Food Research International 45 (2012) 402–414

Contents lists available at SciVerse ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Impact of phenolic and polysaccharidic composition on commercial value of Argentinean Malbec and Cabernet Sauvignon wines

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ARTICLE INFO

Article history:
Received 15 July 2011
Accepted 3 November 2011

Keywords:
Phenols
Polysaccharides
Red wine
Malbec
Cabernet Sauvignon
Commercial value

ABSTRACT

Knowledge of the chemical composition of wine and its association with the commercial value constitutes an objective tool to assess quality and can be used as a marketing strategy. Phenolic compounds are very important quality parameters of wines because of their impact on color, taste and health properties, and together with polysaccharides contribute to the chemical stability and sensory perception of the products. In this context, the major aims of the present study were to describe the phenolic and polysaccharidic composition of Argentinean Malbec and Cabernet Sauvignon wines of different price segments, and assessing their impact on the commercial value. Thirty wines representative of three retail price segments (US$ 5–7, 18–20, and >40) were evaluated. In general, there was a trend towards greater concentration of these compounds with increasing the commercial value of wines. Particularly, it was found that general phenolic composition, color-related compounds, main flavonoid groups and polysaccharides appear as relevant variables differing among segments and showing some differences between varieties. Additionally, the sensory wine description was in good agreement with the analytical results. The wines of greater commercial value, with the best visual and gustatory scores, coincided with higher levels of the phenolic parameters determined. This study provides an interesting insight, no reported so far, on the impact of phenolic and polysaccharidic composition in the final quality of the products and therefore in its market value.

1. Introduction

Wine is a product of particular characteristics, since the degree of differentiation that can reach responds to an imperfectly competitive market, where different products compete for the same demand but each with unique styles. Argentina ranks fifth in world wine production, with about 13 million hectoliters in 2009, representing ~5% of the global amount (OIV, 2010). Over 70% of Argentinean wine is produced in Mendoza province. Malbec (*Vitis vinifera* L.) is the main red grape variety (29%) and is considered the emblematic cultivar of Argentina. This variety, of French origin, has well adapted to the soil and climate of Mendoza, finding the optimal ecological conditions for their development, and allowing obtaining wines with a distinctive style (Fanzone, Peña-Neira, Jofré, Assof, & Zamora, 2010; INV, 2009). For that reason, Malbec has a leading place in the Argentinean wine market by offering a wide range of products resulting from the influence of various factors (geographical location of the vineyard, grape maturity, viticultural practices, winemaking techniques, etc.).

In view of the needs and demands of the current wine market, it becomes increasingly necessary producing wines of the highest quality possible. The wine quality can be defined by different criteria, being subject to the evaluation parameters employed, and always designed to fulfill requirements of consumers. It should also be noted that the concept of quality is closely related to commercial value. In many cases, the quality is evaluated through sensory analysis by trained panelists that characterize the products according to their organoleptic attributes. Then, these data are correlated to consumer liking or acceptance judgments from typical and targeted groups of consumers. Furthermore, sensory analysis techniques have been widely used as an adjunct to quality control and as a diagnostic tool to characterize product differences (Ferreira et al., 2009; Goldner & Zamora, 2007).

Additionally, the identification and quantification of the minor chemical components is a promising approach to explain the sensory description of a wine, and to assess their stability, origin and authenticity, and thus its commercial quality (Sáenz-Navajas, Tao, Dizy, Ferreira, & Fernández-Zurbano, 2010b). The relationship between sensory evaluation and chemical composition of wine is a critical topic of research in oenology. Some authors have investigated the influence of volatile composition on the organoleptic characteristics

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doi:10.1016/j.foodres.2011.11.010

of wines (Escudero, Campo, Farina, Cacho, & Ferreira, 2007; Sáenz-Navajas, Campo, Fernández-Zurbano, Valentin, & Ferreira, 2010a), while others have examined relationships between phenolic compounds and their sensory attributes (Chira, Pacella, Jourdes, & Teissedre, 2011; Granato, Katayama, & de Castro, 2011; Holt, Francis, Field, Herderich, & Iland, 2008).

Phenolic compounds are one of the most important quality parameters in red wines, and involve two main groups of compounds, non-flavonoids (hydroxybenzoic and hydroxycinnamic acids and their derivatives, stilbenes, and phenolic alcohols) and flavonoids (anthocyanins, flavanols, flavonols, and dihydroflavonols). These compounds contribute to organoleptic characteristics of wines such as color, astringency, and bitterness, are also active in biochemical processes, and have nutraceutical effects on human health, including antimicrobial, anticarcinogenic, and antioxidant properties (Renaud & de Lorgeril, 1992). According to some studies, there is close link between high quality wines and high phenolic composition (Langlois, Ballester, Campo, Dacremont, & Dominique, 2010; Sáenz-Navajas, Tao, Dizy, Ferreira, & Fernández-Zurbano, 2010b).

During winemaking and aging, the flavonoids are able to interact between them and with other wine constituents, such as proteins or polysaccharides, contributing to the chemical stability and modifying the sensory perception of wines. Major wine polysaccharides include mannoproteins (MPs) originating from yeasts, and arabinogalactan-proteins (AGPs), arabinans and rhamnogalacturonans (RG-I and RG-II) coming from cell walls of grape berries. They play an important role in the colloidal stability of wines through their ability to interact and aggregate with tannins, and have a positive effect on the organoleptic quality modifying gustatory structure, fullness and body, and softening tannin astringency of wines (Fernández, Martínez, Hernández, Guadalupe, & Ayestarán, 2011; Terrier, Poncet-Legrand, & Cheynier, 2009).

Based on these considerations, it can establish that phenolic compounds and polysaccharides are of great importance for the organoleptic quality of red wines. Moreover, its biosynthesis in plants, their concentration in grapes at harvest and subsequent extraction into wine, give rise to obtain products of different qualities, which are reflected in the final market value. To best of our knowledge, there is to date no report on the individualized chemical composition of Argentinean red wines of different commercial value. In this context, the aims of our study were to describe the chemical composition (in particular, phenolic and polysaccharidic) of Argentinean Malbec and Cabernet Sauvignon wines of different price segments, and assessing their impact on the commercial value. Together with Malbec, we decided to work with Cabernet Sauvignon since it is also a red variety very produced in this country and widely spread in the world.

2. Materials and methods

2.1. Wine samples

Thirty red wines produced at commercial scale were collected in bottles (750 mL) directly from the 9 collaborating wineries of Mendoza (Argentina), which produce monovarietal wines and, therefore, guarantee the 100% purity. The samples corresponded to five different monovarietal Malbec (MB) and Cabernet Sauvignon (CS) wines for each of the price segments assessed. The three segment evaluated were: retail values between US$ 5–7 per bottle (low segment), US$ 18–20 per bottle (medium segment), and > US$ 40 per bottle (high segment). All wines were selected attending to sales criteria to obtain representative samples of Argentinean red wine market. Particularly, the vintage of these wines range from 2007 (3 samples for each variety) to 2008 (2 samples for each variety) for high segment, from 2008 (4 samples for each variety) to 2009 (1 sample for each variety) for medium segment, while only from 2009 for the low segment. They were stored in darkness at 12–15 °C, and each wine bottle was opened immediately before the analyses. Due to the time required for completing all analyses (about 2 month), the wine samples were transferred under nitrogen gas stream to completely filled amber bottles for ensuring their preservation.

2.2. Standards and reagents

Standards of gallic acid [149-91-7], syringic acid [530-57-4], caffeic acid [331-39-5], *p*-coumaric acid [501-98-4], ethyl gallate [831-61-8], tryptophol [526-55-6], (+)-catechin [7295-85-4], (−)-epicatechin [490-46-0], resveratrol [501-36-0], myricetin [529-44-2], kaempferol [520-18-3], and quercetin-3-glucoside [21637-25-2], *p*-dimethylaminocinnamaldehyde [6203-18-5], ammonium formate [540-69-2], L-ascorbic acid [50-81-7], phloroglucinol [108-73-6], and polyvinylpolypyrrolidone [25249-54-1] were purchased from Sigma-Aldrich (St. Louis, MO); tyrosol [501-94-0] was purchased from Fluka (St. Louis, MO); while protocatechuic acid [99-50-3], quercetin [117-39-5], (−)-epigallocatechin [970-74-1], (−)-epicatechin-3-gallate [1257-08-5], and malvidin-3-glucoside chloride [7228-78-6] were supplied by Extrasynthese (Lyon, France). A pullulan calibration kit Shodex P-82 (P-5, Mw = 5.9 kDa; P-10, Mw = 11.8 kDa; P-20, Mw = 22.8 kDa; P-50, Mw = 47.5 kDa; P-100, Mw = 112 kDa; P-200, Mw = 212 kDa; P-400, Mw = 404 kDa; P-800, Mw = 788 kDa) was obtained from Waters (Barcelona, Spain), while a pullulan 1.3 kDa and the four dextrans BioChemika (12, 25, 50 and 80 kDa) from Fluka (St. Louis, MO). The polysaccharides used as external standards were pectins from citrus and dextrans synthesized by *Leuconostoc mesenteroides*e purchased from Sigma-Aldrich (St. Louis, MO). Sodium chloride and sodium metabisulphite were purchased from Anedra (Buenos Aires, Argentina). Ammonium iron (II) sulfate and butanol were obtained from Dalton (Mendoza, Argentina). Ethyl ether and ethyl acetate were acquired from Sintorgan (Buenos Aires, Argentina). Sodium sulfate anhydrous, potassium dihydrogen phosphate, sodium acetate, vanillin, gelatin, acetaldehyde, hydrochloric acid, acetic acid, formic acid, ethanol, chromatography grade methanol and acetonitrile were purchased from Merck (Darmstadt, Germany). All reactive were analytical grade or superior. Ultra pure water was obtained from a RiO/Elix3-Sinergy185 purification system (Millipore, Sao Pablo, Brazil). Cellulose filter (3 μm pore size) and 0.45 μm pore size nylon membrane were supplied by Microclar (Buenos Aires, Argentina). Sep-Pak Plus (400 mg) and Environmental (900 mg) tC_{18} cartridges were obtained from Waters (Milford, MA). Nitrogen gas was supplied by Linde S.A. (Mendoza, Argentina).

2.3. Spectrophotometric analyses

Absorbance measurements were made with a Perkin-Elmer UV–vis spectrophotometer model Lambda 25 (PerkinElmer, Hartford, CT).

Total phenols were determined by direct reading of the absorbance of the samples (1:100 dilution) at 280 nm (Ribéreau-Gayon, Glories, Maujean, & Dubourdieu, 2000). Total phenols were calculated from a calibration curve made with standard solutions of gallic acid (five replicates) in the range between 0 and 50 mg/L ($R^2 = 0.99$), and expressed as milligrams of gallic acid equivalents per liter of sample (GAE, mg/L).

Total anthocyanins were measured by diluting the extract with 2% hydrochloric acid in ethanol and by comparing spectrophotometric readings at 520 nm of single aliquots treated with either sodium metabisulphite or water (Ribéreau-Gayon et al., 2000). Total anthocyanins were expressed as milligrams per liter of malvidin-3-glucoside. Free and combined anthocyanins were calculated using the PVPP index (Glories, 1984a).

