characteristics in the diet, beneficial to human health, in addition to its chemical and mineral composition, and bioactive compounds containing elements like phenols, flavonoids, lycopene, â-carotene, anthocyanins and others (Guedes *et al.*, 2014; Ferreira & Mercadante, 2010).

They can be consumed *in natura* or processed. This use becomes necessary, as the fruits have a fragile structure when ripe and a high respiratory activity, with relatively short postharvest conservation (Souza *et al.*, 2015).

The bioavailability of anthocyanin and phenolic compounds present in fruits can be affected mainly by their use, cultivars, hybrids and climate conditions. Bromatological compounds are generally found in small fruits (Rotili *et al.*, 2021; Rigolon *et al.*, 2020; Guedes *et al.*, 2013). Some studies were carried out with blackberry, regarding the qualification of these compounds (Teixeira *et al.*, 2019), however, this influence on ripening and post-harvest conservation is not well known.

A large number of mineral compounds (macro and microelements) are essential for human nutrition, performing specific functions in the body. Maro *et al.* (2013) and Curi *et al.* (2015) studied some macro and microele-

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ments present in small fruits of *Rubus* genus, among which stood out the presence of nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, boron, copper, manganese, zinc and iron. In addition to these compounds, natural pigments such as anthocyanin also stand out because it's attractive coloring in other products using small fruits.

Due to these characteristics, blackberry has been attracting the interest of producers and consumers, mainly due to the consumption potential associated with its beneficial properties to health.

Because it is a temperate fruit, the largest Brazilian production comes from the Rio Grande do Sul State, but in the subtropical regions located above the Brazilian temperate zone have favorable conditions for fruit production, due there is your winter with low temperatures, which however prints characteristics distinct from the fruits of these regions, highlighting the need for further studies.

Given the above, the objective of this study was to evaluate the bromatological, mineral and bioactive compounds of four blackberry cultivar and two hybrids grown in a subtropical region.

MATERIAL AND METHODS

Blackberry fruits from cultivars Tupy, Arapaho, Chickasaw and Navaho, the hybrids Boysenberry and Olallie were used on experiment. The blackberry plants are cultivated in the orchard of Unioeste Experimental Farm, *Campus* Marechal Cândido Rondon - Paraná, in geographical coordinates 24° 33' 40" S, 54º 04' 12" W and 420 m altitude.

The seedlings were purchased in April/2015 from a suitable nursey, in the form of root cuttings (Villa *et al.*, 2008). In July/2015, the plants were acclimated and taken to the field. The training system used was in "T", with double parallel wires, posts with dimensions of 0.15 m (diameter) x 1.20 m (height).

During the period of the experiment, the climatic data were monitored and the average monthly temperature, relative humidity of the air and precipitation are shown in Figure 1.

The fruit harvest started in October/2016 and November/2017, occurring every two days, extending until January/2017 and January/2018, respectively. The fruits were harvested in transparent polyethylene containers, when they were in complete maturation and dark color.

Immediately after harvest, the fruits were taken to the Unioeste Food Technology Laboratory for analysis. The samples for sugar reducing, bromatological and mineral analysis were frozen and sent to Fundetec's Laboratory (Cascavel, Paraná) and Laboratory of Chemistry, Biochemistry and Food Analysis at UFLA (Lavras, Minas Gerais). At the Unioeste Laboratory, the first evaluations were carried out, such as firmness, color and respiration. Then, five fruits of each treatment were chosen for juice extraction and analysis of ascorbic acid, pH, total acidity, soluble solids and soluble solids/total acidity ratio.

Fruit pulp firmness was measured using a digital penetrometer (brand Brookfield, USA), and the resulting expressed in Newton (N). The fruit respiration (CO_2) or respiratory activity (mg CO_2 Kg^{-1} h^{-1}) was carried out in gas chromatograph (brand Finnigan, 9001).

