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PHYSICO-CHEMICAL CHARACTERIZATION OF GRAPE CULTIVARS (*Vitis labrusca*) FROM SOUTHEAST REGION OF BRAZIL ACCORDING TO CLIMATIC CONDITIONS

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ABSTRACT

Grapes (*vitis* sp.) are beneficial for health as they are rich in phenolic compounds. These and other important compounds are affected by external factors which they are subjected to during their development, such as sunlight, rain and altitude. The aim of this study is to verify the influence of the climate from the city of Lavras (MG) on the chemical composition of different *Vitis labrusca* grape cultivars. The grapes were harvested when they were ripe and the soluble solids, titratable acidity, pH, ratio, phenolic compounds by High-Performance Liquid Chromatography (HPLC), antioxidant activity using the DPPH * method and the climatic factors of the Lavras region were evaluated over four years. The grapes from Lavras showed a low soluble solids content, high acidity and a high content of phenolic compounds, mainly rutin. The BRS Cora and BRS Rúbea hybrid cultivars showed high antioxidant capacity among the six cultivars analyzed and the Bordô cultivar had the lowest antioxidant activity. Climatic factors from the region favored *Vitis labrusca* cultivars concerning the phenolic compound content.

Keywords: *Vitis labrusca*, fruit quality, phenolic compounds, climatic factors, Lavras climate, antioxidant activity

1. INTRODUCTION

Over the years, interest in determining appropriate sources of antioxidant phenolic compounds in the human diet has increased (Burin et al., 2014). Grapes (*Vitis* sp) are a rich natural source in

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phenolic compounds beneficial for health. According to Xia et al (Xia et al., 2010), its main components are anthocyanins, flavonoids and resveratrol, which are responsible for most biological activities of fruits. The contents of these compounds differ between varieties and are conditioned to external factors to which the grapes are subjected during their development (Ojeda et al., 2002, Chafer et al., 2005, Rockenbach et al.2011). Wine production is influenced by weather conditions (temperature, precipitation, evapotranspiration, wind, sunlight) that interact with the other elements of the production system, influencing the physiology of the vines, their development and grape quality (Back et al., 2013). Incident sunlight and water stress are climatic factors that play a significant role in the content and class of secondary compounds and other important compounds synthesized by grapes (Price et al, 1995, Ojeda et al., 2002). Stressful situations increase the activity of enzymes related to the synthesis of grape compounds, such as: phosphoenolpyruvate (PEP), which operates in malic acid synthesis; phenylalanine ammonia lyase (PAL), a key enzyme in the synthesis of phenols and invertase, which hydrolyzes sucrose (Smart, 1987; Rocha and Nonete, 2008). Vine species require a relatively warm and long growth period to ripen the fruit and the amount of cold required depends on the cultivars. For example, American cultivars (*Vitis labrusca*) are less demanding in the cold than European ones (*Vitis vinifera*) (Back et al., 2013). Considering Tonietto et al. (2006) and Dantas et al. (2007), according to the Koppen climate classification, the climate in Lavras is Cwa, temperate or hot (mesothermal) with dry winters and rainy summers, subtropical and the temperature of the hottest month is higher than 22 °C. In the south and southwest middle region of Minas Gerais, the months that have the highest rainfall are also the hottest months (Roldão, Santos and Oliveira, 2012) and generally coincide with the ripening and harvest of grapes, which is a critical factor for the final quality. Considering the fact that the chemical compounds in grapes may be strongly affected by genetic and environmental factors, the aim of this study was to evaluate the first crop of different cultivars of *Vitis labrusca* and hybrid grapes (Niagara Rosada, Concord, Bordô, Isabel Precoce, BRS Cora and BRS Rúbea) produced in the orchard at the Federal University of Lavras, Minas Gerais, based on weather and chemical parameters, as well as the quality of fruits.

2. MATERIALS AND METHODS

2.1 Samples

The experiment was set up in an institutional orchard at the Federal University of Lavras (MG), at 21°14’06” south latitude, 45°00’00” West longitude and an altitude of 918,841 meters. The grapes were cultivated in the upright trellis system. The bunches of cultivars: Niagara Rosada, Isabel Precoce, Bordô, BRS Cora, BRS Rúbea and Concord were harvested between the twenty-third and the twenty-seventh of December, when they reached 13 to 14 ° Brix (according to the

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cultivar) and after harvesting that occurred , the fruits were transported to the Postharvest Fruit and vegetable Laboratory at the Federal University of Lavras and kept in cold storage at 2 °C until further analized. The soluble solids variables, pH and titratable acidity were evaluated in the Postharvest Fruit and Vegetable laboratory at the Federal University of Lavras. In order to analyze the phenolic compounds and determine the antioxidant activity, the fruits were freeze-dried and taken to the Bioactive Products Laboratory at the Federal University of Rio de Janeiro, Macaé campus.

