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Pre-drying and submerged cap winemaking: Effects on polyphenolic compounds and sensory descriptors. Part II: BRS Carmem and Bordô (*Vitis labrusca* L.)

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ABSTRACT

Brazilian wine production is dominated by the use of American grape cultivars (*Vitis labrusca* L.) and their hybrids. In this context, this study analyzed the phenolic composition and sensory profile of Bordô and BRS Carmem red wines elaborated from traditional and two alternative winemaking technologies: grape pre-drying and submerged cap of chaptalized musts. Anthocyanins and pyranoanthocyanins apparently seemed to be affected by the thermal process (60 °C), causing their degradation. In addition, the decrease of the concentration of these compounds could be suggested as a result of possible oxidation and hydrolysis reactions of anthocyanin 3-glucosides. Stilbenes were also affected by thermal degradation; however, flavan-3-ols and HCAD seemed to be less affected by the drying process. Submerged cap winemaking resulted in an increase of the anthocyanin and pyranoanthocyanin compounds due to the constant contact between the must and pomace during the alcoholic fermentation. The antioxidant capacity seemed not to be affected by thermal degradation, since the products of Maillard reaction also present antioxidant properties. Pre-dried wines were described as structured due to their higher flavan-3-ols content, and with high color intensity probably due to the formation of Maillard reaction products. The submerged cap wines presented an intense violet hue due to their high anthocyanin derivative concentrations and showed strong correlation with all other classes of the phenolic compounds.

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1. Introduction

Vitis vinifera is the most used grape for wine production throughout the world, however in Brazil, the wines are mostly elaborated from the American grapes (*Vitis labrusca*) and their hybrids known as table wines, which have surpassed the production of wines elaborated from European grapes (Biasoto, Netto, Marques, & Da Silva, 2014). This fact is probably due to the tropical climatic conditions of the major viticulture regions of Brazil, which present features that are unfavorable for the growth of *V. vinifera* grape cultivars. Additionally, the American grapes present strong adaptation to hot climates, versatility in relation to the crop planning and their rusticity is an interesting feature related to their high resistance to the major diseases of the vine (De Castilhos, Conti-Silva, & Del Bianchi, 2012).

Despite the above-mentioned advantages, the American grapes and their hybrids present low soluble solids content and reduced color intensity on their optimal stage of ripening. Thus, there is a need to improve these features in order to produce table wines that are more attractive for the consumers, as a result of the enhancement of the red pigments extraction from grape berries by variation on the winemaking process or genetic improvement (Camargo & Ritschel, 2008).

In this context, the Brazilian agro-farming research agency EMBRAPA Grape and Wine has been developing new hybrid grape cultivars with higher sugar content and color indexes under normal growth conditions. Among the new cultivars developed, it is possible to highlight the 'BRS' type cultivars such as: BRS Carmem, BRS Rúbea, BRS Cora, BRS Violeta and others. Of these one can highlight the BRS Carmem, which was a grape originated in 2008 as a result of the crossing between Muscat Belly A and BRS Rúbea producing red wines with an intense violet hue and typical raspberry aroma and flavor (Camargo, Maia, & Ritschel, 2008). In addition to these grapes developed by means of genetic improvement, Bordô grape (*V. labrusca* L.), already a well-known grape cultivar in Brazil, which produces wines with intense red-purple color, fruity aroma and usually used as a blend with wines presenting low color hues (Lago-Vanzela, Da-Silva, Gomes, García-Romero, & Hermosín-Gutiérrez, 2011).

Additionally to the genetic improvement, the modifications on the winemaking process are usually carried out by wineries aimed at improving the quality of red wines by the enhancement of the phenolic compound extraction during the alcoholic fermentation. Among the possible variations in the winemaking process, grape drying (Marquez, Serratosa, Lopez-Toledano, & Merida, 2012) is one of the procedures applied in order to gain wine color as a result of the irreversible damage to the cellular structure of the grape skin caused by the heat that facilitates the extraction of anthocyanins and other phenolic compounds (Figueiredo-González, Cancho-Grande, & Simal-Gándara, 2013; Margaris & Ghiaus, 2007). The submerged-cap during the wine maceration is another alternative winemaking procedure that facilitates the contact between the pomace and the must, which promotes higher extraction of the phenolic compounds from the grapes (Bosso et al., 2011). However, these studies are restricted to the analysis of the phenolic compounds from red wines elaborated by *V. vinifera* grapes and studies that assessed the response of these winemaking procedures in wines elaborated from *V. labrusca* grapes and hybrids are practically non-existent.

The maximum levels of these wine pigments are observed during the early days of the maceration and approximately 30–40% of the anthocyanins remain in the crushed skins (Marquez et al., 2012). During the maceration, anthocyanins and tannins are extracted from the solid parts of the berries allowing the oxidation and condensation reactions and absorption phenomena that cause a balance between extraction and loss. The anthocyanin content decreases during the maceration time by the reactions of coupled oxidation catalyzed by polyphenoloxidase (PPO) in the presence of residual oxygen. The submerged-cap winemaking procedure aims at avoiding the contact between the solid parts and the residual oxygen in order to increase the anthocyanin content of the resulting wine (Bosso et al., 2011).

Considering that the quality of the red wines is based on the assessment of their sensory attributes, any variation in the winemaking process can change their phenolic composition, antioxidant capacity, as well as their sensory features, promoting changes on the wine quality. A similar previous work was done assessing the phenolic and sensory profiles of BRS Rúbea and BRS Cora red wines submitted to alternative winemaking procedures (De Castilhos et al., 2015) and another study with BRS Violeta, a *teinturier* grape, is being carried out. These studies present a strong contribution to the enological area since the response of these winemaking procedures on the chemical and sensory profiles of the red wines elaborated from these new grape cultivars are yet unknown.

Thus, the aim of this work was to evaluate the detailed composition of the most relevant phenolic compounds, the antioxidant capacity and sensory descriptive attributes of Bordô and BRS Carmem red wines elaborated from traditional (T) and two alternative winemaking procedures: grape pre-drying (PD) and submerged cap (SC). In addition to the influence of these techniques on chemical and sensory profiles, a chemometric approach was generated in order to allow for a relationship between both profiles.

2. Material and methods

2.1. Chemicals

All solvents were of HPLC quality, all chemicals were of analytical grade (>99%) and the water was of Milli-Q quality. The following commercial standards from Phytolab (Vestenbergsgreuth, Germany) were used for the identification of the phenolic compounds: malvidin 3-glucoside, malvidin 3,5-diglucoside, peonidin 3,5-diglucoside, *trans*-piceid, *trans*-caftaric acid, (−)-epigallocatechin and (−)-gallocatechin, as also the following commercial standards from Extrasynthese (Genay, France): cyanidin 3-glucoside, cyanidin 3,5-diglucoside, procyanidins B1 and B2, kaempferol, quercetin, isorhamnetin, myricetin, syringetin and the 3-glucosides of kaempferol, quercetin, isorhamnetin and syringetin. In addition, the following commercial standards from Sigma Aldrich (Tres Cantos, Madrid, Spain) were used: *trans*-resveratrol, caffeic acid, (+)-catechin, (−)-epicatechin, (−)-epicatechin 3-gallate and (−)-gallocatechin 3-gallate. Other non-commercial flavonol standards such as myricetin 3-glucoside, quercetin 3-glucuronide and laricitrin 3-glucoside were previously isolated from Petit Verdot grape skins (Castillo-Muñoz et al., 2009). Procyanidin B4 was kindly supplied by Prof. Fernando Zamora (Department of Biochemistry and Biotechnology, Universitat Rovira i Virgili, Spain). The *trans* isomers of resveratrol and its 3-glucosides (piceid) were converted into their respective *cis* isomers by UV irradiation (366 nm light for 5 min in quartz vials) of 25% MeOH solutions of the *trans* isomers.

All the standards were used for identification and quantitation by calibration curves covering the expected concentration ranges. When a standard was not available, the quantitation was done using the calibration curve of the most similar compound: malvidin 3,5-diglucoside for 3,5-diglucoside anthocyanin type and malvidin 3-glucoside for the 3-glucoside type, quercetin 3-glucoside for flavonol 3-glycosides and their free aglycones, caffeic acid for hydroxycinnamic acid derivatives, (+)-catechin for polymeric flavan-3-ols (total proanthocyanidins), and individual flavan-3-ol monomers and dimers by their corresponding standards considering their total sum as (+)-catechin equivalents.

2.2. Winemaking

Six red wines were produced: traditional Bordô wine (BT), pre-dried Bordô wine (BPD), submerged cap Bordô wine (BSC), traditional Carmem wine (CART), pre-dried Carmem wine (CARPD) and submerged cap Carmem wine (CARSC). The grapes were harvested in

the city of Jales (20° 16′ 7″ south and 50° 32′ 58″ west), São Paulo state, Brazil, at their usual complete maturity levels and in good sanitary conditions. The Bordô and Carmem grapes presented, at the start of the winemaking procedure, soluble solid contents of 16.4 ± 1.0 °Brix and 17.5 ± 0.5 °Brix, and pH values of 3.37 ± 0.01 and 3.30 ± 0.01, respectively.

All the treatments followed the standard winemaking procedure described by De Castilhos, Cattelan, Conti-Silva, and Del Bianchi (2013), which started with de-stemming and manual crushing of the grapes allowing the release of the juice. The must and pomace were then inserted into 10 L fermentation vessels and sulfur dioxide was added at the proportion of 150 ppm of potassium bisulfite (approximately 86.5 ppm of SO_2). Alcoholic fermentation was induced by the 200 ppm inoculation of active dry Saccharomyces cerevisiae Y904 (Amazon Group®). After dejuicing, the pomace was gently pressed and placed into another vessel allowing for the malolactic fermentation. After the completion of the malolactic fermentation, followed by thin layer chromatography (TLC) (Ribéreau-Gayon, Paynaud, Sudrad, & Ribéreau-Gayon, 1982), the wines were racked, stored at low temperatures, and then bottled.

The submerged cap treatment provided the effect of the constant maceration of the grape's solid parts by using stainless steel screens to maintain the cap at the bottom of the fermentative vessel, avoiding its rise due to the production of carbon dioxide. Traditional and submerged cap were chaptalized by the addition of 52.2 $g \cdot L^{-1}$ and 42.3 $g \cdot L^{-1}$ of sugar for Bordô and Carmem wines, respectively. The pre-drying treatment consisted of drying the grapes to 22 °Brix to avoid chaptalization and obtain wines with an alcoholic strength between 8.6 and 14 °GL, as required by Brazilian legislation (Brasil, 2005). This winemaking process was carried out using a convective drying method with a tray dryer at 60 °C and airflow of 1.1 $m \cdot s^{-1}$ (De Castilhos et al., 2013). At the end of drying procedure, both the Bordô and Carmem wines presented 22.6 °Brix, with 20.6% and 20.4% of the water evaporated in relation to the initial weight, respectively. All the winemaking trials were carried out in duplicate.

The following conventional enological parameters were measured: total and volatile acidities (TAC and VAC, as $g \cdot L^{-1}$ tartaric acid and acetic acid, respectively) and pH (Brasil, 2005); total dry extract (EXT) ($g \cdot L^{-1}$) (AOAC, 2005); reducing sugars (RSG) ($g \cdot L^{-1}$) by the Lane-Eynon method (AOAC, 2005), alcoholic content (ALC) (% volume/volume) (AOAC, 2005) and total phenolic content using gallic acid as standard (Slinkard & Singleton, 1977).