For color analysis, a colorimeter was used (brand Konica Minolta, model Sensy CR 400) and the color expressed by the rectangular coordinate system L* a* b* (CIE, 1986), where L* = percentage of brightness values (0% = dark and 100% = white), a* = red (+) or green (–) colors and b* = yellow (+) or blue (–) colors.

For chemical analysis, ascorbic acid was evaluated (or vitamin C), determined by titration with 2.6-dichlorephenol-indophenol (modification from Benassi & Antunes, 1988) and with results expressed in mg of ascorbic acid per 100 mL^{-1} of juice. For pH, ph meter was used and for SS (°Brix), a refractometer (brand Atago pocket). For total acidity (g 100 g^{-1}) by titration.

The total phenolic compounds (antioxidants) were determined according to the conventional Folin-Ciocalteu spectrophotometric procedure (Georgé *et al.*, 2005). The concentrations of antioxidants were expressed as gallic acid equivalents (mg AG g^{-1}), calculated using a curve constructed with 805 concentrations ranging from 10 to 60 mg L^{-1}.

Anthocyanin was determined using the differential pH methodology proposed by Lee *et al.* (2005). The absorbance readings of 510 and 700 nm were performed on a digital spectrophotometer (brand Shimadzu, UV-1800) with results of anthocyanin content expressed in mg Ci-3-Gly g^{-1}. For the analysis of reducing sugars (g 100 g^{-1}), the methodology of the Instituto Adolfo Lutz was followed (IAL, 2008).

Bromatological (moisture, lipids, proteins, fibers, dry biomass) and mineral analyzes were carried out at the Chemistry, Biochemistry and Food Analysis Laboratory and Plant Mineral Nutrition Laboratory, both at UFLA (Lavras, Minas Gerais), following the IAL (2008) methodology.

For mineral analysis, the fruits were ground in a Willey mill, according to methodology of Marschner *et al.* (2012), with results expressed in percentages for N, P, K, Ca, Mg and S, in mg Kg^{-1} for the others (B, Cu, Fe, Mn e Zn). The data obtained were subjected to the Shapiro-Wilk test for normality and subsequently to analysis of variance the means were compared by the Tukey test, at 5% probability of error, using the Sisvar (Ferreira, 2011) statistical software.

RESULTS AND DISCUSSION

Table 1 showed the significant results presented for firmness and respiration in blackberry fruits, in two consecutive harvests. Firmness is an important attribute in fruit quality and shelf life, as it affects transport resistance, attack by microorganisms and sensory characteristics of fruits (Guedes *et al.*, 2013). Among the cultivars and hybrids studied, no statistical difference was observed for fruit firmness regardless of harvests.

The results found in the cultivar Arapaho were similar to those verified in the same cultivar, in fruits harvested in Lavras (MG) by Guedes *et al.* (2013), although for the cultivar Tupy, the resistance of the fruits at the stage of harvest on this present study was greater than fruits harvested in Lavras (Table 1).

Combined with firmness, respiration is a parameter linked to the fragility of the fruits, acting on their storage potential. Blackberry is a small fruit with a fragile structure, well known for having high respiratory rates (Gonçalves *et al.*, 2012), which it gives the species characteristics of climacteric fruit and it gives respiration an important role in defining its storage potential. Among the cultivars, there was variation in respiratory rates, especially Boysenberry and Navaho, with higher and lower respiratory rates, respectively (Table 1), which allows us to infer different behaviors in relation to post-harvest conservation, although this was not the focus of this study.

It is also observed that the hybrids showed a high respiratory rate in both harvests, higher than the blackberry cultivars, which it may be associated with a more accelerated degradation of these hybrids soon after harvest, due to the presence of a more fragile epidermis (Gonçalves *et al.*, 2012).

Table 2 shows the fruits color of the blackberry cultivars and hybrids, in the 2016/2017 and 2017/2018 harvests. Color is considered an important parameter for producers and consumers, as it indicates whether the fruit presents ideal conditions for commercialization and consumption (Chitarra & Chitarra, 2005).