2.2 Climatological data

In order to study the climatic factors and their influence on the development of the grapes, time series of daily minimum and maximum temperatures, sunlight and rainfall were used from 2010 to 2014 recorded at the DEG/UFLA weather station at the Federal University of Lavras, located in Lavras-MG (21°14'06" south latitude, 45°00'00" West longitude and an altitude of 918,841 meters)

2.3 Chemical quality analysis

For the chemical variables, the must obtained from five grams of sample per cultivar was used. The soluble solids (SS) content was evaluated using an ATAGO PR-100 digital refractometer and the results were expressed as %; titratable acidity (TA) using the titrimetry method neutralizing the sample with NaOH solution (0.1M) and the results expressed as % of tartaric acid; pH using a digital pHmeter (Tecnal-TEC 3M) and soluble solids/ titratable acidity (SS/TA) relation. All the analyses were followed in accordance with the recommendations from the Association of Official Analytical Chemists (AOAC, 2007)

2.4 Reagents and standards

The reference substances of gallic acid, catechin, epicatechin, rutin, coumarin, *p*-coumaric acid, chlorogenic acid, caftaric acid and quercetin used to prepare the reference solutions were purchased from Sigma-Aldrich (St. Louis, MO, USA). The stock solution of the reference substances were prepared in methanol at a concentration of 1.3 mg mL^{-1}. The solutions of gallic acid, catechin, *p*-coumaric acid, chlorogenic acid, caftaric acid and quercetin used to quantfy the phenolic compounds in grapes were prepared from these concentrations of 2, 4, 8, 32, 65 and 130 µg mL^{-1}, while the solutions of epicatechin, rutin and coumarin were prepared at concentrations of 4, 8, 32, 65 and 130 µg mL^{-1}. All the solutions used methanol as the solvent. The solutions were stored at -20 °C and protected from light. The acetonitrile, acetic acid and methanol, HPLC degrees, used to prepare the mobile phases and reference solutions were obtained from Tedia (Fairfield, OH, USA).

2.5 Determining the phenolic compounds by HPLC

The phenolic compounds were identified and quantified in high-performance liquid chromatography equipment (Shimadzu, Kyoto, Japan) consisting of a LC-20AT quaternary gradient pump, a SIL-20A auto injector, a SPD-M20A diode array detector, a CBM-20A controller, CTO-20A oven, a DGU-20A$_5$ degasser (Shimadzu, Kyoto, Japan) and a data acquisition system using LCsolution® software version 1.25SP1. In the chromatographic separation, the Ascentis Express C$_{18}$ chromatographic column (100 x 4.6mm) and particle 2.7□m Supelco (Bellefonte, PA, USA) were used. For the mobile phase, A (water: acetic acid, 5% v/v) and B (acetonitrile) were used. Elution was conducted in gradient mode: 0 - 5 min 1% B; 5.1 - 15 min, 1 - 100% B; 15.1 - 24 min, 100% B with a flow rate of 1ml/min and injection volume of 4□□L at a temperature of 35 °C. The HPLC analysis was monitored in the ultraviolet range of 200-400 nm.

2.6 Preparation of extracts

The extracts were prepared in triplicate by weighing 1 g of the freeze-dried material mixed with 10 mL of methanolic solution (80% MeOH + 20% HCl 1 Meq) taken to ultrasound for 15 minutes and centrifuged for another 15 minutes. The extraction procedure was repeated once under the same conditions and the two supernatants were combined, via rotary evaporation at 35 °C and partitioned (3 x 5 mL ethyl acetate), and again via rotary evaporation, filtered and stored at -80 °C under light until being analyzed.

2.7 Determination of antioxidant capacity by radical DPPH.

The free radical scavenging activity DPPH * method (2,2-diphenyl-1-picrylhydrazyl) was estimated based on the method by Williams, Cuvelier & Berset (1995). An aliquot of 50 µL of the DPPH* solution 300 µM was added to 125 µL of methanol extracts from samples at concentrations of 60, 30, 15, 7.5, 3.75, 1.87 and 0.93 mg.mL. After 30 minutes in the dark, the absorbance at 517 nm was read in a Benchmark Plus Microplate Spectrophotometer (Bio-Rad, California, USA). As a standard, the gallic acid solution was used. The IC$_{50}$ was calculated using the straight line equation by substituting the value of y for 50 to obtain the sample concentration able to reduce 50% of the DPPH * (Negri et al., 2009). The results were expressed in □g.mL equivalent to gallic acid (EAG).