For total proanthocyanidins, the analytical method applied was the acid butanol assay (Porter, Hritsch, & Chan, 1986). This method is based on the acid-catalyzed oxidative cleavage of the C – C interflavanic

bond of proanthocyanidins in butanol–HCl. Total proanthocyanidins were expressed as milligrams per liter of (+)-catechin.

Color intensity (CI), percentage of yellow (%Yellow), percentage of red (%Red) and percentage of blue (%Blue) was estimated using the method described by Glories (1984a,b). The CIELAB coordinates, lightness (L^*), chroma or saturation (C^*), hue angle (h), red-greenness (a^*) and yellow-blueness (b^*) were determined according to Ayala, Echávarri, and Negueruela (1997) and the data were processed with the MSCV® software (Ayala, Echávarri, & Negueruela, 2001). The total color difference (ΔE^*) between two samples was obtained following the method proposed by Pérez-Magariño and González-Sanjosé (2003).

The contribution of copigmented anthocyanins to the total wine color at pH 3.6 (color due to copigmentation, %CC), and the degree of anthocyanins polymerization (color due to polymeric pigments, %CP), were determined following the method described by Hermosín Gutiérrez (2003).

Other chemical parameters measured in the samples were gelatin index (Glories, 1984b) and molar concentration of flavanols by *p*-dimethylaminocinnamaldehyde assay (Vivas, Glories, Lagune, Saucier, & Augustin, 1994). Titratable acidity, pH, and ethanol content were determined as described by Zoecklein, Fugelsang, Gump, and Nury (2001).

2.4. HPLC analysis of anthocyanins

The chromatographic system employed was a Perkin-Elmer Series 200 high-performance liquid chromatograph equipped with a diode array detector, a quaternary pump, and an autosampler (HPLC-DAD; PerkinElmer, Shelton, CT). Separation was performed on a reversed phase Chromolith Performance C_{18} column (100 mm × 4.6 mm I.D., 2 μm; Merck, Darmstadt, Germany) with a Chromolith guard cartridge (10 mm × 4.6 mm) at 25 °C. A gradient consisting of solvent A (water/formic acid, 90:10, v/v) and solvent B (acetonitrile) was applied at a flow rate of 1.1 mL/min from 0 to 22 min and 1.5 mL/min from 22 to 35 min as follows: 96–85% A and 4–15% B from 0 to 12 min, 85–85% A and 15–15% B from 12 to 22 min, 85–70% A and 15–30% B from 22 to 35 min; followed by a final wash with 100% methanol and re-equilibration of the column. Two milliliters of wine was filtered through a 0.45 μm pore size nylon membrane, and then 100 μL was injected onto the column. Diode array detection was performed from 210 to 600 nm, and the quantification was carried out by peak area measurements at 520 nm. Anthocyanin amount was expressed by using malvidin-3-glucoside chloride as standard for a calibration curve ($R^2 = 0.99$). Identification and confirmation of anthocyanic pigments were performed by HPLC-DAD/ESI-MS as described by Monagas, Núñez, Bartolomé, and Gómez-Cordovés (2003a).

2.5. HPLC analysis of low molecular weight phenolic compounds

Sodium chloride (1 g) was added to 50 mL of wine and extracted three times with 20 mL of ethyl ether and three times with 20 mL of ethyl acetate. The organic fractions were combined, dehydrated with 2.5 g sodium sulfate anhydrous, filtered throughout a 3 μm pore size cellulose filter, and evaporated to dryness under a gentle nitrogen gas stream at 35 °C. The solid residue was dissolved in 2 mL of methanol/water (1:1, v/v) and filtered through a 0.45 μm pore size nylon membrane, and then 30 μL was injected in the same HPLC system employed for anthocyanins. Separation was performed on a reversed phase Nova-Pak C_{18} column (300 mm × 3.9 mm I.D., 4 μm; Waters Corp., Milford, MA) at 25 °C. Two mobile phases were employed for elution: A (water/acetic acid, 98:2, v/v) and B (water/acetonitrile/acetic acid, 78:20:2, v/v/v). The gradient profile was 0–55 min, 100–20% A and 0–80% B; 55–57 min, 20–10% A and 80–90% B; 57–70 min, 10% A and 90% B isocratic; 70–80 min, 10–0% A and 90–100% B; 80–125 min, 100% B isocratic; followed by a 100% methanol washing and re-equilibration of the column. The flow rate was 0.9 mL/min from 0 to 55 min and 1.0 mL/min from 55 to 125 min. Diode array detection was performed by scanning from 210 to 360 nm with an acquisition speed of 1 s. The identification of specific compounds was carried out by comparison of their spectra and retention time with those of standards. All the individual phenolic compounds were confirmed by HPLC-DAD/ESI-MS as described by Monagas, Suarez, Gómez-Cordovés, and Bartolomé (2005). Quantitative determinations were made by using the external standard method with commercial standards. The calibration curves were obtained by injection of standard solutions, under the same conditions as for the samples analyzed, over the range of concentrations observed ($R^2 \geq 0.94$). The compounds for which no standards were available were quantified with the curves of quercetin (dihydroflavonols), quercetin-3-glucoside (quercetin and flavonol glycosides), myricetin (myricetin glycosides), resveratrol (*trans* and *cis*-resveratrol glucoside), caffeic acid (fertaric, caftaric and coutaric acids), gallic acid (gentisic acid), ethyl gallate (methyl gallate), and (+)-catechin (procyanidins).

2.6. Analysis of flavanols

2.6.1. Fractionation of flavanols into monomers, proanthocyanidins oligomers and polymers

Wine samples were fractionated using the solid phase extraction method described by Sun, Leandro, Ricardo da Silva, and Spranger (1998a). Briefly, 5 mL of wine was concentrated to dryness in a vacuum evaporator (Univapo 100ECH, Uniequip, Martinsried, Germany) at <30 °C. The residue was dissolved in 20 mL of 67 mM phosphate buffer (pH 7.0). Two C_{18} Sep-Pak cartridges were assembled (900 mg and 400 mg of sorbent weight on top and at the bottom, respectively) and conditioned sequentially with methanol (10 mL), pure water (2 × 10 mL), and phosphate buffer (10 mL). Samples were passed through the cartridges at a flow rate of 2 mL/min, and phenolic acids were then eliminated by elution with 10 mL of phosphate buffer. The cartridges were dried with nitrogen gas and eluted sequentially with 25 mL of ethyl acetate (fraction FI + FII containing monomeric and oligomeric flavanols) and with 15 mL of methanol (fraction FIII containing polymeric proanthocyanidins). The ethyl acetate eluate was taken to dryness under vacuum, redissolved in 20 mL of phosphate buffer, and reloaded onto the same series of cartridges that had been conditioned again as described above. The cartridges were dried with nitrogen and eluted sequentially with 25 mL of ethyl ether (fraction FI) and 15 mL of methanol (fraction FII). Fractions FI, FII, and FIII were evaporated to dryness under vacuum and redissolved in 5 mL of methanol. The total content of flavanols in each fraction was determined by the vanillin assay described by Sun, Ricardo da Silva, and Spranger (1998b).

2.6.2. Analysis of polymeric proanthocyanidins following acid-catalysis with phloroglucinol

Acid-catalysis cleavage in the presence of excess phloroglucinol (Kennedy & Jones, 2001) was used to analyze monomeric proanthocyanidins composition and its mean degree of polymerization (mDP). Reversed-phase HPLC analysis was carried out for the determination of the structural composition of proanthocyanidins, which are characterized by the nature of their constitutive extension units (released as flavanols phloroglucinol adducts) and terminal units (released as flavanols). To calculate the apparent mDP, the sum of all subunits (flavanol monomers and phloroglucinol adducts, in moles) was divided by the sum of all flavanol monomers (in moles). The total proanthocyanidin concentration was considered as the addition of all terminal and extension subunits. In our study it was applied the procedure described by Kontoudakis et al. (2011a).

2.7. Analysis of polysaccharides

2.7.1. Extraction of polysaccharides from the wine samples

Wine samples were processed using the methodology described by Ayestarán, Guadalupe, and León (2004). Briefly, 10 mL of wine was centrifuged (9500×*g*, 20 min, 4 °C) by 5810R equipment (Eppendorf, Hamburg, Germany), and the supernatant concentrated to a final volume of 2 mL employing a vacuum evaporator (Univapo 100ECH, Uniequip, Martinsried, Germany). Total soluble polysaccharides were precipitated by addition of 10 mL cold acidified ethanol (ethanol 99%, 0.3 M HCl) and kept for 24 h at 4 °C. Then, the samples were centrifuged (9000×*g*, 10 min, 4 °C), the supernatants were discarded, and the pellets were washed four times with cold ethanol to remove the interference materials. Finally, the precipitates were dissolved in 1 mL of ultra pure water, frozen to −80 °C and freeze-dried using an equipment model L-I-E300-CRT (Rificor, Buenos Aires, Argentina).

2.7.2. Determination of polysaccharides by HRSEC-RID

In order to determine the molecular distribution and quantifying the polysaccharides obtained from wines, the soluble fractions were analyzed by high-resolution size-exclusion chromatography (HRSEC). The lyophilized samples were resuspended in 1 mL of 30 mM ammonium formate, filtered through a 0.45 μm pore size nylon membrane, and then 100 μL was injected onto the column. HRSEC was performed using an Agilent 1200 Series liquid chromatograph equipped with a G1362A refractive index detector (RID), a G1311A quaternary pump, a G1316A column oven, and G1329A autosampler (Agilent Technologies, Palo Alto, CA). Separation was carried out at 20 °C using two Shodex OHpak SB-803 HQ and SB-804 HQ columns connected in series (300 mm × 8 mm I.D.; Showa Denko, Japan). The mobile phase consists of an aqueous solution of 30 mM ammonium formate applied with a constant flow of 0.6 mL/min for 60 min, and the temperature of cell RID was 35 °C. The molecular weight distribution of the wine fractions was followed by calibration with pullulans and dextrans standards of different molecular weight, described above. The apparent molecular weights were deduced from the calibration equation:

$$\log \mathrm{Mn}\ (\mathrm{kDa}) = [(t_R - 43.67)/-4.45]/1000 \quad (1)$$

were t_R = column retention time at peak maximum, and $R^2 = 0.99$.

The quantification of polysaccharides was performed according to the peak area for each fraction, using the external standard method with pectins and dextrans commercial standards. The calibration curve was obtained by injection of standard solutions, under the same conditions as for the samples analyzed, in the range between 0 and 2 g/L ($R^2 = 0.99$).