2.3. Analysis of the phenolic compounds

2.3.1. Preparation of the wine for the determination of the non-anthocyanin phenolic compounds

The flavonol fractions were isolated from diluted wine samples following the procedure described by Castillo-Muñoz, Gómez-Alonso, García-Romero, and Hermosín-Gutiérrez (2007), using Bond Elute Plexa PCX solid phase extraction cartridges (Agilent; 6 cm^3, 500 mg of adsorbent). The flavan-3-ols (monomers, B-type dimers and polymeric proanthocyanidins) and stilbenes were isolated following the procedure described by Rebello et al. (2013), using SPE C18 cartridges (Waters® Sep-Pak Plus, filled with 820 mg of adsorbent).

2.3.2. HPLC-DAD-ESI-MS^n analysis of the phenolic compounds

The HPLC separation, identification and quantitation of the phenolic compounds were carried out on an Agilent 1100 Series HPLC system (Agilent, Germany) equipped with DAD (G1315B) and a LC/MSD Trap VL (G2445C VL) electrospray ionization mass spectrometry (ESI-MS^n) system, coupled to an Agilent ChemStation (version B.01.03) data-processing unit. The mass spectra data were processed using the Agilent LC/MS Trap software (version 5.3).

The anthocyanin and non-anthocyanin compounds were analyzed according to a previously described method (Lago-Vanzela et al., 2011). The wine samples were injected (10 μL for anthocyanin analysis and 20 μL for non-anthocyanin flavonol analysis) onto a Zorbax Eclipse XDB-C18 reversed-phase column (2.1 × 150 mm; 3.5 μm particle; Agilent, Germany) with the temperature controlled at 40 °C.

For identification, the ESI/MS-MS was used in both the positive (anthocyanins) and negative (flavonols and hydroxycinnamic acid derivatives) ionization modes set for the following parameters: dry N_2 gas with a flow of 8 $L \cdot min^{-1}$ at a drying temperature of 325 °C; and N_2 nebulizer at 50 psi. The ionization and fragmentation parameters were optimized by direct injection of the appropriate standard solutions (malvidin 3,5-diglucoside solution in the positive ionization mode; quercetin 3-glucoside and caftaric acid in the negative ionization mode) using a scan range of 50–1200 m/z. Identification was based on the spectroscopic data (UV–vis and MS/MS) obtained from the aforementioned authentic standards or using previously reported data (Barcia, Pertuzatti, Gómez-Alonso, Godoy, & Hermosín-Gutiérrez, 2014; Lago-Vanzela et al., 2013; Lago-Vanzela et al., 2014; Nixdorf & Hermosín-Gutiérrez, 2010; Rebello et al., 2013). For quantitation, the DAD chromatograms were extracted at 520 nm for anthocyanins, 360 nm for flavonols and 320 nm for the hydroxycinnamic acid derivatives (HCAD). The analyses were carried out in duplicate.

2.3.3. Identification and quantitation of the flavan-3-ols and stilbenes using Multiple Reaction Monitoring (MRM) HPLC-ESI-MS/MS

The analysis was carried out using a HPLC Agilent 1200 series system equipped with DAD (Agilent, Germany) and coupled to an AB Sciex 3200 TRAP (Applied Biosystems) with triple quadrupole, turbo spray ionization (electrospray assisted by a thermonebulization) mass spectroscopy system (ESI-MS/MS). The chromatographic system was managed an Agilent ChemStation (version B.01.03) data-processing unit, and the mass spectra data was processed using the Analyst MSD software (Applied Biosystems, version 1.5).

Structural information concerning the proanthocyanidins was obtained using the pyrogallol-induced acid-catalyzed depolymerization method (Bordiga, Coïsson, Locatelli, Arlorio, & Travaglia, 2013). The reaction consisted of adding 0.50 mL of the pyrogallol solution (100 $g \cdot L^{-1}$ pyrogallol plus 20 $g \cdot L^{-1}$ of ascorbic acid in 0.3 N HCl) to 0.25 mL of the sample in MeOH and incubating 40 min at 30 °C. The hydrolysis reaction was stopped by adding 2.25 mL of sodium acetate (67 mM). An aliquot of 2 mL of the reacted sample was placed in a vial and injected directly into the equipment for analysis.

The samples, before and after the acid-catalyzed depolymerization reaction, were injected (20 μL) onto an Ascentis C18 reversed-phase column (150 mm × 4.6 mm with 2.7 μm of particle size), with the temperature controlled at 16 °C. The solvents and gradients used for this analysis and the two MS scan types used (Enhanced MS — EMS and Multiple Reaction Monitoring — MRM) as well as all the mass transitions (m/z) for identification and quantitation were according to the methodology reported by Lago-Vanzela et al. (2011).

2.4. Determination of the antioxidant capacity by the DPPH assay

The procedure consisted of adding 100 μL of wine diluted in methanol to 2.9 mL of a methanolic DPPH (2,2-diphenyl-1-picrylhydracyl, Fluka Chemie) radical solution (6×10^{-5} $mol \cdot L^{-1}$) (Brand-Williams, Cuvelier, & Berset, 1995). After 25 min, the decrease in the percent absorbance at 515 nm was measured. For this measurement, the range should be between 20 and 80% of the initial DPPH absorbance and thus the dilution of the wine with methanol was adjusted in order to enter this range; for red wines the usual dilution factors are between 1/10 and 1/20. Quantitation of the antioxidant capacity was achieved using calibration curves obtained with methanolic solutions of Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid, Fluka, Chemie).

2.5. Sensory analysis

Descriptive analysis was used to profile the six red table wines (two grapes × three treatments in duplicate). Ten panelists (Embrapa Grape and Wine, Brazil) with more than 15 years of wine tasting experience took part in a session using representative wine samples and reference standards. After a discussion, a list of eleven attributes was established, two attributes for appearance (color intensity, violet hue) and nine for taste (sweetness, acidity, bitterness, flavor intensity/body, structure/tannins, herbaceous taste, astringency, pungency and persistence). The evaluation sessions took place in a sensory analysis room with individual booths under daylight at ambient temperature. Aliquots of 30 mL of the red wines at 18 °C were poured into transparent glass cups and for each wine, the panelists evaluated each descriptor on a horizontal unstructured 9 cm scale anchored by the minimum and maximum extremes. All the samples were coded with three random digits and were presented in a monadic and randomized form. The panelists evaluated the samples in triplicate (Girard, Yuksel, Cliff, Delaquis, & Reynolds, 2001). The Ethical Issues regarding the sensory analysis were approved by the Ethics in Research Committee of the Institute of Biosciences, Humanities and Exact Sciences, São Paulo State University (process n. 15159913.3.0000.5466).

2.6. Data analysis

All the data were treated using a one-way analysis of variance (ANOVA) followed by Tukey's post-hoc test (when P value < 0.05) and the relationship between the chemical properties and the sensory attributes was determined using the Principal Component Analysis (PCA). All the statistical tests were applied at a significance level of 0.05 using the Statistica 10 software (StatSoft Inc., Tulsa, OK).

3. Results and discussion

3.1. Conventional enological parameters

The enological parameter results measured according to the official analysis for wine of the AOAC (2005) and Brasil (2005), for the Bordô and Carmem wines were expressed in Table 1. All the enological parameters of Bordô wines were influenced by the winemaking procedures and pre-dried sample (PDB) presented the higher values for all enological properties, except for alcohol content. A similar result was observed for Carmem wines for all enological parameters, except for alcohol content, which presented no significant differences when the winemaking procedures were compared, pH and volatile acidity, being PDC the wine that showed lower results.

The high acidity and reducing sugar content of the pre-dried wines was an expected result due to the water evaporation and consequent concentration of the fixed organic acids and non-fermentable sugars, respectively, corroborating the results from De Castilhos et al. (2013). In addition, pre-dried wines, regardless the grape cultivar, presented higher dry extract content (above 30 $g \cdot L^{-1}$), considering them as full-bodied wines (Jackson, 2008), and high total phenolic content, suggesting that the heat did not negatively affect these compounds. Submerged cap wines presented no significant differences when compared with traditional treatment and this result suggested the discrete potential of this technique as an alternative winemaking procedure.

3.2. Anthocyanin and pyranoanthocyanin profiles

The data concerning the anthocyanins and pyranoanthocyanins profiles were obtained based on MS/MS and UV–vis spectroscopic data (Blanco-Vega, López-Bellido, Alía-Robledo, & Hermosín-Gutiérrez, 2011; Lago-Vanzela et al., 2011; Nixdorf & Hermosín-Gutiérrez, 2010). The 3,5-diglucosides of the five expected wine anthocyanidins (delphinidin, cyanidin, petunidin, peonidin and malvidin) were identified and quantitated by UV–vis spectra with the different forms of malvidin as the principal anthocyanidin (Table 2, Fig. 1).

Regarding the occurrence of the anthocyanidin 3-glucosides, peonidin-3-glucoside was detected and quantitated only in the Bordô wines, while malvidin-3-glucoside was only detected and quantitated in the BRS Carmem wines. The acylated anthocyanidin 3-glucoside forms were not found in both Bordô and Carmem red wines. This result can be explained due to the formation of the pyranoanthocyanins, which can only be formed from the anthocyanidin 3-glucosides (Blanco-Vega et al., 2011; Nixdorf & Hermosín-Gutiérrez, 2010).

It was possible to detect 27 different pyranoanthocyanins by means of their MS, MS/MS and UV–vis characteristics, most of them being hydroxyphenyl-pyranoanthocyanins, resulted from the reaction between the anthocyanins and hydroxycinnamic acids. The latter compounds were mainly 10-(3″-hydroxyphenyl) (10-HP; reaction products with *p*-coumaric acid) and 10-(3″,4″-dyhydroxyphenyl) (10-DPH; reaction products with caffeic acid) derivatives of the five anthocyanidin 3-glucosides and some of their 6″-acetyl or 6″-*p*-coumaroyl derivatives (Blanco-Vega et al., 2011). The A-vitisin types (10-carboxy-pyranomalvidin forms) were also detected in both Bordô and BRS Carmem wine samples, being the 3-glucoside form detected only in Bordô wine (10-carboxy-pyrmv-3glc), the acetylated form detected and quantitated only in BRS Carmem wines (10-carboxy-pyrmv-3acglc) and the *p*-coumaroylated form detected and quantitated in both Bordô and Carmem red wines (10-carboxy-pyrmv-3cmglc). The formation of these A-vitisin type pigments is a result of the reaction between anthocyanins and pyruvic acid, a yeast metabolite (Blanco-Vega et al., 2011).

The 3-(6″-*p*-coumaroyl)-glucoside-5-glucoside (3-cmglc-5-glc) derivatives of the five aforementioned anthocyanidins were also detected. It was assumed that the glucose moiety was linked to the C-5 position and the 6″-*p*-coumaroyl-glucose moiety to the C-3 position as previously reported (Mazzuca, Ferranti, Picariello, Chianese, & Addeo, 2005). It was possible to detect the delphinidin and cyanidin 3-(6″-*p*-coumaroyl)-glucoside-5-glucosides, as well as the *cis* (22.9 min, 25.3 min and 26.3 min) and *trans* (27.4 min, 29.6 min and 30.5 min) forms of petunidin, peonidin and malvidin in both red wines, respectively,

Table 1
Results (mean ± standard deviation) of the conventional enological parameters.