Regarding coloration, Boysenberry hybrid was the one that showed the highest luminosity (L) in both harvests, although in the 2016/2017 crop other genotypes were equal

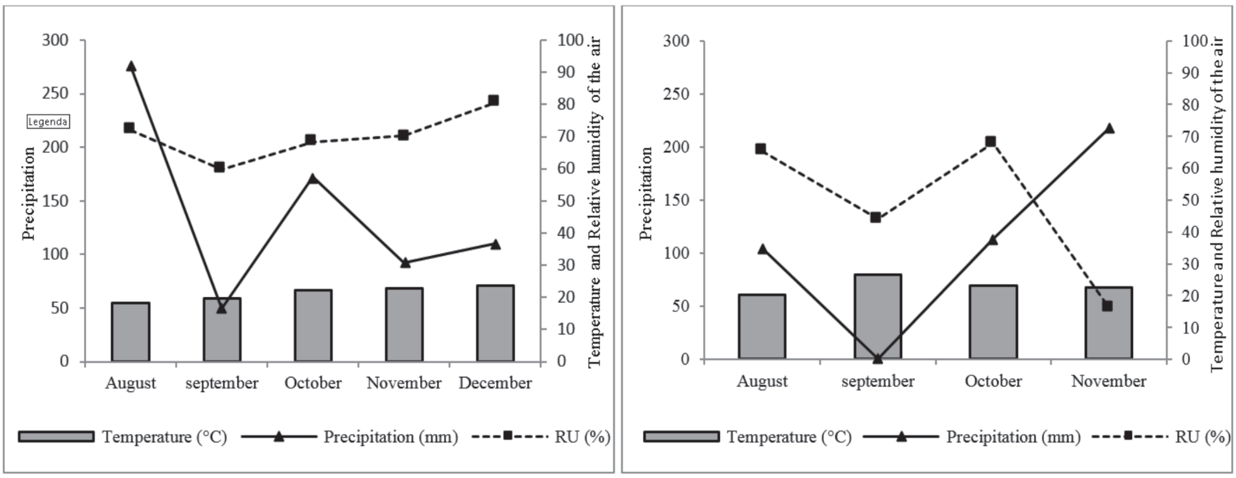

Figure 1: Average monthly temperature, relative humidity of the air and precipitation during productive cycles 2016/2017 (A) e 2017/2018 (B), in Marechal Cândido Rondon, Paraná State, Brazil. Unioeste, *Campus* Marechal C. Rondon, PR. 2020.

Table 1: Firmness and respiration in fruits of blackberry varieties, in two harvests

Varieties	Harvest 2016/2017	Harvest 2017/2018	Harvest 2016/2017	Harvest 2017/2018
	Firmness (N)		CO_2 (mg CO_2 kg^{-1} h^{-1})	
Tupy	0.49 a*	0.49 a	121.66 e	164.97 c
Arapaho	0.51 a	0.44 a	206.55 d	157.70 c
Chickasaw	0.47 a	0.50 a	328.05 b	224.93 b
Navaho	0.43 a	0.49 a	92.63 f	95.11 d
Hybrids				
Boysenberry	0.48 a	0.50 a	348.32 a	328.19 a
Olallie	0.47 a	0.48 a	238.20 c	227.53 b
CV(%)	12.52	7.74	3.53	5.70

*Averages followed by the same lowercase letter differ from each other in the column, by the Tukey test, at 5% probability of error.

to it, however not differing also from genotypes with lower luminosity. According to the CIE (1986) interpretation, L is an approximate measure of luminosity, which it is the property according to which each color can be considered equivalent to a gray scale member, between black or white (Granato & Masson, 2010), that is, in a simplified is a way of classifying the color of the fruit saying whether they tend to have a weaker or more intense color.