2.8. Descriptive sensory analysis

All the wines were tasted by a group of 10 trained panelists (4 females and 6 males) from the National Institute of Agricultural Technology (INTA, Mendoza), all of them part of a sensory group with a long experience in tasting of Malbec and Cabernet Sauvignon wines from different features. A previous training session was carried out to standardize criteria among the panelists. In this first evaluation we elected, by consensus, the most suitable and uniform attributes among the panelists to describe the wines. Subsequently, it was performed five sessions of 60 min (2 per week) during three weeks. Through a session, each panelist had to assess two flights consisting of three wines of different commercial value for each variety (6 wines per session). Approximately 30–40 mL of wine was served in a completely randomized order, at 18–20 °C, in clear wine tasting glasses (ISO 3591, 1977) labeled with three-digit code. In order to ascertain judges' consistency one sample was replicated in each session. For each wine, it was evaluated six sensorial attributes: visual (color intensity), gustatory (fullness, bitterness, astringency, and persistency) and global quality, on a 10-point scale. Panelists were only informed about the grape variety of the wine samples.

2.9. Statistical analysis

All analyses (including extractions) were carried out in triplicate. Statistical analysis was assessed with Statgraphics Plus version 4.0 software (Copyright 1994–1999, Statistical Graphics Corp., Warrenton, VA). All of the results were tested for homogeneity of variance using Cochran's test, and analyzed by one-way or multifactor analysis of variance (ANOVA) and Tukey's honestly significant difference (HSD) test. A $p<0.05$ was considered to be statistically significant. Discriminant analyses were performed for examining price segment differences in Malbec and Cabernet Sauvignon wines, using the individual phenolic parameters.

3. Results and discussion

3.1. General chemical composition

Table 1 presents a summary of the general analytical parameters evaluated in the red wines studied. The chemical data of MB and CS wines have been submitted to the ANOVA test in order to explore the "commercial value" effect ($p<0.05$). Among all of the samples analyzed, both for MB and CS, it was observed a low dispersion in titratable acidity, pH and ethanol content without significant differences for the price segments assessed.

For all samples, total phenols ranged from 2667.5 to 3905.0 and from 2765.3 to 3944.3 mg/L in MB and CS, respectively. Significant differences were observed among wines of different commercial value. On average, the wines of high segment showed the highest level of this parameter, while the lowest content was observed in the low segment. These results are comparable to those reported for other authors in wines from the same cultivars (Fanzone et al., 2010; Ginjom, D'Arcy, Caffin, & Gidley, 2010).

Proanthocyanidins were the major phenolics quantified in the samples, with concentrations similar to those published in previous works (Fanzone et al., 2010; González-Neves et al., 2004). Only for MB wines, there was a positive influence of these compounds on the commercial value, showing a significantly greater content in the high and medium segments with regard to the low segment. This could be due to several factors that favored their accumulation in grapes, as well as to winemaking practices made to achieve a greater extraction from the berries. The molar concentration of flavanols and the gelatin index showed a parallel behavior of proanthocyanidins, with values from 1.7×10^{-3} to 2.2×10^{-3} mol/L and from 72.9 to 74.2%, respectively. With regard to CS, the same trend was not observed as in MB, with levels of proanthocyanidins and GI comparable without significant differences among wines of different price segments.

An overall view of color composition indicates their significant incidence on the commercial value of wines. Specifically, MB and CS wines of high segment showed higher values of CI, C^*, a^* and b^*. By contrast, L^* had the opposite tendency indicating that the wines of lower commercial value (low segment) had less color compared to the rest. The higher CI in MB was principally related to the blue component of the color (%Blue), while in CS was due to the red component (%Red). Analyzing the global effect of the variety (Table 1), we can see that MB wines showed a significantly higher %Blue and a smaller %Yellow and values of the CIELAB coordinates h and b^*, compared with CS.

In order to evaluate the colorimetric difference amongst wines of different commercial value, the total color difference (ΔE^*) was determined. This parameter could be very important for the wine industry as expresses the human eye's ability to discriminate between the

Table 1
General analytical parameters of Malbec and Cabernet Sauvignon wines of different commercial value. Probability values for variety and price segment.

Parameter	Malbec			Cabernet Sauvignon			Factor		
	Price segment						Variety	Segment	Variety × segment[d]
	High	Medium	Low	High	Medium	Low	p_{value}[e]		
Titratable acidity (tartaric acid, g/L)	$6.0^{a} \pm 0.2$	$5.6^{a} \pm 0.3$	$5.5^{a} \pm 0.1$	$6.4^{a} \pm 0.1$	$5.9^{a} \pm 0.2$	$5.3^{a} \pm 0.4$	0.4640	0.0405	0.4671
pH	$3.66^{a} \pm 0.03$	$3.65^{a} \pm 0.02$	$3.62^{a} \pm 0.04$	$3.57^{a} \pm 0.01$	$3.56^{a} \pm 0.05$	$3.71^{a} \pm 0.04$	0.8096	0.7872	0.4414
Ethanol (% v/v)	$15.1^{a} \pm 0.2$	$14.7^{a} \pm 0.1$	$14.2^{a} \pm 0.2$	$14.4^{a} \pm 0.1$	$14.5^{a} \pm 0.2$	$14.3^{a} \pm 0.2$	0.1275	0.0497	0.2576
TA (malvidin-3-glucoside, mg/L)	$411.0^{a} \pm 37.4$	$369.9^{a} \pm 24.4$	$324.8^{a} \pm 26.9$	$320.7^{b} \pm 18.9$	$307.3^{b} \pm 18.7$	$216.4^{a} \pm 13.8$	0.0006	0.0050	0.6879
FA (malvidin-3-glucoside, mg/L)	$170.2^{a} \pm 25.3$	$185.2^{a} \pm 13.8$	$164.0^{a} \pm 15.7$	$141.8^{a} \pm 11.1$	$143.9^{a} \pm 15.1$	$101.4^{a} \pm 13.5$	0.0052	0.1870	0.6140
CA (malvidin-3-glucoside, mg/L)	$240.9^{b} \pm 24.1$	$184.7^{ab} \pm 16.0$	$160.8^{a} \pm 13.3$	$178.9^{b} \pm 10.7$	$163.4^{b} \pm 5.5$	$115.0^{a} \pm 9.5$	0.0030	0.0007	0.4419
CI (A 420 nm + 520 nm + 620 nm) ∗ 10	$21.5^{b} \pm 1.9$	$16.1^{ab} \pm 1.4$	$11.9^{a} \pm 0.8$	$21.8^{c} \pm 0.7$	$16.1^{b} \pm 1.2$	$11.0^{a} \pm 0.5$	0.8520	<0.0001	0.8594
%Yellow	$33.8^{a} \pm 0.6$	$34.8^{a} \pm 1.1$	$36.1^{a} \pm 0.8$	$34.7^{a} \pm 0.4$	$37.1^{ab} \pm 1.2$	$38.3^{b} \pm 0.9$	0.0180	0.0112	0.7040
%Red	$52.7^{a} \pm 0.7$	$52.4^{a} \pm 1.2$	$51.5^{a} \pm 0.7$	$53.3^{a} \pm 0.4$	$50.8^{a} \pm 1.3$	$50.1^{a} \pm 1.1$	0.2915	0.0812	0.4450
%Blue	$13.5^{b} \pm 0.2$	$12.8^{ab} \pm 0.2$	$12.5^{a} \pm 0.3$	$12.0^{a} \pm 0.1$	$12.1^{a} \pm 0.2$	$11.7^{a} \pm 0.2$	<0.0001	0.0087	0.1000
L^*	$29.9^{a} \pm 2.8$	$39.0^{ab} \pm 2.8$	$48.1^{b} \pm 2.5$	$31.3^{a} \pm 0.9$	$40.3^{b} \pm 2.4$	$52.0^{c} \pm 1.5$	0.2502	<0.0001	0.8003
C*	$56.1^{b} \pm 1.3$	$54.9^{ab} \pm 1.9$	$48.9^{a} \pm 1.7$	$61.0^{b} \pm 0.2$	$55.9^{b} \pm 2.2$	$47.5^{a} \pm 2.0$	0.2780	<0.0001	0.1843
h	$18.9^{a} \pm 2.0$	$16.4^{a} \pm 1.5$	$14.1^{a} \pm 1.6$	$25.5^{a} \pm 1.3$	$23.4^{a} \pm 2.1$	$19.7^{a} \pm 2.1$	0.0002	0.0206	0.9108
a^*	$53.5^{b} \pm 0.6$	$52.6^{ab} \pm 1.9$	$47.4^{a} \pm 1.8$	$54.9^{b} \pm 0.4$	$51.1^{b} \pm 2.1$	$44.6^{a} \pm 1.9$	0.4673	0.0001	0.4182
b^*	$18.2^{b} \pm 2.1$	$15.6^{ab} \pm 1.6$	$11.8^{a} \pm 1.1$	$26.4^{b} \pm 1.4$	$22.2^{ab} \pm 2.2$	$16.0^{a} \pm 1.8$	0.0002	0.0003	0.5169
CC (%)	$6.0^{a} \pm 1.1$	$6.7^{a} \pm 0.7$	$8.0^{a} \pm 0.7$	$3.9^{a} \pm 0.7$	$4.2^{a} \pm 0.9$	$8.0^{b} \pm 0.7$	0.0263	0.0007	0.2813
CP (%)	$45.8^{a} \pm 1.4$	$47.1^{a} \pm 1.6$	$43.0^{a} \pm 1.6$	$52.6^{b} \pm 0.9$	$48.4^{ab} \pm 1.5$	$46.3^{a} \pm 1.5$	0.0063	0.0162	0.2491
TP (GAE, mg/L)	$3905.0^{b} \pm 267.8$	$3110.6^{ab} \pm 274.4$	$2667.5^{a} \pm 87.6$	$3944.3^{b} \pm 348.3$	$3251.6^{ab} \pm 256.0$	$2765.3^{a} \pm 115.9$	0.4054	0.0014	0.8361
PA (catechin, mg/L)	$6222.1^{b} \pm 352.7$	$5759.1^{b} \pm 145.8$	$4502.3^{a} \pm 138.9$	$4947.8^{a} \pm 448.3$	$5171.4^{a} \pm 406.5$	$4688.9^{a} \pm 206.7$	0.0618	0.0119	0.0336
FL (catechin, mol/L)	$2.2 \times 10^{-3b} \pm 1.0 \times 10^{-4}$	$2.1 \times 10^{-3b} \pm 6.6 \times 10^{-5}$	$1.7 \times 10^{-3a} \pm 2.4 \times 10^{-5}$	$2.4 \times 10^{-3b} \pm 9.1 \times 10^{-5}$	$1.9 \times 10^{-3a} \pm 9.5 \times 10^{-5}$	$1.9 \times 10^{-3a} \pm 1.2 \times 10^{-4}$	0.5301	0.0001	0.0274
GI (%)	$74.2^{a} \pm 1.5$	$72.9^{a} \pm 2.7$	$73.1^{a} \pm 1.3$	$66.8^{a} \pm 10.3$	$71.7^{a} \pm 3.4$	$74.4^{a} \pm 2.9$	0.3230	0.6580	0.4592

TA, total anthocyanins; FA, free anthocyanins; CA, combined anthocyanins; CI, color intensity; CIELab coordinates (L^*, lightness; C^*, chroma; h, hue; a^*, red-greenness; b^*, yellow-blueness); CC, color due to copigmentation; CP, color due to polymeric pigments; TP, total phenols; PA, proanthocyanidins; FL, molar concentration of flavanols; GI, gelatin index. All data are expressed as the arithmetic mean ± standard error (n = 5). Different letters within the same row indicate significant differences ($p < 0.05$) among price segments for the same variety, according to a Tukey HSD test.