Wines	Enological parameter						
	Total acidity ($g \cdot L^{-1}$)	Volatile acidity ($g \cdot L^{-1}$)	pH	Alcohol content (%v/v)	Dry extract ($g \cdot L^{-1}$)	Reducing sugar ($g \cdot L^{-1}$)	Total phenolic content ($mg \cdot L^{-1}$)
BT	7.29 ± 1.13 ab	0.59 ± 0.03 b	3.37 ± 0.01 b	11.73 ± 0.28 a	29.25 ± 0.60 b	3.44 ± 0.46 a	1446.4 ± 27.5 c
BPD	8.03 ± 0.23 a	0.73 ± 0.03 a	3.40 ± 0.01 a	10.80 ± 0.20 b	39.41 ± 2.32 a	3.73 ± 0.54 a	1618.8 ± 22.8 a
BSC	6.65 ± 0.16 b	0.59 ± 0.03 b	3.41 ± 0.01 a	10.90 ± 0.91 ab	29.87 ± 1.59 b	2.54 ± 0.21 b	1509.8 ± 45.3 b
CART	7.00 ± 0.25 b	0.57 ± 0.03 a	3.37 ± 0.01 a	12.81 ± 0.19 a	29.08 ± 0.48 b	3.28 ± 0.22 ab	1515.9 ± 43.5 a
CARPD	8.17 ± 0.79 a	0.37 ± 0.08 b	3.33 ± 0.02 b	12.41 ± 0.60 a	34.26 ± 3.11 a	3.61 ± 0.44 a	1483.2 ± 56.0 a
CARSC	6.00 ± 0.09 c	0.49 ± 0.06 a	3.40 ± 0.00 a	11.75 ± 1.15 a	27.24 ± 0.41 b	2.90 ± 0.22 b	1325.7 ± 60.3 b

Abbreviations: BT, traditional Bordô wine; BPD, pre-dried Bordô wine; BSC, submerged cap Bordô wine; CART, traditional Carmem wine; CARPD, pre-dried Carmem wine; CARSC, submerged cap Carmem wine. Different letters in the same column indicate significant differences (ANOVA, Tukey's post-hoc test, $\alpha = 0.05$).

Table 2
Anthocyanin and pyranoanthocyanin profiles determined by HPLC/MS/MS (mean value ± standard deviation) for Bordô and BRS Carmem young red wines.

Anthocyanins and pyranoanthocyanins	Peak	R_t (min)	Molecular ion;product ions (m/z)	BT	BPD	BSC	CART	CARPD	CARSC
Anthocyanins (mg·L^{-1})				415.5 ± 2.86 b	273.5 ± 0.41 c	564.6 ± 4.18 a	301.2 ± 51.4 ab	199.6 ± 1.29 b	469.6 ± 66.8 a
Dp-3,5diglc	1	4.5	627;465,303	19.06 ± 0.20 b	13.50 ± 0.54 c	34.71 ± 0.35 a	6.47 ± 3.01 a	3.73 ± 0.04 a	13.25 ± 7.86 a
Cy-3,5diglc	2	6.5	611;449,287	9.84 ± 0.15 b	9.97 ± 0.30 b	12.15 ± 0.55 a	6.37 ± 0.07 a	2.95 ± 0.03 c	5.12 ± 0.39 b
Pt-3,5diglc	3	9.5	641;479,317	34.59 ± 0.28 b	23.57 ± 0.72 c	51.24 ± 2.84 a	19.34 ± 4.32 a	9.56 ± 0.07 a	27.88 ± 6.79 a
Pn-3,5diglc	4	12.1	625;463,301	33.22 ± 0.45 ab	25.65 ± 0.02 b	41.03 ± 3.45 a	25.60 ± 0.55 a	13.27 ± 0.06 b	23.64 ± 2.29 a
Mv-3,5diglc	5	14.0	655;493,331	173.83 ± 1.66 b	117.42 ± 0.28 c	213.36 ± 7.25 a	113.90 ± 15.60 ab	80.88 ± 0.22 b	159.68 ± 12.86 a
Pn-3glc	6	16.1	463;301	0.32 ± 0.02 a	0.19 ± 0.06 a	0.27 ± 0.09 a	ND	ND	ND
Pt-3acglc-5glc	7	18.2	683;521,479,317	2.47 ± 0.18 b	1.49 ± 0.53 b	4.46 ± 0.45 a	3.26 ± 0.89 a	1.98 ± 0.03 a	5.06 ± 0.91 a
Mv-3glc	8	19.2	493;331	0.25 ± 0.04 a	0.41 ± 0.10 a	0.19 ± 0.03 a	ND	ND	ND
Pn-3acglc-5glc	10	20.4	667;505,463,301	3.52 ± 0.05 a	2.80 ± 0.84 a	2.75 ± 0.65 a	4.16 ± 0.19 a	2.55 ± 0.98 a	3.28 ± 0.74 a
Mv-3acglc-5glc	13	21.7	697;535,493,331	5.20 ± 0.12 a	2.66 ± 0.76 b	5.52 ± 0.34 a	8.91 ± 0.86 b	6.84 ± 0.03 b	13.57 ± 1.45 a
Cis-Pt-3cmglc-5glc	14	22.9	787;625,479,317	1.64 ± 0.04 a	1.49 ± 0.19 a	2.04 ± 0.98 a	ND	ND	ND
Dp-3cmglc-5glc	16	23.6	773;611,465,303	12.43 ± 0.07 b	8.87 ± 0.16 b	31.82 ± 5.17 a	5.14 ± 3.26 a	4.19 ± 0.10 a	14.72 ± 10.80 a
Cis-Pn-3cmglc-5glc	17	25.3	771;609,463,301	1.16 ± 0.15 a	0.78 ± 0.03 a	0.97 ± 0.06 a	ND	ND	ND
Cy-3cmglc-5glc	18	25.8	757;595,449,287	4.60 ± 0.04 b	3.68 ± 0.06 c	6.83 ± 0.06 a	5.31 ± 0.57 a	2.85 ± 0.00 b	5.28 ± 0.30 a
Cis-Mv-3cmglc-5glc	19	26.3	801;639,493,331	3.11 ± 0.17 a	1.31 ± 0.02 c	2.40 ± 0.05 b	1.66 ± 0.79 a	2.08 ± 0.01 a	7.42 ± 7.25 a
Mv-3cfglc-5glc	21	27.2	817;655,493,331	ND	ND	ND	NQ	NQ	NQ
Trans-Pt-3cmglc-5glc	22	27.4	787;625,479,317	20.59 ± 0.08 b	14.73 ± 0.04 b	36.70 ± 2.52 a	15.28 ± 5.59 a	11.67 ± 0.32 a	31.95 ± 9.85 a
Trans-Pn-3cmglc-5glc	26	29.6	771;609,463,301	9.79 ± 0.19 b	4.96 ± 0.08 c	14.55 ± 0.69 a	12.01 ± 1.41 a	5.61 ± 0.00 b	15.66 ± 1.10 a
Trans-Mv-3cmglc-5glc	27	30.5	801;639,493,331	79.85 ± 0.37 b	40.05 ± 0.08 c	105.63 ± 6.13 a	72.40 ± 15.90 b	50.03 ± 0.08 b	140.81 ± 4.49 a
Mv-3cmglc	34	35.9	639;331	NQ	NQ	NQ	NQ	NQ	NQ
Pyranoanthocyanins (mg·L^{-1})				61.78 ± 0.05 b	70.88 ± 0.04 a	62.22 ± 0.36 b	78.49 ± 1.49 a	73.85 ± 0.79 b	80.94 ± 0.73 a
10H-pyrpt-3glc	9	19.8	503;341	ND	ND	ND	4.59 ± 0.25 a	4.38 ± 0.03 a	4.80 ± 0.07 a
10HP-pyrcy-3cfglc	11	20.9	727;565,403	NQ	NQ	NQ	ND	ND	ND
10-Carboxy-pyrmv-3glc (vitisin A)	12	21.3	561;399	NQ	NQ	NQ	ND	ND	ND
10-Carboxy-pyrmv-3acglc (ac-vitisin A)	15	23.0	603;399	ND	ND	ND	4.52 ± 0.01 a	4.64 ± 0.01 a	5.91 ± 1.45 a
10-Methyl pyrdp-3glc	20	26.8	503;341	NQ	NQ	NQ	ND	ND	ND
10-Carboxy-pymv-3cmglc (cm-vitisin A)	23	27.7	707;399	4.31 ± 0.00 a	4.31 ± 0.01 a	4.24 ± 0.15 a	4.08 ± 0.03 b	4.19 ± 0.06 ab	4.37 ± 0.03 a
10-Methyl-pyrmv-3glc	24	28.3	531;369	NQ	NQ	NQ	ND	ND	ND
10HP-pyrdp-3glc	25	28.9	581;419	2.04 ± 0.08 b	8.77 ± 0.08 a	2.21 ± 0.08 b	4.20 ± 0.08 b	7.13 ± 0.03 a	4.13 ± 0.09 b
10DHP-pyrdp-3cmglc	28	31.2	743;435	NQ	NQ	NQ	NQ	NQ	NQ
10DHP-pyrpt-3glc	29	31.7	611;449	2.55 ± 0.03 b	2.29 ± 0.09 b	3.32 ± 0.08 a	4.38 ± 0.11 ab	4.13 ± 0.00 b	4.55 ± 0.04 a
10HP-pyrcy-3glc	30	32.8	565;403	NQ	NQ	NQ	ND	ND	ND
10DHP-pyrpt-3acglc	31	34.1	653;449	NQ	NQ	NQ	NQ	NQ	NQ
10HP-pyrpt-3glc	32	34.6	595;433	4.55 ± 0.01 b	4.14 ± 0.02 c	4.37 ± 0.00 a	4.27 ± 0.09 a	4.11 ± 0.00 a	4.32 ± 0.02 a
10HP-pyrdp-3cmglc	33	34.8	727;419	NQ	NQ	NQ	NQ	NQ	NQ
10DHP-pyrmv-3glc	35	36.7	625;463	5.45 ± 0.00 ab	3.07 ± 0.94 b	7.46 ± 0.37 a	5.79 ± 0.05 b	5.14 ± 0.08 b	7.01 ± 0.25 a
10DHP-pyrpt-3cmglc	36	37.5	757;449	NQ	NQ	NQ	ND	ND	ND
10DPH-pyrpn-3glc	37	37.7	595;433	NQ	NQ	NQ	ND	ND	ND
10HP-pyrpt-3acglc	38	38.0	637;433	ND	ND	ND	NQ	NQ	NQ
10HP-pyrpn-3glc	39	38.2	579;417	4.06 ± 0.00 a	4.21 ± 0.02 a	4.17 ± 0.07 a	4.02 ± 0.04 b	4.13 ± 0.00 b	4.40 ± 0.09 a
10HP-pyrcy-3cmglc	40	38.6	711;403	NQ	NQ	NQ	NQ	NQ	NQ
10DHP-pyrmv-3acglc	41	39.5	667;463	NQ	NQ	NQ	NQ	NQ	NQ
10HP-pyrmv-3glc	42	39.6	609;447	4.47 ± 0.00 b	4.12 ± 0.04 c	4.66 ± 0.03 a	4.42 ± 0.03	NQ	4.30 ± 0.03
10HP-pyrpt-3cmglc	43	40.3	741;433	4.21 ± 0.00 b	4.01 ± 0.01 c	4.28 ± 0.00 a	4.30 ± 0.08	NQ	4.52 ± 0.04
10HP-pyrpn-3acglc	44	41.1	621;417	NQ	NQ	NQ	NQ	NQ	NQ
10DHP-pyrmv-3cmglc	45	41.5	771;463	8.93 ± 0.03 a	9.52 ± 0.69 a	9.76 ± 0.18 a	7.49 ± 0.18 a	8.60 ± 0.67 a	9.20 ± 0.69 a
10HP-pyrpn-3cmglc and 10HP-pyrmv-3acglc (coelution)	46	41.9	725/651;417/447	10.21 ± 0.07 b	13.26 ± 0.02 a	7.73 ± 0.33 c	14.53 ± 0.54 a	13.97 ± 1.11 a	11.05 ± 1.33 a
10HP-pyrmv-3cmglc	47	42.2	755;447	11.14 ± 0.03 b	13.13 ± 0.29 a	9.80 ± 0.17 c	11.85 ± 1.04 a	13.39 ± 0.31 a	12.34 ± 0.44 a