2.8 Statistical analysis

The data were analyzed using analysis of variance and the mean comparison was carried out using the Tukey test at a significance level of 5%. The non-parametric Spearman correlation was used to evaluate the correlation between antioxidant activity and phenolic compounds. All the tests used the R software version 3.2.2 and the "ExpDes.pt" package, version. 1.1.2.

3. RESULTS AND DISCUSSION

3.1 Weather conditions during the development of the cultivars

The development of the studied vines were characterized by the pruning period in the first week of August and resulted in early budding. Flowering began in September and the bunches began to grow until the end of October and early November. Ripening took place in November and the harvest was at the end of December.

When the grapes from 2012 harvest were still growing in the field, there was little variation of sunlight from the pruning period to when the bunches were fully grown and the maturation phase (November) had less sunlight. There was a linear increase in rainfall during development, reaching maximum rainfall in November, which corresponds to a period when there are more bunches and ripening, as well as a slight decrease in rainfall in December, which is harvest time. The ripening period of the grapes in this study was characterized by balanced sunlight and high rainfall. The harvest period had lower rainfall compared to the ripening phase, however with only a slight difference. The flowering and fruiting period of this study presented dry and sunny weather, but with temperatures higher than those considered ideal by Mandelli (1999) (Table 1). According to the author, temperatures close to 20 °C would be the most appropriate. Sugars stored in the grapes are mostly synthesized in the vine leaves through photosynthesis and translocated to the berries (Hardy, 1968; Mullins et al., 1992). Vine leaves reach optimal photosynthetic response at temperatures between 25 and 30 °C. Temperatures above 30 °C decrease the photosynthetic rate, reaching zero when the temperature exceeds 45 °C due to enzymatic inactivation and closing the leaves´ stomatal pores (Kriedermann, 1968). The sunlight during the development of the 2012 crop did not show a great variation, but was lower during the ripening and harvest periods. The maximum temperatures reached in the 2012 crop (Table 1) according to Kriedemann (1968) can be considered excellent, however high rainfall during the ripening and harvest periods may have contributed to an unfavorable balance of the sugar/ acidity ratio (Table 2), as cited by other authors (Mandelli, 1999; Amorin et al., 2005). Previous studies (Matthews et al, 1987;. Ojeda et al., 2002;. Martinez-Lüsher et al, 2014) report that water stress results in changes in the sugar, organic acid, flavonoid and anthocyanin concentration. According to the rainfall data for the period 2010 to 2014 (Fig. 1 B), the high rainfall in the summer is a characteristic factor of the climate in Lavras and this can result in fruits with an unfavorable sugar/acidity balance. Moreover, the data concerning sunlight (Fig. 1 A) also shows that the initial stages of the vine development are marked by dry and sunny weather, but with temperatures exceeding the ideal ones.