[d] Interaction effect between variety and price segment.

[e] Considered significant when $p_{value} < 0.05$.

colors of two wines. It is generally accepted that tasters can only distinguish the color of two wines through the glass when $\Delta E^* \geq 5$ units (Pérez-Magariño & González-Sanjosé, 2003). In our study, the mean ΔE^* among MB samples of different price segments were 20.5 (between high and low), 14.0 (between medium and low), and 10.0 units (between high and medium); and for CS, 25.7, 16.8 and 11.8 units, respectively. These values obtained indicate its actual impact on the visual quality of wine.

Parallel to that observed in the color, the total anthocyanin concentration showed a positive upward trend with increasing the commercial value of wines. This behavior was similar for combined anthocyanins, while for free anthocyanins there was no difference among price segments. The higher proportion of combined anthocyanins in high-end wines could be explained by the higher level of flavanols found in those segments, which confirm the condensation reaction between both compound families (Terrier et al., 2009). In addition, when comparing both cultivars it was observed a significant difference ($p<0.05$), with higher anthocyanin content in MB than in CS wines (Table 1). These results are in agreement with those obtained by other authors in wines from the same varieties (Fanzone et al., 2010; Kontoudakis et al., 2011b).

Analyzing the contribution of %CC and %CP to the total wine color we observed an opposite pattern, showing an increase in %CP and a decrease in %CC with augmenting the commercial value of wines, particularly in the CS variety. The high proportion of copigmentation in low segment wines was probably due to their short aging time (wines of the year) compared to the rest. This is in agreement with Boulton (2001) who suggested that up to 30–50% of the red color of young red wines is dependent on the development and concentration of copigmented anthocyanins. By contrast, the polymerization observed in the upper segments confirms the obtained levels of combined anthocyanins, and it supposes the formation of new pigments by means of condensation and cycloaddition reactions (Monagas & Bartolomé, 2009; Terrier et al., 2009). Finally, when analyze the pooled data of the wines, we observed a significant difference between varieties in the level of the parameters mentioned, with a higher proportion of %CP in CS wines (Table 1).

3.2. Anthocyanins and derived pigments

The identified and quantified compounds in the wine samples are summarizes in Table 2. They were grouped in non-acylated glucosides, acetyl-glucosides, coumaroyl-glucosides, and a group formed by more complex anthocyanin-derived pigments (pyranoanthocyanins). All identified compounds were detected in all of the wines studied. The overall results were similar to those obtained by spectrophotometry, although the values were significantly lower. This is because HPLC analysis only detects free anthocyanins, whereas spectrophotometric analysis overestimates their total amount including other pigments (Canals, Llaudy, Canals, & Zamora, 2008).

Remarkable quantitative differences could be noticed in the anthocyanin profile of wines from different commercial value, reconfirming the richness of the upper segments. Coincident with the spectrophotometric determination, the MB and CS wines of high segment had the highest content of total monomeric anthocyanins (188.0 and 158.7 mg/L, respectively), showing a significant difference between varieties (Table 2). A similar tendency was observed in monoglucosides and pyranoanthocyanins for the cultivar MB; and in all of the groups for CS wines.

The mean proportions of some anthocyanic forms were different between varieties, but the relations amongst anthocyanic groups seem to be characteristic of them (Table 2). The group of monoglucosides represented the highest proportion of all anthocyanins, ranging from 61.2 to 65.9% (MB) and from 56.5 to 62.2% (CS). These results are in agreement with those published by others authors for the same cultivars (Fanzone et al., 2010; González-Neves et al., 2007; Hermosín Gutiérrez, Sánchez-Palomo Lorenzo, & Vicario Espinosa, 2005; Puértolas, Hernández-Orte, Saldaña, Álvarez, & Raso, 2010). Considering the acylated derivatives, both varieties showed a similar proportion of acetyl-glucosides, whereas presented a significant difference with regard to coumaroyl-glucosides. These results are consistent with the literature (Fanzone et al., 2010; González-Neves et al., 2007; Monagas, Núñez, Bartolomé, & Gómez-Cordovés, 2003a).

As shown in Table 2, the malvidin was the most abundant anthocyanidin in MB and CS samples while the cyanidin derivatives showed the lowest proportion, confirming its behavior observed in previous studies (Cerezo, Cuevas, Winterhalter, García-Parrilla, & Troncoso, 2010; Fanzone et al., 2010; González-Neves et al., 2007).

Pyranoanthocyanins are of interest for winemakers because they have high stability during the aging of red wines, are more resistant to elevated pH values and bisulphite bleaching than anthocyanins, and express more color than other pigments at the typical pH of wine (Monagas, Núñez, Bartolomé, & Gómez-Cordovés, 2003a). In our study, the MB and CS wines of high segment contained the highest levels of all derived pigments, which support the greater proportion of combined anthocyanins and polymeric pigments obtained by spectrophotometry (Table 1).

Taken together, these results indicate the great incidence of the main compounds responsible for wine color on the commercial value of wines.

3.3. Low molecular weight phenolic composition

Table 3 presents the concentration of the low molecular weight phenolic compounds, individually and grouped and the relative proportions of each group, in the wine samples analyzed. Within the family of non-flavonoids, we identified 6 hydroxybenzoic acids/derivatives, 6 hydroxycinnamic acids/derivatives, 2 stilbenes, and 2 phenolic alcohols. While among the flavonoids, we found 8 flavanols, 10 flavonols, and 3 dihydroflavonols.

Coincident with the results obtained so far, there was a trend towards a higher content of non-anthocyanin phenolics with increasing the commercial value of wines, showing significant differences between varieties for some groups of compounds (Table 3). Flavonoids were the most abundant fraction (mean, 78.1% in MB and 72.7% in CS) compared to non-flavonoids (mean, 21.9% in MB and 27.3% in CS), as reported by other authors (Fanzone et al., 2010; Granato et al., 2011; Monagas et al., 2005). With regard to the non-flavonoids, hidroxybenzoic acids/derivatives and phenolic alcohols were the most abundant groups found in our samples, without significant differences among price segments for both varieties. Gallic acid showed by far the highest concentration of all benzoic derivatives (mean, 16.2 mg/L in MB and 17.6 mg/L in CS), and tyrosol was the main phenolic alcohol found (mean, 22.2 mg/L in MB and 23.5 mg/L in CS).

The hydroxycinnamic acids quantified in our wines were *trans*-caffeic and *trans*-*p*-coumaric acids, being CS richer than MB (Table 3). Analyzing their precursors (caftaric and coutaric acids), we observed a higher content of these compounds than of the free acids in all of the wines evaluated, according to other authors (Puértolas et al., 2010; Sáenz-Navajas, Tao, Dizy, Ferreira, & Fernández-Zurbano, 2010b). In addition, CS wines of high segment presented a greater content of these precursors compared with wines of lesser commercial value.

Stilbenes were the minority non-flavonoid group in the wines analyzed, showing higher concentrations in MB compared to CS wines. These differences may be due not only to the grape variety but also to fungal infections, winemaking procedures, and weather conditions (Vitrac, Monti, Vercauteren, Deffieux, & Mérillon, 2002). In this work we detected *trans*- and *cis*-resveratrol glucoside, with a greater abundance of the *trans* isomer, in accordance with other authors (Monagas et al., 2005; Vitrac et al., 2002). Of particular

Table 2
Anthocyanins quantified in Malbec and Cabernet Sauvignon wines of different commercial value. Probability values for variety and price segment.