Abbreviations: Dp, delphinidin; Cy, cyanidin; Pt, petunidin; Pn, peonidin; Mv, malvidin; 3,5-diglc, 3,5-diglucosides; 3-acglc-5-glc, 3-(6″-acetyl)-glucoside-5-glucoside; 3-cmglc-5-glc, 3-(6″-p-coumaroyl)-glucoside-5-glucoside; 3-glc, 3-glucoside; 3-acglc, 3-(6″-acetyl)-glucoside; 3-cmglc, 3-(6″-p-coumaroyl)-glucoside; 10-HP, 10-(3″-hydroxyphenyl); 10-DHP, 10-(3″,4″-dihydroxyphenyl); pyrdp: pyranodelphinidin; pyrcy: pyranocyanidin; pyrpt: pyranopetunidin; pyrpn: pyranopeonidin; pyrmv: pyranomalvidin; BT, traditional Bordô wine; BPD, pre-drying Bordô wine; BSC, submerged cap Bordô wine; CART, traditional BRS Carmem wine; CARPD, pre-drying BRS Carmem wine; CARSC, submerged cap BRS Carmem wine; ND, not detectable; NQ, not quantifiable. Different letters in the same row indicate significant differences (ANOVA, Tukey's post-hoc test, $\alpha = 0.05$).

the latter at high concentrations. The MS/MS spectra showed the detection of malvidin-3-(6″-caffeoyl)-glucoside-5-glucoside (mv-3-cfglc-5-glc) (molecular ion m/z 817; ion products m/z 655, 493, 331) in the BRS Carmem wines and this anthocyanin was also found in other American grapes (Barcia et al., 2014).

The 3-(6″-acetyl)-glucoside-5-glucoside (3-acglc-5-glc) derivatives of petunidin and peonidin were also quantitated in both Bordô and BRS Carmem wines, which also presented certain concentration of the *trans* malvidin-3-(6″-acetyl)-glucoside-5-glucoside at 21.7 min, since the *cis*-malvidin form at 18.7 min was only detected and quantitated in the BRS Carmem samples. In addition to the detection of up to 47 anthocyanin and pyranoanthocyanin compounds, a detection of a new anthocyanin compound was observed at 41.3 min with molecular ion m/z 947; product ions at m/z 639 and 331, suggesting that this compound could be the malvidin 3-(6″-coumaroyl)-glucoside-5-(6″-coumaroyl)-glucoside. However, other detailed analyses should be carried out in order to confirm the detection of this compound, since this area of the chromatogram presents coelution of many compounds due to the change of the gradient solvents. The suggested compound presented a MS/MS signal in its MS^2 spectra, corresponding to the loss

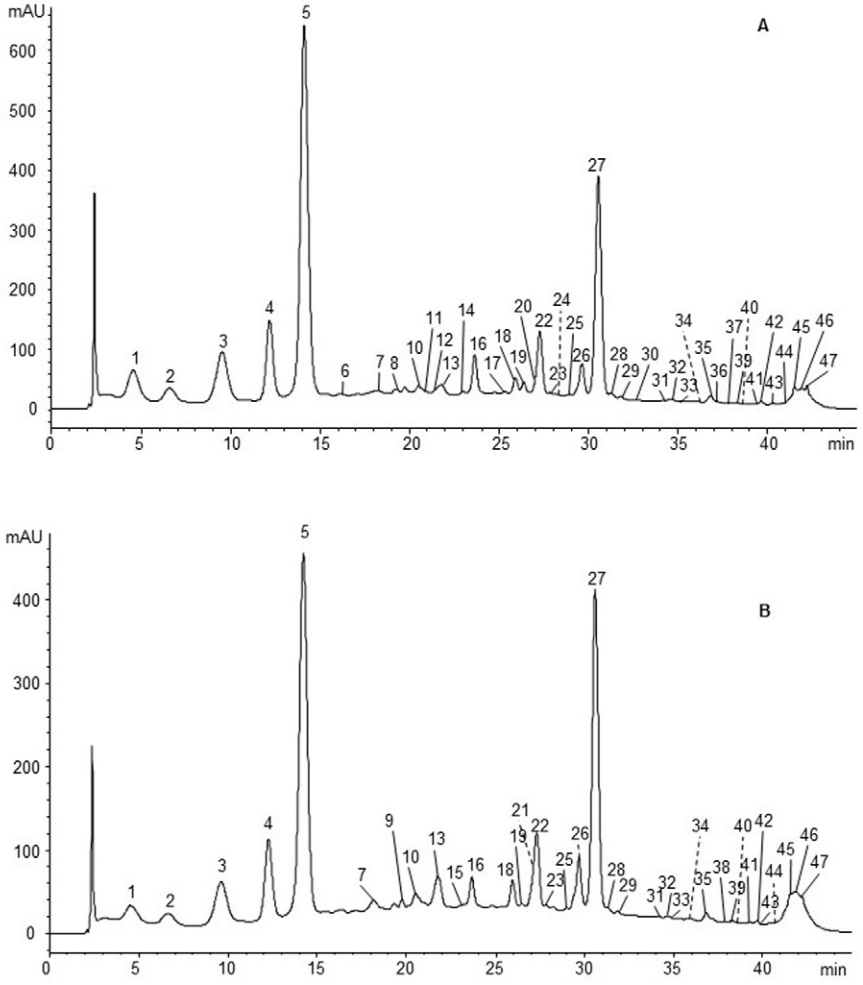

Fig. 1. HPLC DAD-chromatogram (detection at 520 nm) of Bordô (A) and BRS Carmem (B) young red wines anthocyanins. For peak assignation see Table 2. Peak nos. 9, 15, 21, and 38 were not detectable for Bordô samples. Peak nos. 6, 8, 11, 12, 14, 17, 20, 24, 30, 36 and 37 were not detectable for BRS Carmem samples.

of two 6″-coumaroyl-glucose moieties — $[M\text{-cmglc-cmglc}]^+$, suggesting that this loss occurred at C-3 and C-5 positions of the anthocyanidin (Fig. S1 — Supplementary material).

Despite the quite similar anthocyanin profiles of the two red wines, the total number of anthocyanins and pyranoanthocyanins varied according to the winemaking procedures, most of them presenting lower concentrations for pre-drying treatment. In both red wines assessed, the pre-drying winemaking procedure decreased the pigment contents, very likely due to the thermal degradation of these compounds caused by oxidation, the cleavage of the covalent bonds or the hydrolysis of the anthocyanin 3-glucosides. In almost all anthocyanin and pyranoanthocyanin compounds quantitated, when statically differences were observed ($P < 0.05$, Table 2), the submerged cap wines presented large amounts of these aforementioned compounds when compared to the traditional wines for both Bordô and BRS Carmem wines. This result suggests a disagreement with Bosso et al. (2011), who reported the decrease of the extraction of the phenolic compounds during fermentative maceration using submerged cap in comparison to the traditional floating-cap maceration, arguing a limited effect of the pumped must on the solid parts of the berries during the alcoholic fermentation. However, the same authors stated that, after pressing the pomace, the wines submitted to the submerged cap winemaking resulted in higher amounts of anthocyanin compounds, suggesting that the anthocyanin compounds remained attached to the pomace, allowing for the release after pressing.

3.3. Profile of the flavonols and hydroxycinnamic acid derivatives (HCAD)

The 3-glucosides (3-glc) of the five aglycones (Q, quercetin; M, myricetin; L, laricitrin; S, syringetin and I, isorhamnetin) were detected and quantitated in both the Bordô and BRS Carmem wines (Table 3, Fig. 2). In addition, the 3-glucuronides (3-glcU) of M and Q; the 3-galactoside (3-gal) of M; and the free forms of M and Q were detected in the Bordô and BRS Carmem wines. The 3-glucoside of M and the free M presented the highest concentrations in both red wines. The latter results were in accordance with those reported for the other red wines produced from the hybrid cultivar BRS Violeta (Lago-Vanzela et al., 2013) and Bordô grapes (Lago-Vanzela et al., 2011), defined by high concentrations of myricetin based flavonols. In both the Bordô and BRS Carmem red wines, the M-3glc was the most important type of flavonol, followed by free M, L-3glc and S-3-glc, which were not found in relevant amounts in the latter aforementioned studies. No significant differences for flavonol concentrations were observed when the winemaking procedures were compared to Bordô wines, however, for Carmem wines, the differences were significant ($P < 0.05$) for free M and free Q, and the submerged cap winemaking showed higher values for both compounds.

With regard to the hydroxycinnamic acid derivatives (HCAD), high amounts of caffeic and *p*-coumaric acids were observed for both red wines (Table 3, Fig. 3), when compared to most widespread *V. vinifera* wines, and could be a very likely explanation for the high amount and

Table 3
Flavonol and HCAD profile determined by HPLC/MS/MS (mean value ± standard deviation) for Bordô and BRS Carmem young red wines.