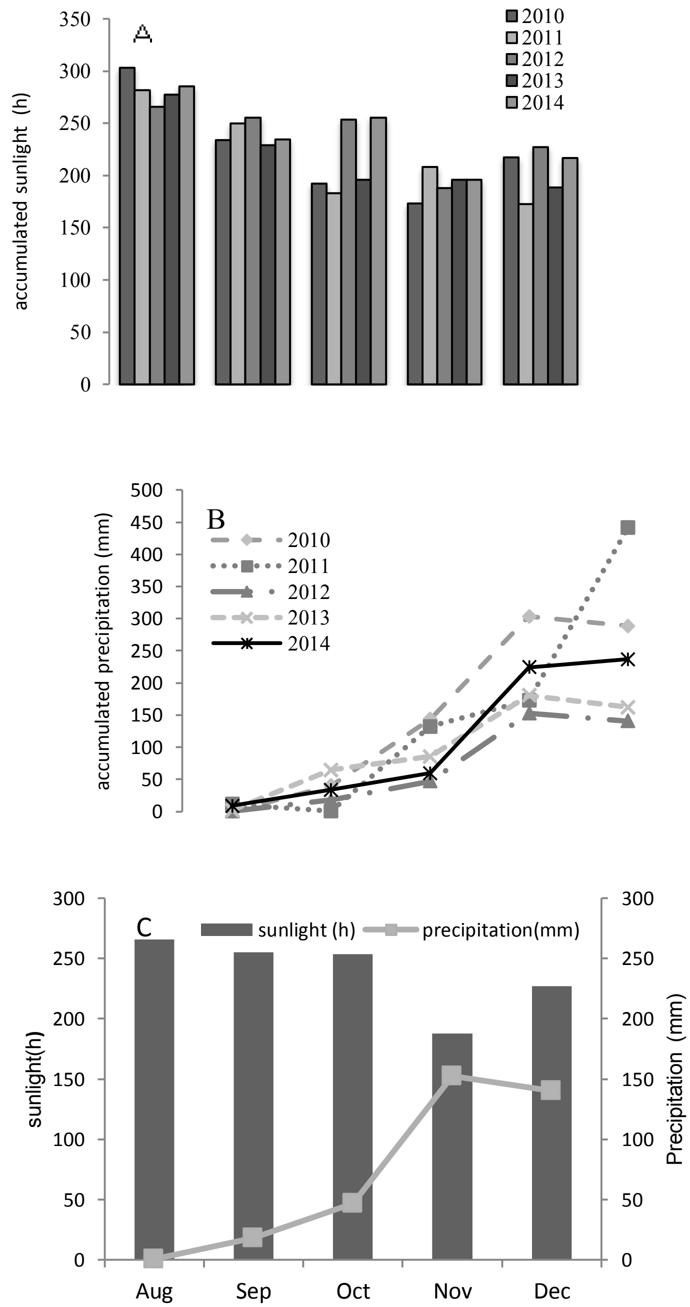

Figure 1. Values of accumulated sunlight (A) and accumulated precipitation (B) for the development period (August to December) of grapes (*Vitis labrusca*) from Lavras (MG) between 2010 and 2014. Accumulated precipitation and sunlight (C) registered for development period of

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grapes harvested in 2012. Data were obtained from weather station at Federal University of Lavras.

Table 1. Climatics conditions of 2012 crop of *Vitis labrusca* grapes.

Month	Max. T[1](°C)	Min. T[2](°C)	PP[3] (mm)	Sun[4] (h)	PA (mm)[5]	T. range[6] (°C)	SA[7]
Aug	25.2	12.3	0.4	8.6	0.4	12.93	266.0
Sep	28.5	14.0	5.7	8.5	17.1	14.41	255.4
Oct	30.6	16.8	4.3	8.2	46.9	13.81	253.8
Nov	27.9	17.7	9.0	6.3	152.7	10.26	187.8
Dec	30.5	19.5	9.4	7.3	140.4	11.05	226.9
Total	142.70	80.24	28.71	38.86	357.50		1189.9
Average per crop	28.54	16.05	5.74	7.77	71.50	12.49	237.98

1= MaximumTemperature, 2= Minimum temperature, 3= Average precipitation, 4= Average sunlight , 5= precipitation accumulated to each month, 6= Temperature range, 7= Sunlight accumulated to each month

3.2 Chemical evaluation of the berries

Although the cultivars studied did not show significant differences in relation to the °Brix content, the BRS Cora and Concord cultivars had the lowest soluble solids values (SS) while Bordô, BRS Rúbea and Niagara Rosada had the highest °Brix (Table 2). For the Isabel Precoce cultivar, the °Brix presented a lower value than that found by Rizzon and Miele (2006) in the 1999 to 2000 crops in fruits from Serra Gaucha, however they are within the values found by Sato et al., (2009) which varied from 13.4 to 16.8 °Brix for fruit from Rolândia (PR).