Compound	Malbec			Cabernet Sauvignon			Factor		
	Price segment						Variety	Segment	Variety × segment[c]
	High	Medium	Low	High	Medium	Low	p_{value}[d]		
Delphinidin-3-glucoside	$10.8^{b} \pm 1.5$	$9.2^{ab} \pm 0.9$	$6.5^{a} \pm 0.4$	$8.7^{a} \pm 0.4$	$8.9^{a} \pm 1.4$	$5.4^{a} \pm 0.7$			
Cyanidin-3-glucoside	$2.4^{b} \pm 0.4$	$1.7^{ab} \pm 0.1$	$1.3^{a} \pm 0.1$	$2.2^{ab} \pm 0.2$	$2.3^{b} \pm 0.4$	$1.2^{a} \pm 0.1$			
Petunidin-3-glucoside	$17.1^{b} \pm 1.4$	$14.2^{b} \pm 0.7$	$10.3^{a} \pm 0.5$	$10.9^{b} \pm 0.2$	$10.5^{b} \pm 0.9$	$6.8^{a} \pm 0.6$			
Peonidin-3-glucoside	$11.7^{b} \pm 0.8$	$10.2^{ab} \pm 0.8$	$8.4^{a} \pm 0.5$	$9.4^{ab} \pm 0.2$	$10.1^{b} \pm 1.1$	$5.8^{a} \pm 0.6$			
Malvidin-3-glucoside	$73.0^{a} \pm 4.2$	$66.7^{a} \pm 4.3$	$58.9^{a} \pm 5.0$	$58.5^{b} \pm 5.2$	$54.5^{ab} \pm 4.2$	$41.9^{a} \pm 1.2$			
Total glucosylated	$115.0^{b} \pm 3.2$ (61.2)	$102.0^{ab} \pm 6.2$ (65.0)	$85.4^{a} \pm 6.1$ (65.9)	$89.7^{b} \pm 4.6$ (56.5)	$86.3^{b} \pm 3.6$ (62.2)	$61.1^{a} \pm 3.0$ (60.8)	<0.0001	<0.0001	0.2811
Delphinidin-3-(6″-acetyl)glucoside	$6.0^{b} \pm 0.8$	$3.7^{a} \pm 0.4$	$2.8^{a} \pm 0.3$	$4.5^{b} \pm 0.3$	$4.2^{b} \pm 0.5$	$2.8^{a} \pm 0.2$			
Cyanidin-3-(6″-acetyl)glucoside	$5.8^{b} \pm 0.7$	$4.3^{ab} \pm 0.7$	$2.4^{a} \pm 0.2$	$5.7^{b} \pm 0.8$	$3.5^{a} \pm 0.2$	$2.8^{a} \pm 0.3$			
Petunidin-3-(6″-acetyl)glucoside	$6.0^{b} \pm 0.3$	$4.5^{a} \pm 0.4$	$3.3^{a} \pm 0.4$	$5.2^{b} \pm 0.3$	$3.9^{ab} \pm 0.3$	$3.0^{a} \pm 0.2$			
Peonidin-3-(6″-acetyl)glucoside	$3.9^{a} \pm 0.7$	$3.3^{a} \pm 0.5$	$3.3^{a} \pm 0.4$	$3.8^{a} \pm 0.7$	$3.5^{a} \pm 0.3$	$2.4^{a} \pm 0.1$			
Malvidin-3-(6″-acetyl)glucoside	$9.7^{a} \pm 1.0$	$8.7^{a} \pm 0.9$	$9.3^{a} \pm 1.6$	$14.1^{a} \pm 3.4$	$10.7^{a} \pm 2.1$	$9.9^{a} \pm 0.9$			
Total acetylated	$31.5^{a} \pm 2.2$ (16.8)	$24.5^{a} \pm 2.9$ (15.6)	$21.2^{a} \pm 2.7$ (16.4)	$33.1^{b} \pm 4.8$ (20.9)	$25.8^{ab} \pm 1.8$ (18.6)	$21.0^{a} \pm 0.6$ (20.9)	0.5280	<0.0001	0.8465
Delphinidin-3-(6″-*p*-coumaroyl)glucoside	$1.8^{a} \pm 0.1$	$1.6^{a} \pm 0.2$	$1.3^{a} \pm 0.2$	$1.6^{b} \pm 0.2$	$1.2^{ab} \pm 0.1$	$0.9^{a} \pm 0.1$			
Cyanidin-3-(6″-*p*-coumaroyl)glucoside	$0.20^{a} \pm 0.04$	$0.13^{a} \pm 0.02$	$0.15^{a} \pm 0.02$	$0.20^{a} \pm 0.01$	$0.17^{a} \pm 0.03$	$0.20^{a} \pm 0.04$			
Petunidin-3-(6″-*p*-coumaroyl)glucoside	$0.7^{a} \pm 0.1$	$0.6^{a} \pm 0.1$	$0.6^{a} \pm 0.1$	$0.15^{a} \pm 0.04$	$0.33^{a} \pm 0.03$	$0.13^{a} \pm 0.03$			
Peonidin-3-(6″-*p*-coumaroyl)glucoside	$3.1^{a} \pm 0.7$	$2.0^{a} \pm 0.5$	$1.5^{a} \pm 0.4$	$2.6^{b} \pm 0.4$	$2.3^{b} \pm 0.3$	$0.9^{a} \pm 0.1$			
Malvidin-3-(6″-*p*-coumaroyl)glucoside *cis*	$0.47^{a} \pm 0.10$	$0.30^{a} \pm 0.04$	$0.28^{a} \pm 0.04$	$0.30^{a} \pm 0.01$	$0.37^{a} \pm 0.12$	$0.13^{a} \pm 0.06$			
Malvidin-3-(6″-*p*-coumaroyl)glucoside *trans*	$7.6^{a} \pm 0.9$	$5.4^{a} \pm 0.6$	$5.6^{a} \pm 1.1$	$4.6^{ab} \pm 0.1$	$4.7^{b} \pm 0.4$	$3.1^{a} \pm 0.3$			
Total coumaroylated	$13.9^{a} \pm 1.2$ (7.4)	$10.0^{a} \pm 1.1$ (6.4)	$9.3^{a} \pm 1.7$ (7.2)	$9.4^{b} \pm 0.3$ (5.9)	$9.1^{b} \pm 0.2$ (6.6)	$5.3^{a} \pm 0.5$ (5.3)	0.0001	0.0001	0.0510
Vitisin A	$12.4^{b} \pm 2.5$	$9.3^{ab} \pm 1.7$	$5.2^{a} \pm 0.5$	$12.4^{b} \pm 0.8$	$7.2^{a} \pm 1.2$	$6.0^{a} \pm 1.0$			
Vitisin B	$8.0^{b} \pm 0.5$	$5.6^{a} \pm 0.5$	$4.2^{a} \pm 0.4$	$6.7^{b} \pm 0.1$	$5.1^{b} \pm 0.5$	$3.4^{a} \pm 0.3$			
Peonidin-3-glucoside pyruvate	$3.2^{b} \pm 0.6$	$2.2^{ab} \pm 0.3$	$1.4^{a} \pm 0.1$	$2.9^{b} \pm 0.1$	$2.1^{ab} \pm 0.4$	$1.5^{a} \pm 0.2$			
Malvidin-3-glucoside-ethyl-epicatechin	$3.3^{b} \pm 0.2$	$2.4^{a} \pm 0.2$	$1.9^{a} \pm 0.2$	$3.3^{b} \pm 0.1$	$2.1^{ab} \pm 0.3$	$1.5^{a} \pm 0.2$			
Malvidin-3-glucoside-4-vinylphenol	$0.8^{a} \pm 0.3$	$0.9^{a} \pm 0.2$	$0.9^{a} \pm 0.2$	$1.4^{a} \pm 0.5$	$0.9^{a} \pm 0.1$	$0.7^{a} \pm 0.2$			
Total derivatives	$27.7^{b} \pm 3.9$ (14.7)	$20.4^{ab} \pm 2.6$ (13.0)	$13.6^{a} \pm 1.2$ (10.5)	$26.6^{b} \pm 0.3$ (16.8)	$17.5^{a} \pm 2.3$ (12.6)	$13.0^{a} \pm 1.4$ (12.9)	0.2184	<0.0001	0.6610
Total anthocyanins	$188.0^{b} \pm 7.2$	$156.9^{ab} \pm 11.0$	$129.5^{a} \pm 11.5$	$158.7^{b} \pm 9.5$	$138.7^{b} \pm 2.9$	$100.5^{a} \pm 4.4$	<0.0001	<0.0001	0.5378

All data are expressed as the arithmetic mean (mg/L) ± standard error (n = 5). Different letters in the same row indicate significant differences among price segments for the same variety (Tukey HSD, $p < 0.05$). Values between parentheses refer to the relationship (%) between anthocyanin derivatives by acylation and total anthocyanins.

[c] Interaction effect between variety and price segment.

[d] Considered significant when $p_{value} < 0.05$.

Table 3
Low molecular weight phenolic compounds quantified in Malbec and Cabernet Sauvignon wines of different commercial value. Probability values for variety and price segment.