Flavonols and HCAD	Peak	R_t (min)	Molecular ion;product ions (m/z)	BT	BPD	BSC	CART	CARPD	CARSC
Flavonols ($mg \cdot L^{-1}$)				53.50 ± 42.40 a	71.80 ± 74.40 a	144.52 ± 1.75 a	68.56 ± 13.41 a	50.10 ± 28.20 a	83.94 ± 2.10 a
M-3-glcU	50	20.0	493;317	2.47 ± 1.43 a	4.67 ± 3.48 a	3.75 ± 0.49 a	1.89 ± 0.12 a	1.55 ± 0.75 a	2.09 ± 0.16 a
M-3-gal	51	20.4	479;317	0.50 ± 0.04 a	0.54 ± 0.38 a	0.55 ± 0.00 a	0.53 ± 0.16 a	0.34 ± 0.08 a	0.33 ± 0.03 a
M-3-glc	52	21.5	479;317	20.30 ± 20.80 a	12.10 ± 16.20 a	62.76 ± 1.37 a	34.84 ± 2.80 a	16.16 ± 11.72 a	29.70 ± 0.05 a
Q-3-glcU	53	28.6	477;301	3.18 ± 2.64 a	9.47 ± 9.79 a	4.90 ± 0.94 a	3.99 ± 2.11 a	12.22 ± 7.88 a	4.57 ± 3.25 a
Q-3-glc	54	29.9	463;301	1.45 ± 0.87 a	0.73 ± 0.11 a	1.98 ± 1.97 a	1.50 ± 0.60 a	5.72 ± 3.65 a	1.79 ± 0.05 a
L-3-glc	55	33.0	493;331	4.80 ± 2.17 a	5.01 ± 4.31 a	8.37 ± 0.55 a	5.41 ± 0.24 a	4.24 ± 1.95 a	5.29 ± 0.15 a
Free M	56	33.2	317	13.40 ± 16.40 a	25.20 ± 28.00 a	39.67 ± 2.50 a	10.88 ± 1.85 b	1.99 ± 2.33 c	21.19 ± 0.48 a
I-3-glc	57	40.1	477;315	1.34 ± 0.15 a	2.62 ± 2.81 a	3.91 ± 0.70 a	2.76 ± 0.33 a	2.42 ± 1.72 a	3.27 ± 0.09 a
S-3-glc	58	41.6	507;345	4.52 ± 1.98 a	4.13 ± 1.63 a	0.85 ± 0.08 a	3.53 ± 3.79 a	2.33 ± 1.81 a	5.37 ± 1.47 a
Free Q	59	45.0	301	1.52 ± 0.10 a	7.33 ± 7.99 a	17.75 ± 0.75 a	3.21 ± 2.64 b	3.12 ± 0.07 b	10.34 ± 0.05 a
Hydroxycinnamic acid derivatives (HCAD) ($mg \cdot L^{-1}$)				232.31 ± 34.46 a	252.55 ± 36.29 a	256.23 ± 42.00 a	197.80 ± 11.46 ab	136.40 ± 22.00 b	227.57 ± 13.70 a
Caftaric acid	60	4.1	311;179,149,135	8.99 ± 10.78 a	0.35 ± 0.09 a	7.83 ± 3.18 a	4.86 ± 1.62 a	3.13 ± 3.13 a	7.17 ± 0.35 a
Trans-coutaric acid	61	6.1	295;163,149,119	1.18 ± 0.00 a	2.70 ± 3.10 a	0.65 ± 0.67 a	0.79 ± 0.19 ab	4.17 ± 1.42 a	0.13 ± 0.01 b
Cis-coutaric acid	62	6.5	295;163,149,119	0.83 ± 0.00 a	1.21 ± 0.91 a	2.03 ± 0.40 a	NQ	NQ	NQ
Caffeic acid	63	7.8	179;135	84.80 ± 16.60 a	93.81 ± 3.02 a	117.83 ± 1.01 a	60.12 ± 2.83 a	42.90 ± 22.30 a	77.87 ± 2.92 a
p-Coumaroyl-glucose-1	64	9.0	325;163,145	25.19 ± 5.98 a	27.52 ± 11.83 a	17.41 ± 2.46 a	25.63 ± 1.43 ab	29.61 ± 1.04 a	17.42 ± 3.53 b
p-Coumaroyl-glucose-2	65	11.6	325;163,145	11.23 ± 0.70 a	26.39 ± 12.39 a	9.04 ± 0.28 a	10.86 ± 0.42 b	16.27 ± 0.70 a	9.33 ± 1.26 b
p-Coumaric acid	66	14.4	163;119	85.42 ± 9.45 a	84.48 ± 1.13 a	82.99 ± 2.42 a	85.59 ± 8.54 a	36.61 ± 4.09 b	102.68 ± 8.07 a
Ethyl caffeate	67	46.1	207;179,135	3.53 ± 1.32 ab	1.02 ± 1.10 b	6.39 ± 0.34 a	3.78 ± 1.29 a	1.72 ± 2.16 a	6.05 ± 1.17 a
Ethyl *p*-coumarate	68	55.8	191;163,119	12.10 ± 5.10 a	15.07 ± 0.17 a	12.06 ± 0.00 a	6.15 ± 0.94 a	2.00 ± 0.22 b	6.91 ± 0.57 a

Abbreviations: M, myricetin; Q, quercetin; L, laricitrin; K, kaempferol; S, syringetin; I, isorhamnetin; glcU, glucuronide; gal, galactoside; glc, glucoside; BT, traditional Bordô wine; BPD, pre-drying Bordô wine; BSC, submerged cap Bordô wine; CART, traditional BRS Carmem wine; CARPD, pre-drying BRS Carmem wine; CARSC, submerged cap BRS Carmem wine; NQ, not quantifiable. Different letters in the same row indicate significant differences (ANOVA, Tukey's post-hoc test, $\alpha = 0.05$).

diversity of hydroxyphenyl-pyranoanthocyanins found in these wines as it has been reported in the latter section (Rentzsch, Schwarz, Winterhalter, & Hermosín-Gutiérrez, 2007). An important piece of information was extracted from these data: the both Bordô and BRS Carmem pre-dried wines presented lower concentrations of ethyl esters and BRS Carmem wine showed lower concentration of *p*-coumaric acid; however, almost all the HCAD concentrations in pre-dried wines were higher than the traditional and the submerged cap winemaking treatments. This result was comparable to the reported findings about winemaking by-products of the BRS Violeta and BRS Lorena grapes obtained by drying at 50 °C, in which the drying process apparently did not affect the concentrations of HCAD and its derivatives (Barcia et al., 2014).

No significant differences were observed in the comparison of the different winemaking procedures for Bordô flavonols and HCAD, except for ethyl caffeate, suggesting that the pre-drying and the submerged cap winemaking procedures did not significantly affected the concentration of these compounds; but for BRS Carmem, pre-dried wines showed low concentrations of *p*-coumaric acid and ethyl *p*-coumarate, indicating that this treatment possibly gave rise to the chemical oxidations and thermal degradation of these aforementioned compounds (Patras, Brunton, O'Donnell, & Tiwari, 2010). The submerged cap treatment presented the same behavior as seen for the traditional treatment.

3.4. Profile of the flavan-3-ols and stilbenes

Catechin (C), epicatechin (EC), epicatechin gallate (ECG), proanthocyanidin B1 (PB1), proanthocyanidin B2 (PB2) and proanthocyanidin B4 (PB4) were detected in both red wines, with the exception of ECG that was not detected in the Bordô wines (Table 4). Despite the absence of significant differences, the pre-dried and submerged cap red wines presented the highest concentrations for all flavan-3-ols and B-type proanthocyanidins when compared to traditional red wines, and these differences were well noticed in the Bordô wines. For the Carmem wines, this tendency was also observed, however in a more discreet way.

Figueiredo-González et al. (2013) reported that the grapes lost their physiological integrity during dehydration, thus favoring the diffusion of phenolic compounds, including flavan-3-ols, from the grape skin to the pulp, which could be transferred to the wine during alcoholic fermentation. However, the same authors stated that this could also promote the reaction between the anthocyanidin 3-glucosides and flavan-3-ols, giving rise to polymeric pigments with a parallel decrease in the total flavan-3-ol contents. This fact could explain the results found for the Carmem red wines, since the difference between the concentration of the flavan-3-ols of the pre-dried wines compared to the traditional and submerged cap red wines was lower than the differences obtained for the Bordô wines when the winemaking procedures were compared, suggesting that the Carmem wines presented, at the initial stage of the winemaking, higher concentration of anthocyanidin-3-glucosides.

With respect to the stilbenes, *cis*-resveratrol, *trans*-piceid and *cis*-piceid were detected in both red wines. Despite the absence of significant differences among the concentration of the stilbenes when the winemaking procedures were compared, the results showed that the use of heat promoted the degradation of these compounds and this result was comparable to those previously reported about winemaking by-products of the BRS Violeta and BRS Lorena grapes obtained by drying at 50 °C (Barcia et al., 2014). An opposite result was observed for *cis*-piceid, i.e., the pre-dried wines presented higher concentrations for this compound.

The stilbenes and other phenolic compounds have been the focus of many studies concerning their correlation with antioxidant activity (AA) and health benefits that prevent chronical diseases (Baht, Kosmeder, & Pezzuto, 2001; López-Vélez et al., 2003). However, the wines with higher concentration of phenolic compounds does not always show higher antioxidant activity, i.e., it has been suggested that wine antioxidant properties are intensely related to the types of phenolic compounds occurring in the wines than to their global amounts (Rivero-Pérez, Muñiz, & González-San José, 2007). Furthermore, the formation of the Maillard reaction products such as melanoidins has been described as compounds with antioxidant activity (Borrelli, Visconti, Mennella, Anese, & Fogliano, 2002; Delgado-Andrade & Morales, 2005; Tagliazucchi, Verzelloni, & Conte, 2008). Thus, the different types of phenolic profiles in both the Bordô and BRS Carmem red wines according to the winemaking procedure, along with the likely formation of melanoidins, in the case of pre-drying process, should lead to differences in the antioxidant capacity exhibited by the wines. However,

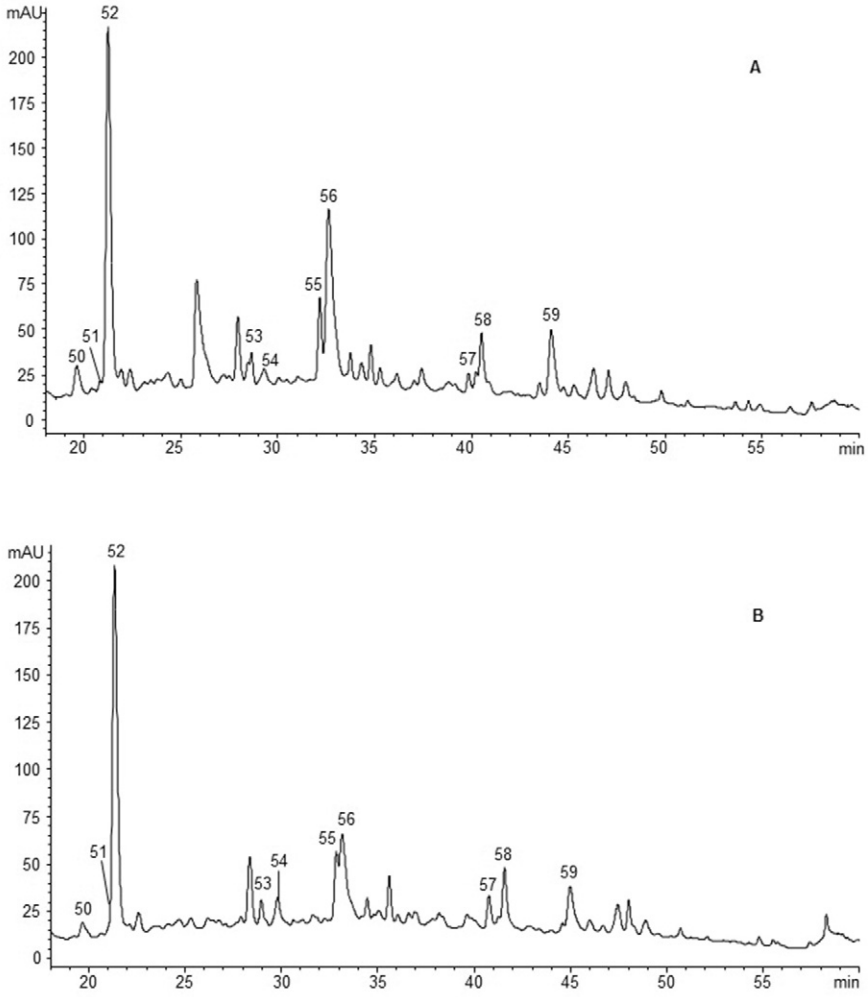

Fig. 2. HPLC DAD-chromatogram (detection at 360 nm) of Bordô (A) and BRS Carmem (B) young red wines flavonols. For peak assignation see Table 3.

the results found for antioxidant capacity did not show significant differences among the winemaking procedures (Table 4).

These apparently contradictory results are very likely caused by the balance in the chemical reactions that produce more antioxidant compounds and, at the same time, with losses in the antioxidant grape polyphenols, i.e., while drying could cause the degradation of the phenolic compounds promoting an antioxidant activity in wines (Makris, Kallithraka, & Kefalas, 2006), drying could also be responsible for the formation of new compounds that present AA, such as the melanoidins resulting from the Maillard reaction (Delgado-Andrade & Morales, 2005).