Ribeiro et al., (2012) found higher values, 21 °Brix for the Isabel Precoce from Petrolina (PE). Camargo et al., (2004) states that the cultivar on average reaches a content of 18 to 20 °Brix. Detoni et al. (2005) found an SS average of 16.2 °Brix for Niagara Rosada grapes from the organic system in Toledo (PR). Hernandes et al. (2013), who studied different systems for Niagara Rosada grapes found an SS average of 15.5 °Brix for summer crops in the region of Jundiái (SP) and the results corroborate with those of this study. The BRS Cora cultivar had an average of 13.7 °Brix, which was below that cited by Camargo and Maia (2004) for the BRS Cora in Petrolina (PE), which had a content of 22.6 °Brix. Borges et al. (2012) found that BRS Rúbea, produced in Rolândia (PR), reached 13.8 °Brix and was below that found in this study. According to Camargo and Dias, on average BRS Rúbea has a sugar content of around 15 °Brix. For the Concord cultivar, Borges et al. (2012) found 12.68 °Brix while the cultivars produced in Lavras had on average 13.7 °Brix, which is a value close to those found by Rizzon and Meneguzzo (2007). Villa et al. (2010) found a variation between 8 and 11 °Brix in ten different vineyards in Caldas (MG) for the Bordô cultivar differing widely from the cultivar studied, which showed a value of 16.33 °Brix, and according to Rizzon and Meneguzzo (2010) for this cultivar, the SS can vary from 13 to 16 °Brix. Since the SS accumulation depends on the sugar synthesized in the photosynthetic process and transported to berries by the phloem (Hardy, 1968;. Mullins et al, 1992), various factors, such as weather conditions (Winkler et al, 1974), altitude, grapevine defoliation or shading can affect the soluble solids content in fruits (Kliewer, 1964; Kliewer and Antcliff, 1970). The altitude significantly influences the soluble solids factor in fruits. Regions located at higher altitudes imply increased cloudiness and reduced sunlight, which reduces solar radiation (Regina et al., 2010), and consequently, the synthesis and accumulation of sugars may occur on a smaller scale. This becomes clear when we find that fruits from Petrolina (PE) showed a much higher content of SS (Sato et al., 2012) compared to fruits from higher altitudes (Villa et al. 2010). The solute accumulation synthesized during the first stage of fruit development remains until harvest (Conde et al., 2007). The dry and warm weather in the early period when the berries were developing was favorable for the sugar synthesis, but the ripening and harvest period was marked by high rainfall and this fact may have contributed to the dilution of compounds found in the berries, which mostly consist of sugars mainly for the Isabel Precoce and BRS cora cultivars.

According to the Brazilian standards (Brasil, 2002), grapes with at least 14 °Brix are considered ripe, and in order to meet international standards, fruits can be harvested showing a variation of 14 to 17.5 °Brix (Choudhury, 2001). Concerning juice production, grapes with SS contents above 14 °Brix are recommended, insofar as depending on the methodology used during processing, must dilution and a reduction in the SS content may occur (Borges et al, 2014). The SS values found for the Niagara Rosada, BRS Rúbea, Isabel Precoce and Bordô cultivars in this study meet the Brazilian legislation, as well as international requirements, whereas the BRS Cora and Concord cultivars had values below those recommended. The acidity was significantly different among the cultivars studied: Concord and BRS Rúbea were the most acidic and Niagara Rosada was the least acidic (Table 2). Borges et al (2012, 2014) found averages of 0.84 and 0.75 % for TA, respectively for the Concord cultivar from Rolândia (PR), and Pereira et al (2008) found an acidity of 1.3% for the same cultivar in Caldas (MG). The same author found a TA of 1.2 and 1.7 %, respectively for Bordô and BRS Rúbea cultivars in Caldas (MG). For the Isabel Precoce and BRS Cora cultivars grown in Petrolina (PE), Ribeiro et al. (2012) found a TA of 0.6 % and 0.8 %, respectively. For the Niagara Rosada cultivar, Detoni et al. (2005) observed a TA around 0.6 to 0.7 %. The cultivars in this study showed an acid variation of 1.3 to 1.9 % (Table 2), i.e., higher than that found in the literature. *Vitis labrusca* cultivars have high acidity as the main characteristic (Rizzon and Miele, 2006). In grapes, the malic and tartaric acids together correspond to a range of 68 to 92 % of the acids found in the fruits and vine leaves, and the tartaric acid is found in significantly higher quantities than the malic acid (Kliewer 1966 ; Wen et

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al. 2013). The malic acid after the development period of the fruit, known as "*véraison*", is then released from the vacuoles to be catabolized by different routes such as gluconeogenesis, the tricarboxylic acid cycle (TAC) and respiration (Conde et al, 2007; Wen et al ., 2013), while tartaric acid does not undergo degradation and, therefore, becomes the predominant acid (Melino et al, 2009;. Wen et al, 2010). The function of the accumulation of this acid *in planta* is still unclear (Debolt et al, 2007; Melino et al., 2009). Its synthesis and accumulation is started within the weeks following flowering, showing that the enzymatic activity of the acid synthesizer system is greater during the early stages of development (Kliewer, 1964). The synthesis of tartaric acid takes place by the catabolism of ascorbic acid. An increase in the expression of the enzyme codifier that gives rise to ascorbate during the day was reported by Tamaoki (2003), suggesting that expression of this encoder is controlled by light. Wen et al. (2013) proposed that high levels of tartaric acid found in Chinese grape cultivars must be related to the slow decrease in L-idonate dehydrogenase (L-IdnDH) levels; the only one identified in the biosynthetic via of ascorbic acid to tartaric acid so far. Considering that tartaric acid is a product of ascorbic acid catabolism, and this is influenced by the incident sunlight and that according to Kliewer (1964), green berries have an amount of acid two times higher than in ripe fruits, a connection between the temperature and sunlight can be established during the growth of the berries, ascorbic acid synthesis and tartaric acid accumulation because of no degradation of the acid and a slow decrease in the L-IdnDH levels, as suggested by Wen et al. (2013) in the fruits studied by us. The levels of this acid showed a large variation for the same cultivars from different regions. A study of the local conditions could clarify what the limiting factors or stimulants are in the ascorbic acid biosynthesis and high acidity of the grapes produced in Lavras. The cultivars studied did not have a high TSS/TA ratio and this is clearly linked to the fact that all of them have presented high acidity. The Niagara Rosada and Bordô cultivars had the highest averages of 11.61 and 11.04, respectively (Table 2), as they were the cultivars which had the lowest TA values. The TSS/TA ratio is an indicator of quality which represents the balance between acidity and sweetness of the product (Rizzon and Link, 2006). According to Choudhury et al. (2001), this ratio must be equal or more than 20 to produce red wine. Thus, the cultivars studied have not reached a good TSS/TA index due to the high acidity.