Compound	Malbec			Cabernet Sauvignon			Factor		
	Price segment						Variety	Segment	Variety × segment[d]
	High	Medium	Low	High	Medium	Low	p_{value}[e]		
Non-flavonoid phenolics									
Gallic acid	$16.6^{a} \pm 0.6$	$14.8^{a} \pm 1.1$	$17.1^{a} \pm 0.9$	$18.5^{a} \pm 0.3$	$17.3^{a} \pm 0.6$	$17.1^{a} \pm 0.4$			
Protocatechuic acid	$1.8^{a} \pm 0.1$	$1.6^{a} \pm 0.1$	$1.7^{a} \pm 0.1$	$2.2^{a} \pm 0.1$	$2.0^{a} \pm 0.1$	$2.1^{a} \pm 0.1$			
Syringic acid	$2.9^{b} \pm 0.1$	$2.0^{a} \pm 0.1$	$2.1^{a} \pm 0.2$	$1.8^{a} \pm 0.1$	$1.7^{a} \pm 0.1$	$1.6^{a} \pm 0.1$			
Gentisic acid	$0.88^{a} \pm 0.02$	$0.98^{a} \pm 0.04$	$0.90^{a} \pm 0.04$	$0.93^{a} \pm 0.05$	$0.96^{a} \pm 0.07$	$0.94^{a} \pm 0.02$			
Methyl gallate	$3.5^{a} \pm 0.3$	$2.6^{a} \pm 0.2$	$2.7^{a} \pm 0.2$	$2.3^{a} \pm 0.1$	$2.5^{a} \pm 0.2$	$2.6^{a} \pm 0.1$			
Ethyl gallate	$8.0^{a} \pm 0.5$	$7.2^{a} \pm 0.5$	$7.6^{a} \pm 0.7$	$9.7^{a} \pm 0.7$	$7.9^{a} \pm 0.5$	$7.6^{a} \pm 0.4$			
Hydroxybenzoic acids/derivatives	$33.7^{a} \pm 1.0$ (8.2)	$29.2^{a} \pm 1.6$ (8.1)	$32.1^{a} \pm 1.7$ (9.2)	$35.4^{a} \pm 1.1$ (10.2)	$32.4^{a} \pm 1.0$ (10.5)	$31.9^{a} \pm 0.7$ (10.7)	0.1255	0.0195	0.3802
trans-Caftaric acid	$4.0^{a} \pm 0.3$	$3.5^{a} \pm 0.3$	$3.1^{a} \pm 0.3$	$8.2^{b} \pm 0.1$	$5.7^{ab} \pm 0.6$	$3.4^{a} \pm 0.4$			
cis-Coutaric acid	$0.82^{a} \pm 0.07$	$0.94^{a} \pm 0.07$	$0.88^{a} \pm 0.04$	$2.25^{b} \pm 0.03$	$1.56^{a} \pm 0.14$	$1.32^{a} \pm 0.06$			
trans-Coutaric acid	$3.0^{a} \pm 0.2$	$3.2^{a} \pm 0.3$	$3.0^{a} \pm 0.3$	$7.3^{c} \pm 0.3$	$5.2^{b} \pm 0.5$	$3.3^{a} \pm 0.2$			
trans-Fertaric acid	$3.4^{a} \pm 0.2$	$3.0^{a} \pm 0.1$	$3.0^{a} \pm 0.1$	$2.95^{a} \pm 0.03$	$3.08^{a} \pm 0.06$	$2.86^{a} \pm 0.15$			
trans-Caffeic acid	$2.6^{a} \pm 0.1$	$2.9^{a} \pm 0.3$	$3.3^{a} \pm 0.3$	$3.4^{a} \pm 0.3$	$3.6^{a} \pm 0.3$	$3.7^{a} \pm 0.3$			
trans-*p*-Coumaric acid	$3.0^{a} \pm 0.2$	$4.2^{ab} \pm 0.5$	$5.0^{b} \pm 0.6$	$4.1^{a} \pm 0.2$	$4.4^{a} \pm 0.3$	$4.5^{a} \pm 0.4$			
Hydroxycinnamic acids/derivatives	$16.8^{a} \pm 0.5$ (4.1)	$17.7^{a} \pm 0.4$ (4.9)	$18.3^{a} \pm 0.4$ (5.3)	$28.2^{c} \pm 0.8$ (8.1)	$23.5^{b} \pm 0.9$ (7.6)	$19.1^{a} \pm 0.2$ (6.3)	<0.0001	<0.0001	<0.0001
trans-Resveratrol-3-glucoside	$4.1^{b} \pm 0.3$	$2.0^{a} \pm 0.2$	$2.1^{a} \pm 0.2$	$1.8^{a} \pm 0.1$	$1.9^{a} \pm 0.2$	$1.8^{a} \pm 0.2$			
cis-Resveratrol-3-glucoside	$3.1^{b} \pm 0.2$	$1.8^{a} \pm 0.2$	$1.9^{a} \pm 0.1$	$1.3^{a} \pm 0.1$	$1.2^{a} \pm 0.1$	$1.3^{a} \pm 0.1$			
Stilbenes	$7.2^{b} \pm 0.5$ (1.7)	$3.8^{a} \pm 0.3$ (1.1)	$4.0^{a} \pm 0.2$ (1.1)	$3.1^{a} \pm 0.1$ (0.9)	$3.1^{a} \pm 0.2$ (1.0)	$3.1^{a} \pm 0.2$ (1.0)	<0.0001	<0.0001	<0.0001
Tyrosol	$22.1^{a} \pm 1.5$	$21.4^{a} \pm 1.3$	$23.2^{a} \pm 1.1$	$23.4^{a} \pm 0.5$	$22.9^{a} \pm 1.5$	$24.2^{a} \pm 1.5$			
Tryptophol	$4.6^{a} \pm 0.3$	$4.3^{a} \pm 0.2$	$5.8^{b} \pm 0.3$	$3.4^{a} \pm 0.1$	$3.6^{a} \pm 0.4$	$3.6^{a} \pm 0.3$			
Alcohols/related compounds	$26.7^{a} \pm 1.5$ (6.5)	$25.7^{a} \pm 1.2$ (7.2)	$29.0^{a} \pm 1.3$ (8.4)	$26.8^{a} \pm 0.3$ (7.7)	$26.5^{a} \pm 1.8$ (8.6)	$27.8^{a} \pm 1.7$ (9.3)	0.9019	0.2593	0.7452
Total non-flavonoids	$84.4^{a} \pm 2.7$ (20.5)	$76.4^{a} \pm 2.5$ (21.3)	$83.4^{a} \pm 2.5$ (24.0)	$93.5^{b} \pm 1.6$ (26.9)	$85.5^{a} \pm 1.3$ (27.7)	$81.9^{a} \pm 1.9$ (27.4)	0.0049	0.0039	0.0267
Flavonoid phenolics									
(+)-Catechin	$33.6^{a} \pm 2.5$	$33.6^{a} \pm 3.3$	$34.2^{a} \pm 1.3$	$32.0^{a} \pm 2.7$	$35.5^{a} \pm 2.9$	$35.8^{a} \pm 2.3$			
(−)-Epicatechin	$15.6^{a} \pm 0.6$	$19.2^{ab} \pm 1.0$	$20.9^{b} \pm 1.5$	$30.8^{b} \pm 2.0$	$21.1^{a} \pm 1.1$	$22.6^{a} \pm 1.2$			
Procyanidin dimer 1	$7.3^{b} \pm 0.4$	$5.8^{a} \pm 0.2$	$7.4^{b} \pm 0.5$	$8.7^{b} \pm 0.3$	$5.3^{a} \pm 0.4$	$5.2^{a} \pm 0.4$			
Procyanidin dimer 2	$53.9^{b} \pm 2.6$	$43.3^{a} \pm 1.1$	$45.6^{a} \pm 1.9$	$55.4^{b} \pm 1.9$	$43.5^{a} \pm 0.4$	$44.1^{a} \pm 2.1$			
Procyanidin trimer 1	$15.1^{a} \pm 1.3$	$15.0^{a} \pm 0.5$	$12.5^{a} \pm 0.8$	$16.0^{b} \pm 0.2$	$12.5^{a} \pm 0.9$	$10.5^{a} \pm 0.6$			
Procyanidin trimer 2	$5.7^{a} \pm 0.3$	$5.1^{a} \pm 0.5$	$5.5^{a} \pm 0.2$	$6.8^{a} \pm 0.4$	$5.9^{a} \pm 0.4$	$6.9^{a} \pm 0.8$			
Procyanidin trimer 3	$7.7^{b} \pm 0.3$	$5.6^{a} \pm 0.7$	$5.5^{a} \pm 0.5$	$7.7^{a} \pm 0.1$	$8.7^{a} \pm 0.6$	$7.9^{a} \pm 0.3$			
Procyanidin trimer 4	$12.2^{b} \pm 0.5$	$9.8^{a} \pm 0.5$	$8.6^{a} \pm 0.4$	$8.5^{b} \pm 0.2$	$7.9^{ab} \pm 0.2$	$7.2^{a} \pm 0.2$			
Flavanols	$151.1^{a} \pm 3.7$ (36.7)	$137.4^{a} \pm 5.6$ (38.2)	$140.2^{a} \pm 3.7$ (40.3)	$165.9^{b} \pm 1.2$ (47.6)	$140.4^{a} \pm 4.6$ (45.2)	$140.2^{a} \pm 5.5$ (47.1)	0.1229	0.0004	0.2678
Myricetin-3-glucuronide	$9.6^{a} \pm 0.7$	$9.1^{a} \pm 0.4$	$8.0^{a} \pm 1.0$	$6.9^{a} \pm 0.1$	$7.9^{a} \pm 0.4$	$7.1^{a} \pm 0.4$			
Myricetin-3-galactoside	$3.9^{a} \pm 0.2$	$3.4^{a} \pm 0.2$	$3.6^{a} \pm 0.2$	$3.3^{a} \pm 0.1$	$3.2^{a} \pm 0.1$	$3.1^{a} \pm 0.2$			
Myricetin-3-glucoside	$14.5^{b} \pm 1.0$	$8.4^{a} \pm 0.5$	$8.0^{a} \pm 0.7$	$6.8^{a} \pm 0.3$	$6.3^{a} \pm 0.1$	$6.5^{a} \pm 0.5$			
Quercetin-3-glucuronide	$10.9^{b} \pm 0.9$	$7.2^{a} \pm 0.6$	$5.7^{a} \pm 0.3$	$9.2^{b} \pm 0.2$	$7.0^{ab} \pm 0.6$	$6.4^{a} \pm 0.7$			
Quercetin-3-glucoside	$8.7^{b} \pm 0.5$	$6.5^{a} \pm 0.5$	$5.6^{a} \pm 0.5$	$7.4^{b} \pm 0.3$	$6.7^{ab} \pm 0.3$	$5.7^{a} \pm 0.5$			
Quercetin-3-rhamnoside	$4.6^{b} \pm 0.5$	$5.0^{b} \pm 0.5$	$1.9^{a} \pm 0.2$	$2.6^{a} \pm 0.2$	$5.0^{c} \pm 0.2$	$3.5^{b} \pm 0.2$			
Isorhamnetin-3-glucoside	$11.0^{b} \pm 0.6$	$7.3^{a} \pm 0.7$	$9.1^{ab} \pm 0.8$	$10.5^{b} \pm 0.4$	$7.4^{a} \pm 0.8$	$6.2^{a} \pm 0.3$			
Syringetin-3-glucoside	$7.2^{a} \pm 0.5$	$5.8^{a} \pm 0.4$	$5.7^{a} \pm 0.7$	$7.4^{b} \pm 0.2$	$5.6^{a} \pm 0.2$	$5.7^{a} \pm 0.2$			
Naringenin	$3.8^{a} \pm 0.3$	$3.0^{a} \pm 0.3$	$2.8^{a} \pm 0.1$	$5.2^{b} \pm 0.2$	$3.3^{a} \pm 0.2$	$3.6^{a} \pm 0.1$			
Kaempferol	$13.1^{a} \pm 1.1$	$11.9^{a} \pm 0.9$	$9.8^{a} \pm 0.9$	$8.0^{a} \pm 0.1$	$8.8^{a} \pm 0.4$	$7.8^{a} \pm 0.4$			
Flavonols	$87.3^{b} \pm 1.8$ (21.3)	$67.6^{a} \pm 2.0$ (18.9)	$60.2^{a} \pm 2.2$ (17.4)	$67.2^{b} \pm 0.2$ (19.3)	$61.2^{ab} \pm 1.6$ (19.7)	$55.5^{a} \pm 1.5$ (18.7)	<0.0001	<0.0001	0.0003
Dihydroquercetin-3-rhamnoside	$12.6^{b} \pm 0.9$	$11.1^{ab} \pm 0.6$	$9.1^{a} \pm 0.5$	$4.7^{a} \pm 0.2$	$4.9^{a} \pm 0.1$	$4.5^{a} \pm 0.4$			
Dihydrokaempferol-3-glucoside	$26.9^{b} \pm 1.8$	$22.9^{ab} \pm 1.8$	$18.6^{a} \pm 1.4$	$9.6^{ab} \pm 0.5$	$10.6^{b} \pm 0.4$	$8.5^{a} \pm 0.3$			
Dihydroquercetin-3-glucoside	$48.9^{a} \pm 3.7$	$44.3^{a} \pm 3.0$	$36.2^{a} \pm 3.7$	$7.4^{a} \pm 0.2$	$7.6^{a} \pm 0.2$	$7.0^{a} \pm 0.3$			
Dihydroflavonols	$88.4^{b} \pm 6.0$ (21.5)	$78.3^{ab} \pm 4.5$ (21.7)	$63.9^{a} \pm 4.9$ (18.3)	$21.7^{ab} \pm 1.0$ (6.2)	$23.1^{b} \pm 0.7$ (7.4)	$20.0^{a} \pm 0.7$ (6.8)	<0.0001	0.0081	0.0248
Total flavonoids	$326.8^{b} \pm 7.0$ (79.5)	$283.3^{a} \pm 10.1$ (78.7)	$264.3^{a} \pm 8.3$ (76.0)	$254.8^{b} \pm 0.5$ (73.1)	$224.7^{a} \pm 5.7$ (72.3)	$215.7^{a} \pm 3.9$ (72.6)	<0.0001	<0.0001	0.2548
Total non-anthocyanins phenolics	$411.2^{b} \pm 8.2$	$359.7^{a} \pm 11.1$	$347.7^{a} \pm 9.2$	$348.3^{b} \pm 1.2$	$310.2^{a} \pm 4.8$	$297.6^{a} \pm 4.5$	<0.0001	<0.0001	0.6030

All data are expressed as the arithmetic mean (mg/L) ± standard error (n = 5). Different letters in the same row indicate significant differences among price segments for the same variety (Tukey HSD, p<0,05). Values between parentheses refer to the relationship (%) between phenolic groups and total phenolics.

[d] Interaction effect between variety and price segment.

[e] Considered significant when $p_{value}<0.05$.

interest, was the high total concentration observed in MB wines of high segment (7.2 mg/L) compared to the other segments. This could be explained by a possible elevated content in grapes. A previous study by our workgroup conducted in the Valle de Uco region (Mendoza) showed a high content of stilbenes in Malbec grape skins (Fanzone, Zamora, Jofré, Assof, & Peña-Neira, 2011). It is important to note that premium Malbec wines are mainly produced in Mendoza from grapes grown in high altitudes, such as Valle de Uco, where agroecological conditions could favor the synthesis of stilbenes.

Flavanols were the major class of non-anthocyanin phenolics present in the wines studied (mean, 38.4% in MB and 46.6% in CS). Also in this case, the amount of flavanols justifies the significant differences observed among wines of different commercial value, especially in CS samples (Table 3). The high segment wines showed the highest levels of these compounds, mainly oligomers (dimers and trimers), confirming the results obtained with regard to the proportion of polymeric pigments (%CP) in CS wines of upper commercial value (Table 1). In both varieties evaluated, the (+)-catechin levels were higher than those of (−)-epicatechin. These results are in agreement with those presented in the literature for the same varieties (Fanzone et al., 2010; Granato et al., 2011; Monagas, Gómez-Cordovés, Bartolomé, Laureano, & Da Silva, 2003b). On the other hand, the content of dimers and trimers was lower than the monomers in all samples, with the exception of compound called "procyanidin dimer 2" that showed greater levels (Table 3).