The Boysenberry and Olallie hybrids were characterized by high values in a*, confirming that the more intense red coloration, which it showed a brilliant purple coloration, what is indicative of fruit maturity and ideal harvest stage. According to Hirsch *et al.* (2012), the appearance of purple color may be related to the amount of phenolic compounds present, favoring the commercialization due to the consumer's preference for bright colored fruits. The low levels of b* can be explained by the predominance of anthocyanin and the almost null presence of carotenoids, such as coloring pigments of these fruits.

The contents of ascorbic acid, pH, total acidity, SS and SS/AT ratio in blackberry fruits were shown in Table 3. Blackberry represents an important source of vitamin C (Souza *et al.*, 2015; Skrovankova *et al.*, 2015). This amount may vary according to the species, cultivation system, fruit maturation, harvest season, pre-harvest climatic conditions, post-harvest management, storage and processing (Jacques & Zambiazi, 2011). The ascorbic acid contents of the blackberries studied were higher than those mentioned in the international literature by Zia-Ul-Haq *et al.* (2014), with a maximum of 44 mg 100 mL^{-1} found in the Loch Ness cultivar grown in Serbia. Also, Kafkas *et al*. (2006) analyzed the levels of ascorbic acid in blackberries and in their study found divergent values of the present work, emphasizing that in their study the Loch Ness cultivar presented mg 100 mL^{-1}.

The cultivar that had the best performance was Tupy, with 68.18 to 75.00 mg 100 g^{-1}, in both harvests, respectively. It was also observed that, in the second harvest, the ascorbic acid concentrations were higher than the previous harvest, influenced by the higher temperatures during fruit ripening (Guedes *et al.*, 2013), which they were 21.3°C in the 2016/2017 crop and 23.1°C in the 2017/2018 crop.

Regarding the acidity of the fruits, regardless of the harvests, the cultivar Arapaho was the one with the lowest acidity and the highest pH (Table 3), possibly due to its lower concentration of organic acids. For the other genotypes, there was no significant difference for acidity, although for pH it was possible to observe great variation among cultivars, but always maintaining the observed patterns.

The acidity found in the fruits is of extreme importance in the industry, as it does not favor the manifestation of microorganisms and, consequently, it gives a longer shelf life of the product. In particular, due to its high perishability and limited consumption *in natura*, blackberry has a strong tendency to industrialization, revealing the importance of acidity in this fruit (Silva *et al.*, 2013b).

In comparison to other studies, the results found for pH and acidity of these cultivars were favorable to cultivation, with fruits of less acidity and pH higher than those verified by Hirsch *et al.* (2012), in Pelotas (Rio Grande do Sul State, Brazil) and lower acidity than Tupy variety, grown in Marechal Cândido Rondon (Paraná State, Brazil) (Campagnolo & Pio, 2012). In comparison to other fruits of nutritional value, blackberry matches acidity and pH to *Dovyalis* sp., allowing consumption *in natura* and in processed form (Rotili *et al.*, 2018).

The soluble solids content of blackberries, which it is indicative of the sugar content, varied between 7.56 and 9.86ºBrix for the cultivars Chickasaw and Tupy, respecti-

Table 2: Color in fruits of blackberry varieties, in two harvests

Varieties	Harvest 2016/2017			Harvest 2017/2018		
	Color					
	L*	a*	b*	L*	a*	b*
Tupy	18.82 ab**	0.62 cd	0.55 d	18.29 b	1.06 c	0.59 c
Arapaho	18.76 abc	2.38 c	1.12 cd	18.84 b	1.27 c	0.90 c
Chickasaw	15.99 bc	0.58 d	0.82 cd	15.58 d	1.20 c	0.87 c
Navaho	14.63 c	1.53 cd	1.25 cd	16.95 c	1.76 c	1.08 c
Hybrid						
Boysenberry	20.66 a	8.50 a	2.78 a	22.37 a	12.24 a	4.75 a
Olallie	18.70 abc	5.10 b	2.01 b	18.53 b	6.43 b	2.69 b
CV(%)	11.67	28.96	20.37	13.56	11.40	31.23