The pH values of the Bordô and Concord cultivars produced in Lavras are in accordance with the values found in the literature (Rombaldi et al., 2004; Pereira et al 2008;. Borges et al, 2014.). The BRS Rúbea cultivar had a pH value matched to that found by Pereira et al. (2008), however below that found by Sato et al. (2008). The Niagara Rosada cultivar had higher pH values found than those found by Detoni et al (2005), while the BRS Cora had a lower pH than that observed by Camargo and Maia (2004) for this cultivar. Camargo (2004) cites that the Isabel Precoce cultivar can reach pH values on average of 3.22, but the cultivar from Lavras showed the highest value (3.4) matching data from Rizzon and Mielle (2006), but lower than that observed by

Pereira et al. (2008). The increase in pH can be caused by absorption of water by the vine roots, which results in higher absorption of K and salification of tartaric acid (Rizzon and Miele, 2002). As the rainfall was high during ripening and harvesting, this may have contributed to the high pH values in the case of the Niagara Rosada cultivar because of the high osmotic K mobility (Mpelasoka et al.2003).

3.3 Phenolic compounds

The results showed significant differences in the concentrations of phenolic compounds of the analyzed grapes, agreeing with Mulero et al. (2010), Rockenbach et al. (2011) Natividade et al. (2013) by emphasizing the influence of the variety of grape compared to the concentration of phenolic compounds found in them. For the first time, a phenolic profile for the Isabel Precoce, BRS Rúbea and BRS Cora hybrid cultivars has been reported, and when compared to their original cultivars (Isabel for Isabel Precoce cultivar; Niagara Rosada x Bordô for BRS Rúbea cultivars and BRS Rúbea x muscat belly A' for BRS Cora cultivars), in this study we observed that BRS Rúbea showed a greater amount of gallic acid, catechin, epicatechin, chlorogenic caftaric acid and quercetin considering the origin cultivars, and for BRS Cora when compared with BRS Rúbea, only catechin, rutin, coumarin and p-coumaric acid had high expressions. The Isabel Precoce cultivar from Lavras had higher quantities of gallic acid, p-coumaric acid, catechin, epicatechin and quercetin than that obtained by Burin et al. (2014) for the Isabel Precoce cultivar. The Concord cultivar showed the lowest concentration for 4 out of the 9 compounds: gallic acid, catechin, epicatechin and chlorogenic acid (Table 2).

The BRS Rúbea cultivar showed the highest concentrations for 5 out of the 9 compounds: gallic acid, epicatechin, chlorogenic acid, caftaric acid and quercetin (Table 2). Rutin was the phenolic compound found in higher concentrations for all the grapes analyzed. Furthermore, the Bordô and BRS Cora cultivars showed the highest concentrations and Isabel Precoce the lowest concentration. The Niagara Rosada cultivar showed intermediate levels for all the compounds. Abe et al. (2007), Lago-Vanzela et al. (2011) and Burin et al. (2014) reported for the Bordô, Concord and Niagara Rosada cultivars, levels of gallic acid, caftaric acid, p-coumaric acid, (+) catechin, (-) epicatechin, rutin and quercetin lower than those found in this study. Unlike our study, Lago-Vanzela et al. (2011) reported that the lowest concentration of phenolic compound for the Bordô cultivar was rutin. The rutin concentrations found by Novak et al. (2008) in skins of different Portuguese grape cultivars reached values of 0.029 mg.g to 0.214 mg.g and this compound is also the most abundant flavonol among the analyzed samples, which is in accordance with our study. Various authors (Chafer et al. 2005, Montealegre et al. 2006; Gomez-Alonso et al. 2007) also found both compounds (quercetin and rutin) in grapes, as in this study. The results concerning the concentrations of both compounds (quercetin and rutin) in this