Concerning to flavonols, their importance in red wines lies in its health properties and its contribution to the color by the phenomenon of copigmentation (Ribéreau-Gayon et al., 2000). The total content in MB and CS samples ranged from 60.2 to 87.3 mg/L and from 55.5 to 67.2 mg/L, respectively, indicating a significant difference between varieties (Table 3). These elevated values for both varieties could be explained by the climatic conditions of Mendoza, characterized by high sunlight radiation during the ripening period of grapes, which appears to be associated with an increased accumulation of flavonols (Makris, Kallithraka, & Kefalas, 2006). Analyzing the distribution of flavonol structures, we can notice different proportions between varieties, in agreement to Mattivi, Guzzon, Vrhovsek, Stefanini, and Velasco (2006). In the pattern of MB wines, the main flavonol was myricetin (mean = 31.7%), followed by quercetin (25.8%), kaempferol (16.3%), isorhamnetin (12.9%), syringetin (8.8%), and naringenin (4.5%), whereas in CS, quercetin (29.1%) was the main flavonol, followed by myricetin (27.9%), kaempferol (13.5%), isorhamnetin (13.0%), syringetin (10.2%), and naringenin (6.5%). Again, following the same tendency observed in other phenolic groups, the level of most of the flavonols was higher in high segment wines showing their positive impact on the commercial value. The particular higher concentration in high-end wines could be related to a greater potential in grapes. In a recent study by Berli, Fanzone, Piccoli, and Bottini (2011), it was observed a significant effect of solar UV-B radiation by promoting the flavonol synthesis in grapes grown in Valle de Uco (Mendoza), a region primarily intended for production of premium wines.

Finally, we want to highlight the presence of dihydroflavonols (dihydroquercetin-3-rhamnoside, dihydrokaempferol-3-glucoside and dihydroquercetin-3-glucoside) in all of the samples analyzed, showing levels 3-fold higher in MB compared to CS (Table 3). According to literature, these compounds contribute to a smaller fraction of total wine flavonoids, and they play functional roles in grape berries (Landrault et al., 2002; Vitrac et al., 2002). However, in previous studies by our research group have been detected elevated contents in Malbec grapes and wines from Mendoza, which could represent a distinctive feature of this variety (Berli et al., 2011; Fanzone et al., 2011; Fanzone et al., 2010). Evaluating the influence of these compounds on the range of wine, only in the case of MB it was observed the same tendency found so far, while CS wines of medium segment showed the highest levels of dihydroflavonols (Table 3).

3.4. Distribution of flavanols according to polymerization degree

Fig. 1 depicts the flavanol content, determined by the vanillin reaction, of MB and CS wine fractions (monomeric, oligomeric, and polymeric) obtained by C_{18} Sep-Pak cartridges. Sun, Leandro, Ricardo da Silva, and Spranger (1998a) indicate that the monomeric fraction (FI) consists only of (+)-catechin, (−)-epicatechin and (−)-epicatechin-3-gallate, whereas the FII fraction is formed by procyanidin dimers, trimers and tetramers, and FIII fraction is composed of polymeric proanthocyanidins (over 4 units). For all red wines analyzed, polymeric proanthocyanidins were predominant (94.9% in MB, 94.7% in CS), followed by oligomeric fraction (4.5% in MB, 4.6% in CS), and monomeric flavanols were presented in the lowest concentration (0.6% in MB, 0.7% in CS).

It is interesting to note the no significant differences found in the content of FI and FII among wines of different commercial value. By contrast, the polymeric fraction tended to increase with the commercial value of wines, especially in CS where the high segment samples showed significantly higher content compared to the rest (Fig. 1).

As seen previously with other parameters, when analyze the pooled data of the wines, we observed a higher content of all fractions in CS samples compared to MB. This could be supported by a greater level of monomers and oligomers determined by HPLC (Table 3) and a larger molar concentration of flavanols by *p*-dimethylaminocinnamaldehyde assay (Table 1), observed in high-end CS wines.

The relative content of the various extractable fractions obtained in this work coincides with data reported in other studies (Cosme, Ricardo-Da-Silva, & Laureano, 2009; Monagas, Gómez-Cordovés, Bartolomé, Laureano, & Da Silva, 2003b). Nevertheless, the levels observed in our study are higher than those reported by these authors in Spanish and Portuguese wines.

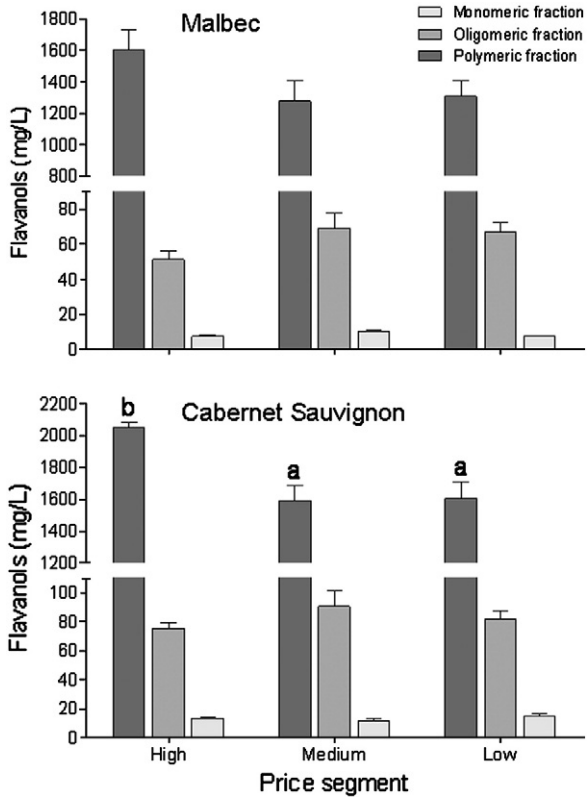

Fig. 1. Monomeric (FI), oligomeric (FII), and polymeric (FIII) fractions of flavanols in Malbec and Cabernet Sauvignon wines of different commercial value. Different letters within the polymeric fraction mean significant differences ($p<0.05$) among price segment for CS variety, according to a Tukey HSD test.

3.5. Characterization of polymeric proanthocyanidins by phloroglucinolysis

Table 4 shows the results of the analysis of proanthocyanidins, in MB and CS wines, by acid-catalysis in the presence of excess phloroglucinol. The total proanthocyanidin concentration measured by this method was lower than those obtained by the acid butanol assay (Table 1), because of incomplete depolymerization of phenolic material into known proanthocyanidin subunits (Kennedy, Ferrier, Harbertson, & Peyrot des Gachons, 2006). However, the tendencies observed by both methods in the wine samples were very similar, the proanthocyanidin concentration of wines being higher when the commercial value was greater, for the MB variety; and without differences found for CS.

This method also allows the mean degree of polymerization (mDP), the percentage of the different monomers and the molecular weight average (aMW) of proanthocyanidins to be measured. Our results indicate that mDP was higher in wines of upper commercial value, without significant differences between varieties ($p = 0.1520$). As was expected, the aMW followed a similar trend to the mDP. These data suggest that high quality wines possibly come from riper grapes with higher density, or from vines subjected to viticultural practices that would reduce the berry size, i.e. increasing the amount of skins proanthocyanidins (Herderich & Smith, 2005; Kennedy, Matthew, & Waterhouse, 2002; Kontoudakis, Esteruelas, et al., 2011a). Analyzing the distribution of monomers, no significant differences ($p > 0.05$) were found among MB and CS wines of different commercial value, with levels similar to those published by other authors (Canals et al., 2008; Kontoudakis, Esteruelas, et al., 2011a; Monagas, Gómez-Cordovés, Bartolomé, Laureano, & Da Silva, 2003b).

Taken together, these observations are consistent with the results described above, where MB and CS wines of high segment showed a higher concentration of polymeric proanthocyanidins (Fig. 1), and justify the strong influence of proanthocyanidin composition on the commercial value, and therefore on the final quality of wines.

3.6. Polysaccharides profile and content of different fractions

First, it is noteworthy that the chromatographic technique used in our study does not allow the separation of polysaccharides according to their chemical nature. Therefore, the fractions obtained of different molecular weight may contain polysaccharides from grapes, from microorganisms (yeasts and bacteria) or, more likely, a mixture of both. However, it is considered an appropriate technique for the purposes of determining its concentration in wines and assessing their impact on the commercial value.

Fig. 2 shows the distribution of the molecular weights of the polysaccharides in MB and CS wines of different price segments. We detected four peaks that eluted at approximately 18.5, 20.5, 23.2 and 25.2 min; and corresponded to fractions with a number average molecular weight of 450 kDa, between 830 and 380 kDa (F1); 150 kDa, between 380 and 70 kDa (F2); 50 kDa, between 75 and 25 kDa (F3); and 15 kDa, and between 25 and 5 kDa (F4). According to the literature these fractions might belong to yeast polysaccharides (mannans and MPs), as well as to other grape polysaccharides such as arabinogalactans, AGPs and RG-II dimers (Ayestarán et al., 2004). The polysaccharides profile observed in our study is similar to previously described in Merlot (Ducasse et al., 2010) and Tempranillo wines (Fernández et al., 2011).

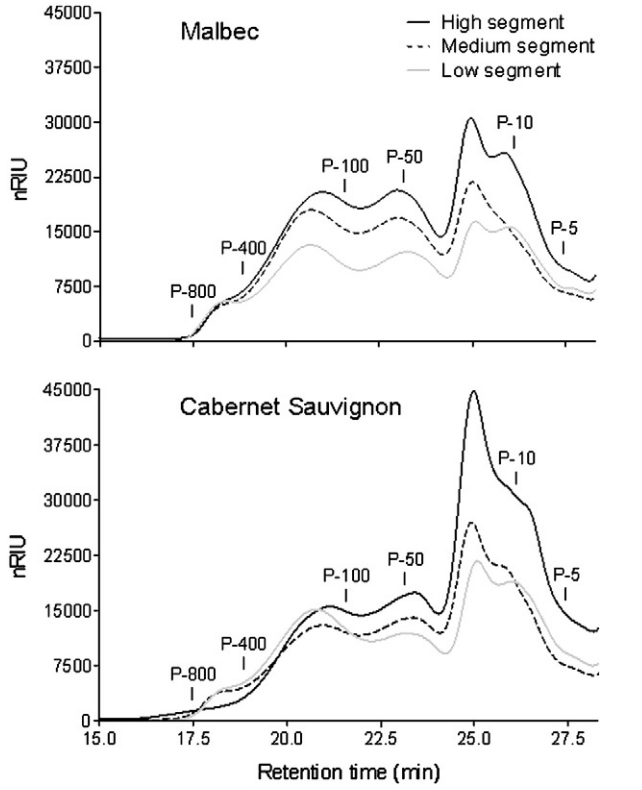

Fig. 2. Molecular weight distribution of polysaccharides soluble fractions, by HRSEC-RID, in Malbec and Cabernet Sauvignon wines of different commercial value. Elution times of pullulan standards (P-5 → P-800) are also shown.