L* = expressed as a percentage the luminosity values (0% = black e 100% = white), a* = colors red (+) or green (–), b* = colors yellow (+) or blue (–). ** Averages followed by the same lowercase letter differ from each other in the column, by the Tukey test, at 5% probability of error.

vely, in the first harvest and 9.12 to 10.54ºBrix for Chickasaw and the Olallie hybrid in the subsequent harvest (Table 3). This variation in values can be attributed to the characteristics of each cultivar, combined with the edaphoclimatic conditions of the cultivation site.

The soluble solids (SS) present in the fruits are an important parameter of evaluation, mainly when they are destined for processing, because a high SS content guarantees higher yield and lower production cost and represents the sugar content balanced with acidity. Although SS and total acidity (TA) are parameters evaluated in isolation, they must be analyzed together, as the flavor of the fruits is given by this relationship (Chitarra & Chitarra, 2005).

Due to the reduced acidity observed in all cultivars and hybrids, a high SS/AT ratio was verified, with emphasis on Arapaho and Tupy, which it obtained values above 30. Based on a high relationship, Curi *et al.* (2015) indicate Caiguangue and Cherokee varieties for consumption *in natura*, already that presented 14 and 8.1ºBrix on average, respectively. Therefore, all cultivars in this study can be consumed fresh, or processed, as they have a minimum SS/TA ratio of 19.8, which it can be considered as high value for this parameter demonstrating that the fruit has a predominance of sugars in detriment to acids, making the flavor sweet and at the same time allowing a high yield in its processing by the food industry.

Due to the great importance of phenolic compounds for health, they have been quantified in several studies with fruit crops. Celant *et al.* (2016) cite 14.98 mg of gallic acid 100 g^{-1} of fruit, lower than that found in the present study. Silva *et al.* (2016) found a variation from 78.91 to 112.37 mg EAG 100 mL^{-1} in species of *Physalis*. This variability in the content of phenols is related to the difference in methodology used for extracting the sample, annual harvests or climate (Jacques & Zambiazi, 2011).

Anthocyanins are pigments that give color to fruits, vary among orange, red and blue and act as natural antioxidants, promoting benefits to human health. They are also the main pigments of blackberry, providing attractive coloring in dairy and processed products (Acosta-Montoya *et al.*, 2010).

The anthocyanin content can vary significantly between cultivars and hybrids, giving specific characteristics to each genotype (Souza *et al.*, 2015). There are a number of factors capable of influencing the concentration of anthocyanin in fruits, including light, temperature, intermolecular pigmentation, presence of metals and pH. Fruits with a lower pH tend to have a higher intensity of red coloring, which it can be seen in the Boysenberry and Olallie hybrids (Table 3).

The Boysenberry hybrid, in both harvests, had higher anthocyanin levels, with 5.11 and 5.08 mg Ci-3-Gly g^{-1}, following by hybrid Olallie (Table 4), which it arouses the commercial interest of the consumer for these genotypes,

Table 3: Ascorbic acid, pH, total acidity (TA), SS (ºBrix) and SS/TA ratio, in fruits of blackberry varieties, in two harvests
Harvest 2016/2017