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study followed the same trend as Iacopini et al. (2008) reported with low concentrations of quercetin (Table 2). In a study on tomatoes, Capanaglu et al. (2012) suggested that the availability of the substrate can have more effect on the rutin content than the enzyme activity itself. Various authors showed an increase in the glycosylated derivative content of quercetin when the plant material was exposed to radiation (Price et al. 1995, Gregan et al. 2012) and do not identify aglycone, suggesting that the synthesized quercetin was used in the synthesis of rutin. The accumulation of flavonoid starts before anthesis and increases in the flowering stages, possibly as a means of protection (Czemmel et al.2012). Under appropriate levels of radiation, genes involved in enzyme coding (PAL and CHS and CHI) of the phenylpropanoid biosynthetic pathway are activated, and thus, result in the accumulation of phenolic compounds that absorb such radiation playing an important role in defense against damage caused by exposure (Pontin et al. 2010). As previously mentioned, various factors induce the synthesis of phenolic compounds. Among them, temperature and solar radiation are regarded as the most influential. When comparing the climatic factors in Caldas (MG) and Serra Gaucha (RS), there is a tendency of high rainfall in Serra Gaucha at the beginning of budding, flowering and fruiting which falls, but no shortage of rain in the ripening and harvest seasons, having an average rainfall per crop of 163.7mm (Tonietto and Mandelli, 2003). For the Caldas region, the trend is the same as that observed in Lavras, with a low amount of rainfall at the beginning of budding and increased rainfall in the ripening and harvest seasons totalling on average 205 mm per crop (Tonietto and Mandelli, 2003). Caldas develops at the beginning with more sunlight, but varies throughout the development (165.4 h on average per harvest) (Tonietto and Mandelli, 2003). In Serra Gaucha, the tendency is to increase sunlight during the development (236.1 average hours per season). Lavras had average rainfall and sunlight from 2010 to 2014 of 117.9 mm and 227.2 h (data not shown). Concerning the studied crop, the average rainfall was the lowest and the average sunlight accumulated was the highest, which may explain the high content of secondary compounds found in cultivars produced in Lavras. Lavras is located approximately 919 m above sea level and is at an intermediate altitude compared to Caldas (1.100 m) and Serra Gaucha (between 400 and 700 m above sea level). This fact could significantly influence the high content of phenolic compounds observed in this study.

3.4 Antioxidant activity by DPPH *

The BRS Rúbea cultivar showed higher antioxidant capacity with 16.4 μgEAG.mL of extract able to reduce 50% of free radicals while the Bordô cultivar showed the lowest antioxidant capacity with 628.1 μgEAG.mL (Table 2). Some studies correlate the antioxidant capacity that the sample shows with the amount of phenolics presented by it. Other authors (Nixdorf and Hermosín-Gutiérrez, 2010; Baiano and Terracone, 2011) correlate the antioxidant capacity with the type of phenolic compound found in the sample. The non-parametric Spearman correlation

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analysis performed in this study suggests that the compounds epicatechin and quercetin significantly influenced the antioxidant activity of the evaluated grapes. The results showed a negative correlation for both epicatechin compounds (R = -0.47) and quercetin (R = -0.90), which means that the higher the concentration of these phenolic compounds, the lower the IC50 value or the higher the antioxidant capacity presented by the grapes (Fig. 2). In a study carried out by Arora et al. (1998), the flavonoid quercetin showed higher antioxidant activity than rutin (its glycosylated form), luteolin, narigenin, hisperetin, coumarin and chrysin. The authors attribute this greater activity to the hydroxyl group (OH) at the C-3 position of the molecule structure. The replacement of hydroxyl in the C-3 position by the disaccharide rutinoside showed a slight decrease in the antioxidant capacity of the compound (Arora et al. 1998). Iacopini et al (2008) also observed a higher antioxidant capacity for quercetin compared to catechin, epicatechin, resveratrol and rutin. The other phenolic compounds showed no significant correlation ($p > 0.5$).