3.5. Sensory assessment

The comparison of the winemaking treatments provided relevant differences with respect to color intensity for both the Bordô and BRS Carmem red wines, and the differences for violet hue and acidity were significant for the BRS Carmem red wines (Table 5). Pre-dried wines showed greater color intensity than the submerged cap wines only in the case of Bordô cultivar (BPD vs. BSC) and did not significantly differ in comparison to traditional treatment in both cases (BPD vs. BT and CARPD vs. CART). Pre-dried wines also showed greater acidity than the traditional treatment, only for the Carmem samples. The other sensory descriptors presented similar scores for the two wines.

Unfortunately, the univariate approach using ANOVA and post-hoc Tukey's test provided no relevant information about the descriptive sensory profiles of the Bordô and BRS Carmem, which were submitted to traditional, pre-drying and submerged cap winemaking procedures. Based on this, the principal component analysis — PCA (chemometric approach) was carried out in order to obtain relevant relationships between the sensory attributes and the chemical compounds. The lack of univariate differences does not exclude the application of the PCA analysis, on the contrary, it allows the assessment of exploratory evidences for all the set of variables, since the multivariate statistical technique evaluates the response of each variable in accordance with the effects of the other several variables included on the analysis, a fact that does not occur in the univariate statistical analysis, which assesses the effect of only one variable in another one (Hair, Black, Babin, Anderson, & Tatham, 2009).

3.6. Chemometric approach

The objective of the chemometric approach was to evaluate the relationship between the chemical (phenolic and antioxidant capacity) and descriptive sensory profiles, using multivariate statistical tools. According to the PCA results (Fig. 4A), 65.85% of the total variance was explained by the first two components, PC1 explained 43.80% and PC2 explained 22.05%. PC1 allowed the differentiation of the winemaking treatments, regardless the grape cultivar, i.e., the submerged cap samples were discriminated from the pre-dried samples. PC2 allowed distinguishing the grape cultivars.

Two groups of variables mainly explained the first PC. The first group was composed of the anthocyanins 3,5-diglc, 3-acglc-5glc and 3-cmglc-5-glc, the myricetin and laricitrin flavonols, caftaric, caffeic, *p*-coumaric

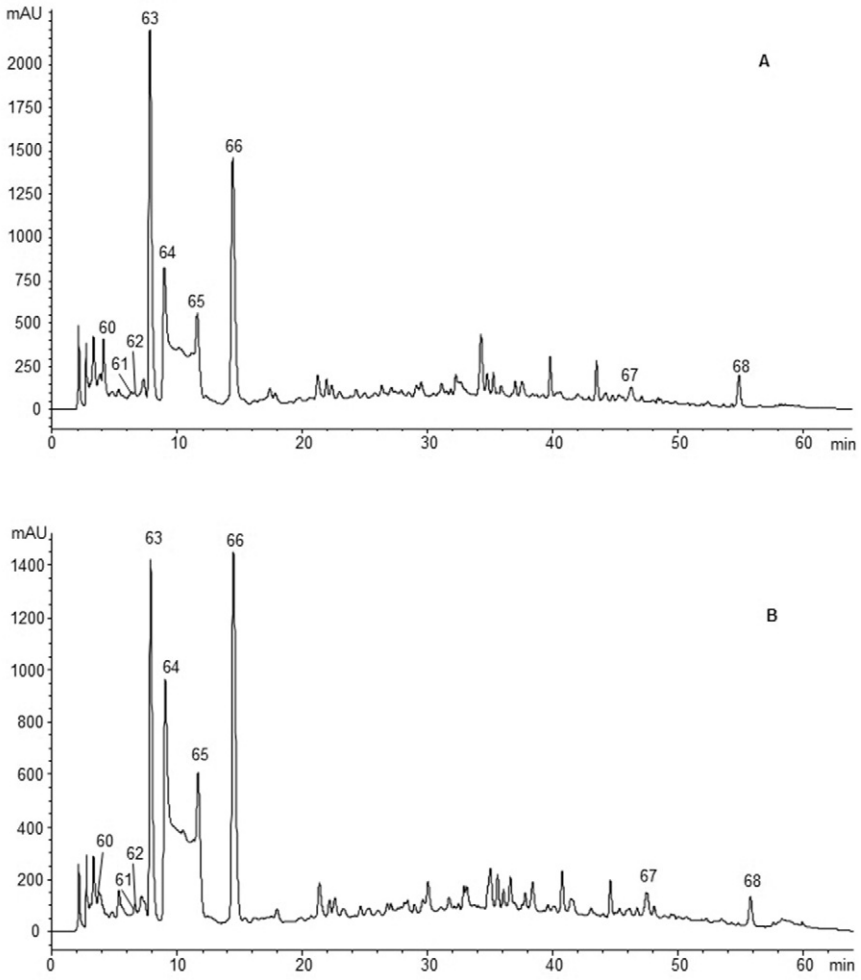

Fig. 3. HPLC DAD-chromatogram (detection at 320 nm) of Bordô (A) and BRS Carmem (B) young red wines hydroxycinnamic acid derivatives (HCAD). For peak assignation see Table 3.

HCAD, ethyl esters, the proanthocyanidins PB1, PB2 and PB4, cis-resveratrol and two sensory descriptors, violet hue and sweetness. The wines covered by these features were the submerged cap wines (BSC and CARSC) (Fig. 4B). On one hand, the formation of inter and intra co-pigmentation complexes by the anthocyanidins could explain the enhancement of the violet hue, which presented relevant correlation with the anthocyanin derivatives, except the anthocyanin monoglucosides, which presented low percentages of concentration; on the other hand, the pyranoanthocyanins are compounds resulting from the condensation of anthocyanins with pyruvic acid,

Table 4
Flavan-3-ol/stilbenes profiles determined by HPLC-ESI-MS/MS (MRM) and antioxidant capacity determined by DPPH radical scavenging (mean value ± standard deviation) for Bordô and BRS Carmem young red wines.

Flavan-3-ols and stilbenes	BT	BPD	BSC	CART	CARPD	CARSC
Flavan-3-ol monomers and dimers ($mg \cdot L^{-1}$)	17.02 ± 21.70 a	76.37 ± 95.00 a	135.85 ± 55.40 a	65.76 ± 4.52 a	46.15 ± 50.40 a	101.58 ± 44.30 a
C	6.01 ± 7.50 a	22.30 ± 25.20 a	31.33 ± 13.02 a	28.95 ± 2.86 a	24.40 ± 24.60 a	40.60 ± 14.50 a
EC	2.31 ± 2.62 a	9.48 ± 9.95 a	16.11 ± 7.35 a	5.70 ± 0.15 a	5.18 ± 5.51 a	9.72 ± 3.91 a
ECG	ND	ND	ND	0.13 ± 0.18 a	0.60 ± 0.65 a	0.09 ± 0.13 a
PB1	4.14 ± 5.53 a	20.90 ± 28.10 a	42.80 ± 16.80 a	19.22 ± 1.98 a	9.30 ± 11.09 a	32.50 ± 16.70 a
PB2	4.08 ± 5.41 a	22.20 ± 29.70 a	42.90 ± 16.60 a	10.15 ± 0.36 a	5.68 ± 7.06 a	16.02 ± 8.27 a
PB4	0.48 ± 0.64 a	1.48 ± 2.04 a	2.71 ± 1.58 a	1.59 ± 0.00 a	1.03 ± 1.46 a	2.63 ± 1.07 a
Proanthocyanidin total content ($mg \cdot L^{-1}$)	54.92 ± 51.50 a	158.34 ± 120.90 a	159.38 ± 22.90 a	23.03 ± 5.23 a	31.17 ± 16.70 a	21.73 ± 4.29 a
Proanthocyanidin structural characterization						
mDP	1.33 ± 0.08 a	1.40 ± 0.23 a	1.66 ± 0.03 a	2.67 ± 0.59 b	1.66 ± 0.54 b	6.43 ± 0.94 a
% galloylation	1.31 ± 0.20 a	1.96 ± 0.53 a	1.35 ± 0.24 a	10.07 ± 4.73 a	18.13 ± 5.59 a	18.63 ± 4.55 a
% prodelphinidin	1.45 ± 0.85 a	2.15 ± 1.08 a	3.94 ± 0.13 a	4.76 ± 2.12 a	1.43 ± 1.32 a	0.60 ± 0.00 a
Stilbenes ($mg \cdot L^{-1}$)	0.61 ± 0.61 a	0.87 ± 0.70 a	1.07 ± 0.17 a	0.33 ± 0.01 a	0.57 ± 0.30 a	0.48 ± 0.32 a
Cis-resveratrol	0.28 ± 0.31 a	0.24 ± 0.25 a	0.52 ± 0.02 a	0.20 ± 0.06 a	0.03 ± 0.05 a	0.42 ± 0.34 a
Cis-piceid	0.26 ± 0.23 a	0.60 ± 0.42 a	0.52 ± 0.12 a	0.09 ± 0.07 a	0.35 ± 0.16 a	0.03 ± 0.01 a
Trans-piceid	0.06 ± 0.05 a	0.02 ± 0.03 a	0.01 ± 0.02 a	0.03 ± 0.00 a	0.18 ± 0.08 a	0.01 ± 0.01 a
Antioxidant capacity ($mmol \cdot L^{-1}$ of Trolox equivalents)	7.74 ± 0.55 a	10.99 ± 1.99 a	7.94 ± 0.07 a	7.06 ± 0.24 a	6.68 ± 1.27 a	5.27 ± 0.76 a

Abbreviations: C, catechin; EC, epicatechin; ECG, epicatechin gallate; PB1, proanthocyanidin B1; PB2, proanthocyanidin B2; PB4, proanthocyanidin B4; mDP, mean degree of polymerization; BT, traditional Bordô wine; BPD, pre-drying Bordô wine; BSC, submerged cap Bordô wine; CART, traditional BRS Carmem wine; CARPD, pre-drying BRS Carmem wine; CARSC, submerged cap BRS Carmem wine; ND, not detectable. Different letters in the same row indicate significant differences (ANOVA, Tukey's post-hoc test, $\alpha = 0.05$).

Table 5
Descriptive sensory profile (mean ± standard deviation) for Bordô and Carmem red wines.

Sensory attributes	Wines					
	BT	BPD	BSC	CART	CARPD	CARSC
Appearance						
Color intensity	7.35 ± 0.90 ab	7.93 ± 0.86 a	6.86 ± 1.11 b	7.70 ± 0.80 a	7.46 ± 0.97 ab	6.98 ± 0.79 b
Violet hue	7.11 ± 0.77 a	7.38 ± 0.88 a	7.03 ± 1.04 a	7.16 ± 1.01 a	6.25 ± 1.18 b	7.08 ± 0.64 a
Taste						
Sweetness	3.23 ± 1.44 a	2.86 ± 1.48 a	3.28 ± 1.44 a	3.21 ± 1.20 a	2.80 ± 1.26 a	2.98 ± 1.08 a
Acidity	4.16 ± 1.30 a	4.50 ± 1.53 a	4.28 ± 1.25 a	4.45 ± 1.35 b	5.38 ± 1.68 a	4.63 ± 1.36 ab
Bitterness	1.00 ± 1.00 a	1.45 ± 1.30 a	1.25 ± 1.44 a	1.55 ± 1.48 a	2.08 ± 2.03 a	1.41 ± 1.19 a
Flavor intensity/body	5.39 ± 1.14 a	5.26 ± 1.17 a	5.46 ± 0.96 a	5.31 ± 0.97 a	5.30 ± 1.37a	5.06 ± 1.10 a
Structure/tannins	4.73 ± 1.78 a	5.00 ± 1.50 a	4.75 ± 1.32 a	4.98 ± 1.33 a	4.93 ± 1.58 a	4.60 ± 1.41 a
Herbaceous taste	1.71 ± 1.03 a	2.05 ± 1.15 a	1.86 ± 1.10 a	2.03 ± 1.19 a	2.55 ± 1.67 a	2.11 ± 1.43 a
Astringency	1.38 ± 1.02 a	1.70 ± 1.18 a	1.61 ± 1.43 a	2.13 ± 1.40 a	2.30 ± 1.63 a	1.73 ± 1.25 a
Pungency	5.40 ± 1.29 a	5.18 ± 1.08 a	5.23 ± 0.98 a	5.45 ± 1.08 a	5.23 ± 1.29 a	5.30 ± 1.14 a
Persistence	5.86 ± 1.40 a	5.53 ± 1.06 a	5.71 ± 1.01 a	5.61 ± 1.00 a	5.43 ± 1.29 a	5.41 ± 1.41 a

Abbreviations: BT, traditional Bordô wine; BPD, pre-drying Bordô wine; BSC, submerged cap Bordô wine; CART, traditional Carmem wine; CARPD, pre-drying Carmem wine; CARSC, submerged cap Carmem wine. Different letters in the same row indicate significant differences (ANOVA, Tukey's post-hoc test, $\alpha = 0.05$).

acetaldehyde, acetoacetic acid, hydroxycinnamic acids or vinylflavanols, giving rise to an orange hue for the red wines (Sánchez-Ilárduya et al., 2014).