Varieties	**Ascorbic acid (mg 100 mL^{-1})**	**pH**	**Total acidity (g 100 g^{-1})**	**S S (ºBrix)**	**Relation SS/TA**
Tupy	68.18 a*	3.21 ab	0.33 a	9.86 a	30.98 a
Arapaho	43.17 b	3.24 a	0.25 b	8.28 ab	32.94 a
Chickasaw	68.18 a	3.16 c	0.38 a	7.56 b	19.68 b
Navaho	68.18 a	3.20 b	0.38 a	9.62 a	25.04 ab
Hybrids					
Boysenberry	63.63 a	3.11 d	0.38 a	7.64 b	19.89 b
Olallie	34.09 c	3.14 cd	0.38 a	7.66 b	19.94 b
CV (%)	5.34	0.53	8.08	11.22	16.93
			Harvest 2017/2018		
Varieties					
Tupy	75.00 a	3.22 ab	0.35 a	9.30c	26.51b
Arapaho	52.26 d	3.24 a	0.25 b	9.22 c	36.88 a
Chickasaw	70.04 c	3.15 c	0.38 a	9.12 c	24.00 c
Navaho	72.72 b	3.20b	0.38 a	10.00 ab	26.31 b
Hybrids					
Boysenberry	70.00 c	3.10 d	0.35 a	9.88 bc	28.22 b
Olallie	40.90 e	3.13 cd	0.38 a	10.54a	27.73 b
CV (%)	5.87	0.52	9.56	2.98	9.44

*Averages followed by the same lowercase letter differ from each other in the column, by the Tukey test, at 5% probability of error.

taking into account the nutraceutical potential. There is a scarce literature with information about the Olallie hybrid on phytochemical aspects (Ryu *et al.*, 2017).

Regarding the sugars present in fruits, Souza *et al.* (2015) state that reducers are the main sugars contained, due to the low concentration of sucrose. The cultivars with highest concentrations of reducing sugars were Arapaho and Chickasaw, although the latter did not differ statistically from Navaho (Table 4). In addition to genetic factors, the relationship between physical and chemical variables helps in understanding the results. The high concentration of reducing sugars in the Arapaho cultivar, together with the low levels of ascorbic acid, decreases the titratable acidity and raises the pH (Table 3), resulting in fruits sweeter.

The contents of moisture, dry matter, lipids, proteins and fibers of the fruits were shown in Table 5. Blackberry fruits had no significant water content among cultivars, with values similar to those found by Hirsch *et al.* (2012), some genotypes studied, observed that the results ranged from 84.8 to 90.3 g 100 g^{-1} in ‘Selection 02/96’ and ‘Cherokee’, respectively. Despite the non-significance among cultivars, the water content can be considered high. Garcia *et al.* (2014) mention the importance of moisture content, reporting that this parameter serves as a quality indicator, since it has a direct influence on storage.

The dry matter values did not show statistical differences among the genotypes (Table 5). According to Crisosto *et al.* (2011), can be considered a quality parameter, positively relating to the SS and TA content, where fruits harvested with higher dry matter are preferred by final consumers.

The lipid content found in the genotypes was low for Arapaho and Chickasaw (Table 5). Regarding the protein content, the fruits studied were also higher than the values described by Souza *et al.* (2015), demonstrating the influence of the maturation stage on the bromatological characterization. Confirming this superiority, especially in hybrids, the protein content in 100 g of fruit represents 17.14 to 19.78% of an adult’s recommended daily intake (RDI).

The amount of fiber was also significantly different among genotypes, with the highest value found in the Tupy cultivar and the lowest in Arapaho (Table 5). Dietary fibers are components of conventional foods and, when possible, it should be part of the daily diet, as adequate consumption directly correlates with the reduction of the risk of diseases (Bernaud & Rodrigues, 2013).

A high fiber content observed in the present study, in addition to benefiting health through the consumption of fresh fruit, favors the development of new nutraceutical processed products, such as flour (Casarin *et al.*, 2016).