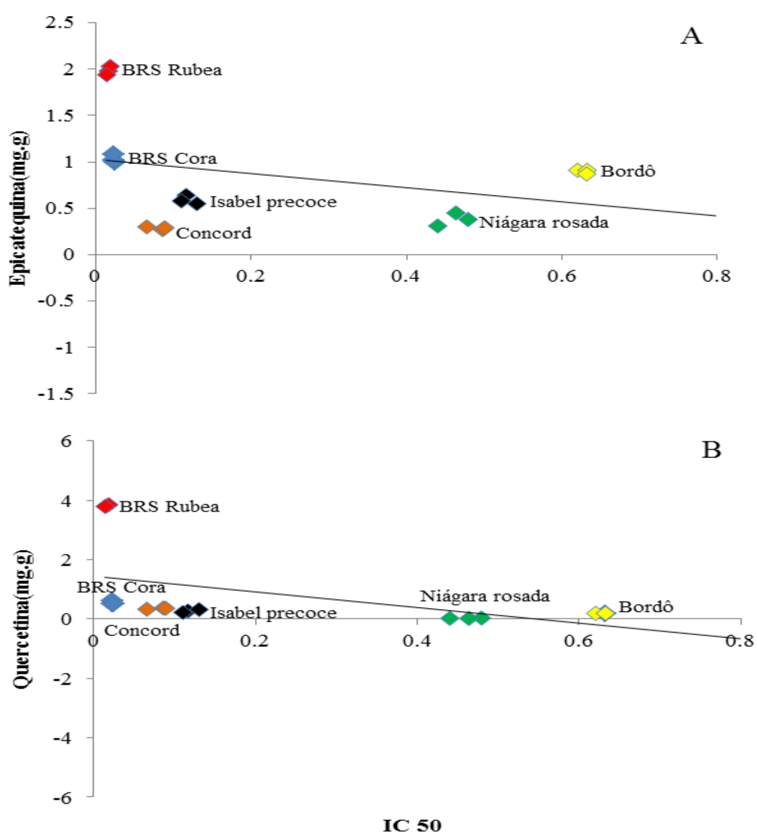

Figure 2. Correlation of epicatequin (A) and quercetin (B) phenolic compounds to IC50 values of 6 different grape cultivars from Lavras, MG.

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Table 2. Chemical composition and antioxidant activity of grapes *Vitis labrusca* from Lavras

	BRS Cora	BRS Rúbea	Niágara Rosada	Isabel Precoce	Bordô	Concord
TSS (°Brix)	13.7 a ±1.2	16.3 a ±1.2	16.3 a ± 0.6	16.0 a ±2.0	16.3 a ±0.6	13.7 a ±1.2
TA(%tartaric acid)	1.8 ba ±0.1	1.9 a ±0.2	1.3 c ±0.1	1.7 cba ±0.2	1.5 cb ±0.3	1.9 a ±0.1
TSS/TA (ratio)	7.40 c ±1.85	8.40 cb ±0.92	11.61 a ±1.34	9.37 cba ±1.7	11.04 ba ±1.39	7.03 c ±0.77
pH	3.37 c ±0.01	3.50 b ±0.06	3.57 a ±0.02	3.40 c ±0.02	3.50 b ±0.00	3.35 c ±0.01
Phenolic compounds (mg.g)						
Galic acid	0.63b	1.00a	0.32d	0.21e	0.52c	0.21e
p-cumaric acid	0.57a	0.25c	0.22c	0.22c	0.42b	0.19c
Caftaric acid	0.32a	0.5a	0.31a	0.39a	0.39a	0.31a
Clorogenic acid	0.29abc	0.41a	0.25bc	0.33abc	0.36ab	0.21c
catequin	0.65b	0.59bc	0.28d	1.38a	0.45c	0.23d
epicatequin	1.03b	1.98a	0.38e	0.59d	0.89c	0.27e
rutin	8.66a	5.11c	3.14e	1.5f	8.13b	4.42d
quercetin	0.54b	3.79a	0.025e	0.27cd	0.19d	0.35c
coumarin	0.9b	0.69c	0.73c	0.73c	1.07a	0.55d
***DPPH(IC_{50})**	23.5a	16.4a	460.9d	118.9c	628.1e	80.0b

Different letters within a line mean statistically significance difference among the cultivars by Tukey's test ($p<0.05$).
*µg.mL Galic Acid Equivalent

3.5 Conclusion

Due to the fact that there is rainfall in Lavras during the ripening and harvesting seasons, this results in grapes with low SS content, but a high content of phenolic compounds, mainly rutin which may be linked to sunlight and the altitude. The hybrid BRS Cora and BRS Rúbea cultivars were those that showed higher antioxidant capacity among the six cultivars analyzed.

CONFLICT OF INTEREST

The authors have no conflict of interest to declare

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