The second group was composed of some HCAD (coutaric and *p*-coumaroyl-glucose), the flavan-3-ol epicatechin gallate (ECG), the *cis* and *trans* resveratrol 3-glucosides (piceids), and two sensory descriptors, structure and color intensity. The wines that presented a distinct connection with these parameters were the pre-dried samples (BPD and CARPD). The panelists defined the wine structure as a perception promoted by the tannins and acids, which provide a harsh palate sensation for the wine. In addition, the results showed that the color intensity was related to the wine structure and this corroborates the findings of Tecchio, Miele, and Rizzon (2007) who reported the correlation between the structure and color intensity of the Bordô wine. These sensory attributes were closely linked to the flavan-3-ols content and to the hydroxycinnamic acids and their derivatives (Jackson, 2008; Ma et al., 2014; Vidal et al., 2003), and the PCA projection corroborated these results.

Furthermore, the panelists defined the color intensity as the obstruction that wine color provides for the light reflection enabling the visualization of the cup bottom. This definition is closely linked to the presence of substances that promotes wine browning, mainly caused by the products of non-enzymatic Maillard reaction. Based on this, it was possible to suggest that the pre-dried wines, produced by grapes that were dried at 60 °C, presented brown compounds resulted from the Maillard reaction, which have occurred to a greater extent than enzymatic reactions caused by the action of PPO, since this enzyme is denatured at 50 °C maximum (Patras et al., 2010). Based on this result, it was possible to suggest the enhancement of the structure of these wines promoted by the pre-drying treatment of the grapes before the winemaking procedure, and it has been considered as a potential winemaking procedure that produces wines with great structure by the enhancement of these aforementioned chemical compounds.

Two groups explained the total variance of the PC2: the first was composed of the catechin, epicatechin and galloylated flavan-3-ols, and three sensory descriptors, acidity, bitterness and herbaceous taste. CARPD and CARSC were the wines connected with these chemical compounds. This result corroborates the findings of Chira, Pacella, Jourdes, and Teissedre (2011) who reported that the bitterness was closely related to monomeric flavan-3-ols. The results showed that the bitterness could also be explained by the high concentration of catechin, epicatechin and galloylated flavan-3-ols, and could also be features of pre-dried wines. It was possible to suggest that the Carmem wines presented high acidity, bitterness and herbaceous taste, and these sensory features were related to intrinsic features of the grape cultivar. However, the application of these winemaking treatments enhanced these sensory features being transferred to the respective wines. The herbaceous taste, which is an undesirable sensory feature for wines produced from American grapes and their hybrids, could be explained by the thermal degradation of the phenolic compounds, using thermal process above 50 °C. According to Patras et al. (2010), this degradation process is a complex and perplexing mechanism, that induces the formation of some (un) expected and (un) desired chemical reactions which (in) directly influence the wine quality.

The second group of the PC2 was composed only of the sensory descriptor persistence, the BT wine being the representative sample. None of the chemical properties studied were related to this attribute. The anthocyanin monoglucosides, pyranoanthocyanins, flavonols quercetin, syringetin, laricitrin, mean degree of polymerization (mDP) and antioxidant capacity (AA) presented weak representation for the both PCs, and three sensory descriptors were not linked to any chemical property, color intensity, body and pungency. Unfortunately, the AA was weakly explained by the first two PCs, however, the AA was located in the same quadrant of the trans-piceid (Fig. 4A), suggesting its influence on AA and also showing that the BT and BPD red wines could probably show a relevant antioxidant capacity (Fig. 4B). The Carmem traditional wine (CART) presented no relationship with chemical compounds or sensory attributes, since it was located close to the origin of the two-dimensional plot and provided no relevant representation for the PCA analysis.

In general, according to the chemometric approach, pre-drying winemaking provided wines with good structure due to the higher flavan-3-ols content. On the other hand, the pre-drying procedure negatively influenced the quality of these samples by the intense herbaceous taste, which could probably be explained by the thermal degradation of the anthocyanins. The submerged cap wines were characterized by the enhancement of the anthocyanin compounds, which were responsible for the intense violet hue. These samples presented high concentration and a great variety of the main analyzed phenolic compounds such as anthocyanins, flavonols, HCAD, high weight flavan-3-ols and stilbenes, suggesting that the submerged cap winemaking had potential in order to enhance the concentration of these compounds and make them more attractive to the consumers.

4. Conclusion

The chemical and sensory profiles provided essential information about the Bordô and BRS Carmem red wines. The HCAD, flavonols and stilbenes appeared to be less influenced by the alternative winemaking treatments. The use of drying procedure may have influenced the formation of products from the Maillard reactions, giving rise to the enhancement of the antioxidant capacity and color intensity of the

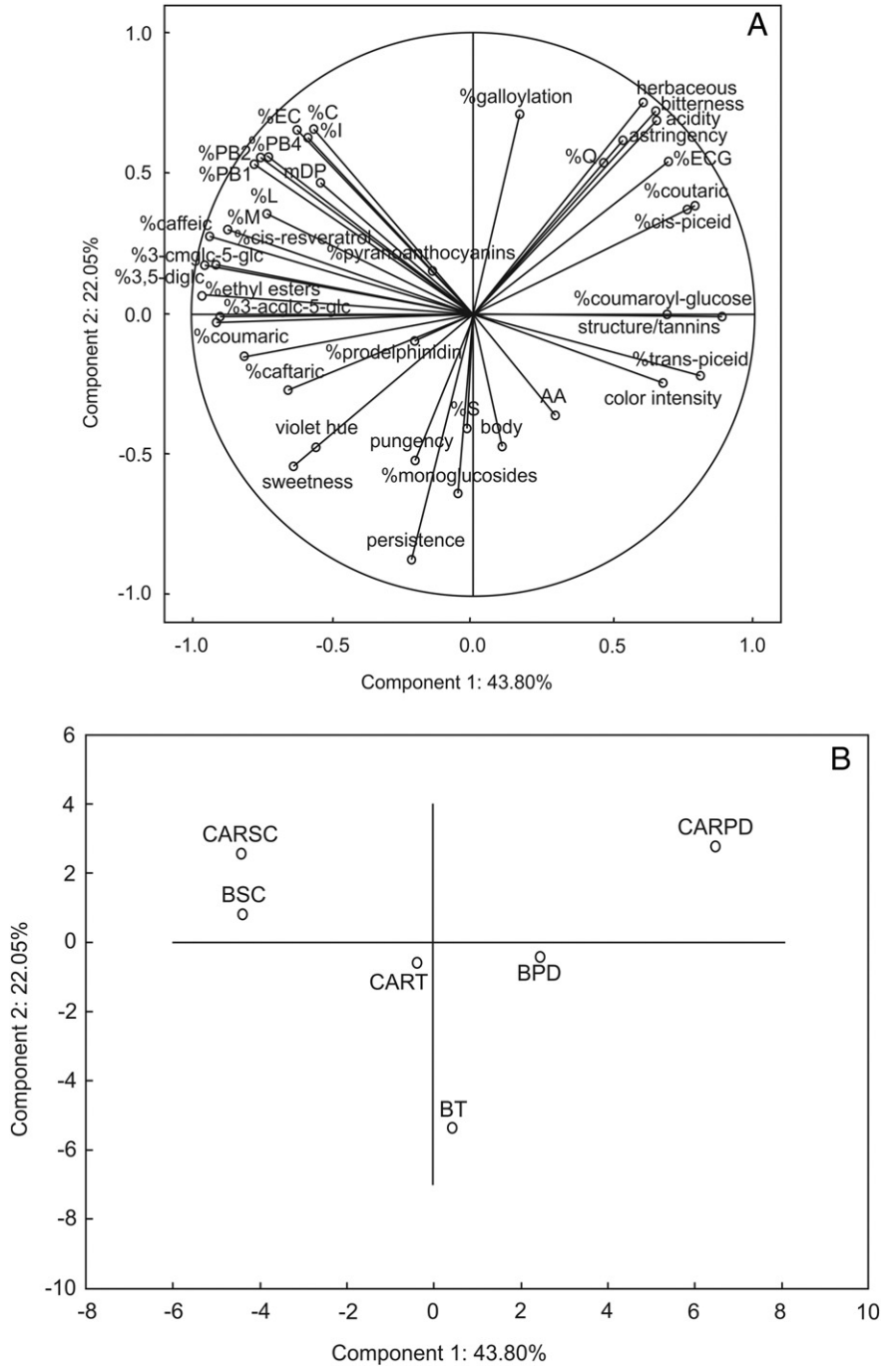

Fig. 4. Projection of the phenolic profile and sensory descriptors (A) and wine samples (B) using PCA. Abbreviations: 3,5-diglc, 3,5-diglucosides; 3-acglc, 3-(6″-acetyl)-glucoside; 3-cmglc, 3-(6″-*p*-coumaroyl)-glucoside; 3-cmglc-5-glc, 3-(6″-*p*-coumaroyl)-glucoside-5-glucoside; M, myricetin; Q, quercetin; L, laricitrin; K, kaempferol; S, syringetin; I, isorhamnetin; C, catechin; EC, epicatechin; ECG, epicatechin gallate; PB1, proanthocyanidin B1; PB2, proanthocyanidin B2; PB4, proanthocyanidin B4; mDP, mean degree of polymerization; BT, traditional Bordô wine; BPD, pre-drying Bordô wine; BSC, submerged cap Bordô wine; CART, traditional Carmem wine; CARPD, pre-drying Carmem wine; CARSC, submerged cap Carmem wine.

pre-dried red wines. The sensory profiles showed that the winemaking procedures were responsible for significant differences between the appearance features (color intensity and violet hue), and the chemometric approach established that the pre-drying winemaking treatment provided wines with great structure due to the flavan-3-ols content. Acidity, bitterness and herbaceous taste were sensory attributes that described the Carmem wines and the pre-drying and submerged cap winemaking procedures possibly influenced the enhancement of these sensory attributes by the use of heat and the constant contact between the pomace and must, respectively. The submerged cap wines presented intense violet hue due to the diglucoside, acetylated and coumaroylated anthocyanin structures. These findings indicate the potential of the drying process in order to obtain more structured red wines from *V. labrusca* L. and their hybrids with high color intensity and the submerged cap technique as an alternative to obtain red wines with an intense violet hue. Both the BRS Carmem and Bordô grape varieties could be treated with pre-drying and submerged cap techniques for improving the quality of the resulting wine, however, the choice of the winemaking procedure must be evaluated by the winery, i.e., pre-drying as a technique that resulted in structured and colorful red wines, and submerged cap as an alternative to elaborate wines with intense violet hue of their red color.