Table 4: Total phenolic compounds, anthocyanin and reducing sugars in fruits of blackberry varieties, in two harvests

Harvest 2016/2017			
Varieties	**Total phenolic compounds (mg EAG100mL^{-1})**	**Anthocyanin (mg Ci-3-Gly g^{-1})**	**Reducing sugars (g 100g^{-1})**
Tupy	1042.47 d*	2.89 d	7.34 cd
Arapaho	1163.32 c	3.03 d	8.28 a
Chickasaw	1368.84 a	2.58 e	8.12 ab
Navaho	1034.10 d	4.14 c	7.71 bc
Hybrids			
Boysenberry	810.48 e	5.11 a	6.94 de
Olallie	1283.28 b	4.35 b	6.88 e
CV(%)	3.688.08	2.74	
Harvest 2017/2018			
Varieties	**Total phenolic compounds (mg EAG100 mL^{-1})**	**Anthocyanins (mg Ci-3-Gly g^{-1})**	**Reducing sugars (g 100 g^{-1})**
Tupy	1094.51 c	2.89 c	-
Arapaho	1233.00 b	2.99 c	-
Chickasaw	1333.56 a	4.18 b	-
Navaho	1090.90 c	2.58 d	-
Hybrids			
Boysenberry	852.82 d	5.08 a	-
Olallie	1335.32 a	4.36 b	-
CV(%)	0.87	3.21	-

*Averages followed by the same lowercase letter differ from each other in the column, by the Tukey test, at 5% probability of error.

Fruits are considered the main sources of minerals needed in the human diet (Hardisson *et al.*, 2001). Among the minerals, macronutrients are found such as nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulfur (S) (Table 6) and micro, such as boron (B), copper (Cu), manganese (Mn), zinc (Zn) and iron (Fe) (Table 7). Among macronutrients, significant differences were observed for P, K and Ca, while for N, Mg and S this difference did not occur.

O N stands out as one of the most significant nutrients in fruits, as it has a structural function and is part of several organic compounds, such as amino acids and proteins, in addition with nitrogenous bases and nucleic acids, performing multiple functions in the coloring of the epidermis, content SS, pulp firmness and fruit size. Despite the non-observance of a significant difference for this nutrient in blackberry genotypes, the values can be considered good.

The P and Ca stood out in the Tupy cultivar, while K concentration was higher among hybrids (Table 6). P in fruits is associated with superior size and quality (Dias *et al.*, 2001), which it is why it is more present in the cultivars Chickasaw and Tupy, with a higher caliber. Mg and S, although they did not show significant difference among genotypes, it can be highlighted due to the nutritional richness of the fruits and their importance in their development and formation (Marschner, 2012). Blackberry plants belong to the Rosaceae botanical family, characterized by the low need for S (Silva *et al.*, 2013a).

Among the micronutrients, there was a significant difference among the genotypes in the content of each, except for Fe. For B levels, only the Chickasaw cultivar showed to be inferior to the others (Table 7). B is an essential micronutrient for the plant, in small amounts and it is not part of any structural compound, having great importance in N metabolism, carbohydrate transport and polysaccharide structure. Thus, its deficiency can harm fruiting and result in malformed fruits, with low commercial value and little resistance (Taiz & Zeiger, 2013).

Zinc is part of the composition of numerous enzymes, in addition to maintaining the structural integrity of the cell membrane. The other micronutrients evaluated (Cu, Mn and Fe) correlate mainly with enzymatic functions, performing structural functions (Marschner, 2012). In

Table 5: Chemical composition, moisture, dry biomass, lipids, proteins and fibers (g 100 g^{-1})] in fruits of blackberry varieties, in the 2016/2017 harvest

Varieties	Harvest 2016/2017				
	Moisture	**Dry biomass**	**Lipids**	**Proteins**	**Fibers**
Tupy	80.03 n.s.	19.96 n.s.	3.77 ab*	9.20 ab	7.23 a
Arapaho	83.09 n.s.	16.91 n.s.	2.59 b	9.28 ab	4.33 b
Chicksaw	82.49 n.s.	17.50 n.s.	4.59 a	8.57 b	6.10 ab
Navaho	80.93 n.s.	19.01 n.s.	3.53 ab	8.84 ab	5.71 ab
Hybrids					
Boysenberry	79.59 n.s.	20.40 n.s.	3.33 ab	9.89 a	5.26 b
Olallie	81.76 n.s.	18.24 n.s.	3.61 ab	9.89 a	6.22 ab
CV(%)	1.27	5.56	9.29	2.80	7.64

*Means followed by the same letter in the column differ from each other statistically by the Tukey test, at 5% probability of error.

Table 6: Mineral composition [N, P, K, Ca, Mg and S (%)] in fruits of blackberry varieties, in the 2016/2017 harvest

Varieties	N	P	K	Ca	Mg	S
Tupy	1.19 n.s.	0.19 a*	0.75 d	0.13 a	0.18 n.s.	0.14 n.s.
Arapaho	1.11 n.s.	0.14 b	0.88 cd	0.08 b	0.15 n.s.	0.12 n.s.
Chicksaw	1.23 n.s.	0.17 ab	0.98 bc	0.01 c	0.16 n.s.	0.12 n.s.
Navaho	1.11 n.s.	0.13 b	0.95 c	0.07 b	0.16 n.s.	0.12 n.s.
Hybrids						
Boysenberry	1.18 n.s.	0.16 ab	1.15 ab	0.09 b	0.18 n.s.	0.12 n.s.
Olallie	1.08 n.s.	0.14 b	1.22 a	0.07 b	0.18 n.s.	0.11 n.s.
CV (%)	5.36	5.65	4.39	7.34	4.38	6.17

*Means followed by the same letter in the column differ from each other statistically by the Tukey test, at 5% probability of error. n.s. = not significance.

Table 7: Mineral composition [B, Cu, Mn, Zn and Fe (mg kg^{-1})] in fruits of blackberry varieties, in the 2016/2017 harvests

Varieties	B	Zn	Cu	Mn	Fe
Navaho	8.80 ab*	8.97 b	8.05 b	67.91 b	44.79 n.s.
Tupy	13.94 a	11.44 ab	13.54 a	50.11 de	49.12 n.s.
Arapaho	9.88 ab	9.65 ab	7.73 bc	58.46 cd	31.22 n.s.
Chickasaw	5.32 b	8.78 b	8.35 b	44.01 e	50.78 n.s.
Hybrids					
Boysenberry	8.72 ab	18.80 a	7.14 bc	63.39 bc	45.01 n.s.
Olallie	9.55 ab	12.78 ab	5.23 c	78.02 a	47.17 n.s.
CV (%)	13.78	18.77	7.46	3.51	11.65

*Means followed by the same letter in the column differ from each other statistically by the Tukey test, at 5% probability of error. n.s. = not significance.

relation to the Cu content, the cultivar Tupy presented fruits with 13.54 mg kg^{-1}, different from the others. As for Mn, the presence was superior to the other micro except for Fe with Chickasaw, which stood out with greater concentration.

Considering that the cultural treatments were the same in all genotypes, the variation in minerals could be attributed to the intrinsic characteristics. It should also be noted that the levels of minerals in fruits are very dependent on edaphoclimatic conditions and cultivars, making it understandable the fluctuation in mineral content.

The results found in the present study with the Tupy, Arapaho, Chickasaw and Navaho varieties and the hybrids Boysenberry and Olallie cultivated in the western region of Paraná State (Brazil) were promising for revealing a high concentration of compounds beneficial to health, however future and more comprehensive studies must be carried out, in order to allow quality fruit to be obtained for fresh consumption and / or processing.

CONCLUSIONS

Hybrids are more perishable, with higher respiratory rates and higher protein content. In Chickasaw cultivar has a higher lipid content.

There is variation in color among the cultivars and hybrids studied. Higher pH is verified in the Tupy and Arapaho varieties. The Arapaho cultivar has less acidic fruits and a higher content of soluble solids.

Blackberry genotypes have a high content of ascorbic acid and fibers, with emphasis on the cultivar Tupy.

Blackberry fruits are a rich source of bioactive and nutritional compounds, with emphasis on cv. Chickasaw and the Boysenberry hybrid.

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