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References

Association of Official Analytical Chemists (2005). *Official methods of analysis of the AOAC International* (18th ed.). Washington: Gaithersburg (Chapter 28).

Baht, K. P. L., Kosmeder, J. W., II, & Pezzuto, J. M. (2001). Biological effects of resveratrol. *Antioxidants and Redox Signaling*, *3*(6), 1041–1064.

Barcia, M. T., Pertuzatti, P. B., Gómez-Alonso, S., Godoy, H. T., & Hermosín-Gutiérrez, I. (2014). Phenolic composition of grape winemaking by-products of Brazilian hybrid cultivars BRS Violeta and BRS Lorena. *Food Chemistry*, *159*, 95–105.

Biasoto, A. C. T., Netto, F. M., Marques, E. J. N., & Da Silva, M. A. A. P. (2014). Acceptability and preference drivers of red wines produced from *Vitis labrusca* and hybrid grapes. *Food Research International*, *62*, 456–466.

Blanco-Vega, D., López-Bellido, F. J., Alía-Robledo, J. M., & Hermosín-Gutiérrez, I. (2011). HPLC-DAD-ESI-MS/MS characterization of pyranoanthocyanins pigments formed in model wine. *Journal of Agricultural and Food Chemistry*, *59*, 9523–9531.

Bordiga, M., Coïsson, J. D., Locatelli, M., Arlorio, M., & Travaglia, F. (2013). Pyrogallol: An alternative trapping agent in proanthocyanidins analysis. *Food Analytical Methods*, *6*, 148–156.

Borrelli, R. C., Visconti, A., Mennella, C., Anese, M., & Fogliano, V. (2002). Chemical characterization and antioxidant properties of coffee melanoidins. *Journal of Agricultural and Food Chemistry*, *50*, 6527–6533.

Bosso, A., Panero, L., Petrozziello, M., Follis, R., Motta, S., & Guaita, M. (2011). Influence of submerged-cap vinification on polyphenolic composition and volatile compounds of Barbera wines. *American Journal of Enology and Viticulture*, *62*, 503–511.

Brand-Williams, W., Cuvelier, M. E., & Berset, C. (1995). Use of a free radical method to evaluate antioxidant activity. *Lebensmittel-Wissenschaft & Technologie*, *28*, 25–30.

Brasil (2005). *Altera dispositivos da Lei n. 7678 de 8 de novembro de 1988.* Brasília: Diário Oficial da União.

Camargo, U. A., Maia, J. D. G., & Ritschel, P. S. (2008). *BRS Carmem: nova cultivar de uva tardia para suco. Comunicado Técnico*, *84*, Embrapa Uva e Vinho (8p.).

Camargo, U. A., & Ritschel, P. (2008). New table and wine grape cultivars: World scenario with emphasis on Brazil. *Acta Horticulturae*, *785*, 89–96.

Castillo-Muñoz, N., Gómez-Alonso, S., García-Romero, E., Gómez, M. V., Velders, A. H., & Hermosín-Gutiérrez, I. (2009). Flavonol 3-O-glycosides series of *Vitis vinifera* cv. Petit Verdot red wine grapes. *Journal of Agricultural and Food Chemistry*, *57*, 209–219.

Castillo-Muñoz, N., Gómez-Alonso, S., García-Romero, E., & Hermosín-Gutiérrez, I. (2007). Flavonol profiles of *Vitis vinifera* red grapes and their single-cultivar wines. *Journal of Agricultural and Food Chemistry*, *55*, 992–1002.

Chira, K., Pacella, N., Jourdes, M., & Teissedre, P. -L. (2011). Chemical and sensory evaluation of Bordeaux wines (Cabernet-Sauvignon and Merlot) and correlation with wine age. *Food Chemistry*, *126*, 1971–1977.

De Castilhos, M. B. M., Cattelan, M. G., Conti-Silva, A. C., & Del Bianchi, V. L. (2013). Influence of two different vinification procedures on the physicochemical and sensory properties of Brazilian non-*Vitis vinifera* red wines. *Lebensmittel-Wissenschaft & Technologie*, *54*, 360–366.

De Castilhos, M. B. M., Conti-Silva, A. C., & Del Bianchi, V. L. (2012). Effect of grape predrying and static pomace contact on physicochemical properties and sensory acceptance of Brazilian (Bordô and Isabel) red wines. *European Food Research and Technology*, *235*, 345–354.

De Castilhos, M. B. M., Corrêa, O. L. S., Zanus, M. C., Maia, J. D. G., Gómez-Alonso, S., García-Romero, E., et al. (2015). Pre-drying and submerged cap winemaking: Effects on polyphenolic compounds and sensory descriptors. Part I: BRS Rúbea and BRS Cora. *Food Research International*, *75*, 374–384.

Delgado-Andrade, C., & Morales, F. J. (2005). Unraveling the contribution of melanoidins to the antioxidant activity of coffee brews. *Journal of Agricultural and Food Chemistry*, *53*, 1403–1407.

Figueiredo-González, M., Cancho-Grande, B., & Simal-Gándara, J. (2013). Effects on colour and phenolic composition of sugar concentration processes in dried-on- and dried-off-vine grapes and their aged or not natural sweet wines. *Trends in Food Science & Technology*, *31*, 36–54.

Girard, B., Yuksel, D., Cliff, M. A., Delaquis, P., & Reynolds, A. G. (2001). Vinification effects on the sensory, colour, and GC profiles of Pinot noir wines from British Colombia. *Food Research International*, *34*, 483–499.

Hair, J. F., Black, W. C., Babin, B. J., Anderson, R. E., & Tatham, R. L. (2009). *Análise Multivariada de Dados* (6th ed.). Porto Alegre: Bookman (593p.).

Jackson, R. S. (2008). *Wine science: Principles and applications* (3rd. ed.). San Diego: Academic Press.

Lago-Vanzela, E. S., Da-Silva, R., Gomes, E., García-Romero, E., & Hermosín-Gutiérrez, I. (2011). Phenolic composition of the edible parts (flesh and skin) of Bordô grape (*Vitis labrusca*) using HPLC-DAD-ESI-MS/MS. *Journal of Agricultural and Food Chemistry*, *59*, 13136–13146.

Lago-Vanzela, E. S., Procópio, D. P., Fontes, E. A. F., Ramos, A. M., Stringheta, P. C., Da-Silva, R., et al. (2014). Aging of red wines made from hybrid grape cv. BRS Violeta: Effects of accelerated aging conditions on phenolic composition, color and antioxidant capacity. *Food Research International*, *56*, 182–189.

Lago-Vanzela, E. S., Rebello, L. P. G., Ramos, A. M., Stringheta, P. C., Da-Silva, R., García-Romero, E., et al. (2013). Chromatic characteristics and color-related phenolic composition of Brazilian young red wines made from the hybrid grape cultivar BRS Violeta ("BRS Rúbea" × "IAC 1398-21"). *Food Research International*, *54*, 33–43.

López-Vélez, M., Martinez-Martinez, F., & Del Valle-Ribes, C. D. (2003). The study of phenolic compounds as natural antioxidants in wine. *Critical Reviews in Food Science and Nutrition*, *43*(3), 233–244.

Ma, W., Guo, A., Zhang, Y., Wang, H., Liu, Y., & Li, H. (2014). A review on astringency and bitterness perception of tannins in wine. *Trends in Food Science & Technology*, *40*, 6–19.

Makris, D. P., Kallithraka, S., & Kefalas, P. (2006). Flavonols in grapes, grape products and wines: Burden, profile and influential parameters. *Journal of Food Composition and Analysis*, *19*, 396–404.

Margaris, D. P., & Ghiaus, A. G. (2007). Experimental study of hot air dehydration of Sultana grapes. *Journal of Food Engineering*, *79*(4), 1115–1121.

Marquez, A., Serratosa, M. P., Lopez-Toledano, A., & Merida, J. (2012). Colour and phenolic compounds in sweet red wines from Merlot and Tempranillo grapes chamber-dried under controlled conditions. *Food Chemistry*, *130*, 111–120.

Mazzuca, P., Ferranti, P., Picariello, G., Chianese, L., & Addeo, F. (2005). Mass spectrometry in the study of anthocyanins and their derivatives: Differentiation of *Vitis vinifera* and hybrid grapes by liquid chromatography/electrospray ionization mass spectrometry and tandem mass spectrometry. *Journal of Mass Spectrometry*, *40*, 83–90.

Nixdorf, S. L., & Hermosín-Gutiérrez, I. (2010). Brazilian red wines made from the hybrid grape cultivar Isabel: Phenolic composition and antioxidant capacity. *Analytica Chimica Acta*, *659*, 208–215.

Patras, A., Brunton, N. P., O'Donnell, C., & Tiwari, B. K. (2010). Effect of thermal processing on anthocyanin stability in foods; Mechanisms and kinetics of degradation. *Trends in Food Science & Technology*, *21*, 3–11.

Rebello, L. P. G., Lago-Vanzela, E. S., Barcia, M. T., Ramos, A. M., Stringheta, P. C., Da-Silva, R., et al. (2013). Phenolic composition of the berry parts of hybrid grape cultivar BRS Violeta (BRS Rubea × IAC 1398-21) using HPLC-DAD-ESI-MS/MS. *Food Research International*, *54*, 354–366.

Rentzsch, M., Schwarz, M., Winterhalter, P., & Hermosín-Gutiérrez, I. (2007). Formation of hydroxyphenyl-pyranoanthocyanins in Grenache wines: Precursor levels and evolution during aging. *Journal of Agricultural and Food Chemistry*, *55*, 4883–4888.

Ribéreau-Gayon, J., Paynaud, E., Sudrad, P., & Ribéreau-Gayon, P. (1982). *Analyse et contrôle des vins.* Traité d'oenologie. Dunod: Paris.

Rivero-Pérez, M. D., Muñiz, P., & González-San José, M. L. (2007). Antioxidant profile of red wines evaluated by total antioxidant capacity, scavenger capacity, and biomarkers of oxidative stress methodologies. *Journal of Agricultural and Food Chemistry*, *55*, 5476–5483.

Sánchez-llárduya, M. B., Sánchez-Fernández, C., Garmón-Lobato, S., Viloria-Bernal, M., Abad-García, B., Berrueta, L. A., et al. (2014). Tentative identification of pyranoanthocyanins in Rioja aged red wines by high-performance liquid chromatography and tandem mass spectrometry. *Australian Journal of Grape and Wine Research*, *20*, 31–40.

Slinkard, K., & Singleton, V. L. (1977). Total phenol analysis: Automation and comparison with manual methods. *American Journal of Enology and Viticulture*, *28*, 49–55.

Tagliazucchi, D., Verzelloni, E., & Conte, A. (2008). Antioxidant properties of traditional balsamic vinegar and boiled must model systems. *European Food Research and Technology*, *227*, 835–843.

Tecchio, F. M., Miele, A., & Rizzon, L. A. (2007). Sensory characteristics of Bordô wine. *Pesquisa Agropecuária Brasileira*, *42*, 897–899.

Vidal, S., Francis, L., Guyot, S., Marnet, N., Kwiatkowski, M., Gawel, R., et al. (2003). The mouth-feel properties of grape and apple proanthocyanidins in a wine-like medium. *Journal of the Science of Food and Agriculture*, *83*, 564–573.