The content of total polysaccharides and polysaccharides per fraction is shown in Table 5. For all samples, total polysaccharides ranged from 524.3 to 691.7 and from 571.3 to 776.5 mg/L in MB and CS, respectively. These values are in the range described in other studies for red varieties (Ayestarán et al., 2004; Fernández et al., 2011). In the pattern of MB wines, the main fraction was F4 (mean = 42.9%), followed by F2 (31.5%), F3 (21.9%), and F1 (3.8%); whereas in CS, the mean proportions changed, with F4 accounted

Table 4
Structural characteristics and composition of polymeric proanthocyanidins from Malbec and Cabernet Sauvignon wines of different commercial value.

Parameter	Malbec			Cabernet Sauvignon		
	Price segment					
	High	Medium	Low	High	Medium	Low
Total proanthocyanidins (mg/L)	$315.6^{b} \pm 17.9$	$232.6^{a} \pm 26.9$	$211.1^{a} \pm 6.7$	$284.6^{a} \pm 32.0$	$290.4^{a} \pm 11.6$	$242.8^{a} \pm 8.4$
mDP	$6.1^{b} \pm 0.4$	$5.0^{ab} \pm 0.2$	$4.5^{a} \pm 0.3$	$5.3^{a} \pm 0.4$	$4.5^{a} \pm 0.1$	$4.7^{a} \pm 0.3$
(+)-Catechin (%)	$13.3^{a} \pm 0.3$	$15.6^{b} \pm 0.7$	$14.2^{ab} \pm 0.5$	$13.8^{a} \pm 0.8$	$14.2^{a} \pm 0.2$	$14.1^{a} \pm 0.5$
(−)-Epicatechin (%)	$57.9^{a} \pm 0.6$	$57.4^{a} \pm 2.1$	$58.2^{a} \pm 1.3$	$58.6^{a} \pm 0.5$	$56.8^{a} \pm 2.2$	$56.2^{a} \pm 2.6$
(−)-Epigallocatechin (%)	$27.0^{a} \pm 0.9$	$25.3^{a} \pm 1.7$	$26.1^{a} \pm 1.2$	$25.5^{a} \pm 1.4$	$27.2^{a} \pm 2.2$	$27.8^{a} \pm 2.3$
(−)-Epicatechin-3-gallate (%)	$1.8^{a} \pm 0.1$	$1.8^{a} \pm 0.1$	$1.6^{a} \pm 0.1$	$2.2^{a} \pm 0.1$	$1.8^{a} \pm 0.2$	$2.0^{a} \pm 0.2$
aMW (Da)	$1770.7^{b} \pm 89.7$	$1450.7^{a} \pm 54.5$	$1312.9^{a} \pm 72.6$	$1561.5^{b} \pm 52.3$	$1302.0^{a} \pm 39.4$	$1323.8^{a} \pm 79.3$

All data are expressed as the arithmetic mean (mg/L) ± standard error ($n = 5$). mDP, mean degree of polymerization; aMW, molecular weight average. Different letters within the same row mean significant differences ($p < 0.05$) among price segments for the same variety, according to a Tukey HSD test.

Table 5
Polysaccharides in Malbec and Cabernet Sauvignon wines of different commercial value.

Polysaccharides	Malbec			Cabernet Sauvignon		
	Price segment					
	High	Medium	Low	High	Medium	Low
F1 (450 kDa)	$32.4^{b} \pm 0.7$ (4.7)	$20.0^{a} \pm 1.1$ (3.1)	$18.2^{a} \pm 1.8$ (3.5)	$18.8^{a} \pm 0.6$ (2.4)	$15.6^{a} \pm 1.0$ (2.8)	$14.4^{a} \pm 2.1$ (2.5)
F2 (150 kDa)	$215.5^{b} \pm 3.0$ (31.2)	$188.0^{ab} \pm 11.5$ (29.5)	$177.4^{a} \pm 10.2$ (33.8)	$146.2^{ab} \pm 3.2$ (18.8)	$132.4^{a} \pm 3.0$ (23.4)	$166.3^{b} \pm 12.2$ (29.1)
F3 (50 kDa)	$143.9^{a} \pm 8.9$ (20.8)	$138.2^{a} \pm 4.0$ (21.7)	$121.4^{a} \pm 4.2$ (23.2)	$150.6^{b} \pm 2.5$ (19.4)	$124.5^{a} \pm 4.8$ (22.0)	$112.8^{a} \pm 5.4$ (19.7)
F4 (15 kDa)	$299.9^{b} \pm 4.7$ (43.4)	$291.2^{b} \pm 16.2$ (45.7)	$207.3^{a} \pm 10.7$ (39.5)	$460.9^{b} \pm 6.6$ (59.4)	$292.4^{a} \pm 6.5$ (51.8)	$277.8^{a} \pm 17.4$ (48.6)
Total	$691.7^{b} \pm 7.1$	$637.4^{b} \pm 18.5$	$524.3^{a} \pm 15.4$	$776.5^{b} \pm 6.5$	$565.0^{a} \pm 8.3$	$571.3^{a} \pm 13.6$

All data are expressed as the arithmetic mean (mg/L) ± standard error (n = 5). Different letters within the same row mean significant differences ($p<0.05$) among price segments for the same variety, according to a Tukey HSD test. Values between parentheses refer to the relationship (%) between the fractions and total polysaccharides content.

for 53.2% of the total polysaccharides, followed by F2 (23.8%), F3 (20.4%), and F1 (2.6%). Once again, significant differences were observed among wines of different commercial value. For both varieties, the wines of high segment showed the highest level of these compounds, while the lowest content was observed in the low segment. These findings support the elevated values of proanthocyanidins and color parameters observed in premium wines, possibly due to the capacity of polysaccharides to enhance or inhibit tannin aggregation playing a significant role in color stability and wine aging (Terrier et al., 2009). In addition, premium wines generally come from riper grapes subjected to prolonged maceration times, increasing the extraction of these compounds into the wine. On the other hand, not all polysaccharides show the same behavior with respect to wines; their influence on wine characteristics will depend not only of the quantity of polysaccharidic compounds but also of their structure, composition, and distribution. Therefore, it is necessary a deep knowledge of the cultural and environmental factors that affect these parameters, to understand their interaction with the other compounds and to predict their expression into the wine, to reach a product with the wanted quality.

3.7. Descriptive sensory analysis

Sensory evaluations of wines were carried out to complement the chemical analyses and to verify if the existent differences among samples of different commercial value can be appreciated by the organoleptic perception.

In this study, there were no significant differences in the scores given by the judges for each attribute ($p>0.05$), indicating that all the panelists used all attributes reproducibly. From the ANOVA of the sensory descriptive data for the 30 wines (MB and CS), it was found that all of the attributes assessed by the panel differed significantly ($p<0.05$) across the samples of different commercial value (Table 6). With regard to color intensity, the scores were significantly higher toward increased commercial value of MB and CS wines, while for the gustatory attributes there were some differences between varieties. In the case of MB, the panel found no difference in bitterness and astringency between low and medium segments, observing the same pattern between medium and high segments for the rest of the attributes. Concerning CS wines, the tasters did not appreciate differences in bitterness, while the other parameters showed a similar trend to MB.

Analyzing the perception of astringency, the highest scores achieved by the wines of upper commercial value justify the observed level of proanthocyanidins (Table 4). According to Vidal et al. (2003) astringency augments when the degree of proanthocyanidin polymerization increases. Given that high-end wines presented higher proanthocyanidin concentration and that their proanthocyanidins also presented a higher mDP, it is logical that their astringency was greater too. However, these results do not agree with the high levels of polysaccharides found, which should diminish the astringency sensation (Vidal et al., 2004).

In general terms, these data obtained in the wine tasting were in good agreement with our previous analytical results. The wines of greater commercial value, with the best visual and gustatory scores, coinciding with higher levels of the phenolic parameters determined.

Table 6
Sensory attributes evaluated in Malbec and Cabernet Sauvignon wines of different commercial value.

Attribute	Malbec			Cabernet Sauvignon		
	Price segment					
	High	Medium	Low	High	Medium	Low
Color intensity	$8.8^{c} \pm 0.1$	$7.3^{b} \pm 0.1$	$6.4^{a} \pm 0.2$	$8.0^{c} \pm 0.2$	$7.0^{b} \pm 0.2$	$6.0^{a} \pm 0.3$
Fullness	$6.1^{b} \pm 0.2$	$5.5^{b} \pm 0.2$	$4.6^{a} \pm 0.2$	$6.1^{b} \pm 0.2$	$5.5^{ab} \pm 0.3$	$4.9^{a} \pm 0.2$
Bitterness	$5.4^{b} \pm 0.2$	$4.4^{a} \pm 0.2$	$4.2^{a} \pm 0.2$	$4.6^{a} \pm 0.3$	$4.2^{a} \pm 0.3$	$3.8^{a} \pm 0.3$
Astringency	$6.4^{b} \pm 0.3$	$5.3^{a} \pm 0.3$	$4.5^{a} \pm 0.2$	$6.3^{b} \pm 0.3$	$4.9^{a} \pm 0.2$	$4.6^{a} \pm 0.2$
Persistance	$7.3^{b} \pm 0.2$	$6.6^{b} \pm 0.2$	$5.7^{a} \pm 0.2$	$6.5^{b} \pm 0.2$	$6.1^{ab} \pm 0.3$	$5.2^{a} \pm 0.2$
Global quality	$7.2^{b} \pm 0.2$	$6.8^{b} \pm 0.3$	$6.0^{a} \pm 0.2$	$7.1^{b} \pm 0.3$	$6.7^{b} \pm 0.1$	$5.4^{a} \pm 0.3$

All data are expressed as the mean scores of 10 judges ± standard error (n = 5). Different letters within the same row mean significant differences among price segments for the same variety, according to a Tukey HSD test ($p<0.05$).

3.8. Classification of wines according to commercial value

In the present study, the different chemical composition observed among the wines analyzed, indicates the influence of the grape cultivar and other factors like environmental conditions, viticultural practices and winemaking techniques on the commercial quality. In order of classifying the samples according to commercial value, independently of variety, we employed the anthocyanin and non-anthocyanin profiles in a separate multivariate analysis. The main reason for this choice is due to the high correlation and dependence between these two groups of variables, as well as with the rest of the chemical parameters determined (seen through an exploratory statistical analysis). Moreover, it is interesting to evaluate the potential for classification of both groups in order to simplify the determinations in future studies.

In the multivariate analysis is first necessary to select appropriate variables for sample classification. To achieve this goal is required the elimination of redundant variables to avoid overfitting problems, by applying different methodologies of feature selection: forward selection, backward selection, principal component analysis or genetic algorithms (Kruzlicova et al., 2009). Canonical discriminant analysis (CDA) with backward selection method was carried out to provide a visualization of data in a reduced-dimension plot, using the information given in Tables 2 and 3. The first CDA, using individual anthocyanins as predictor variables, resulted in two discriminant functions (DF) containing 14 variables that accounted jointly for 100% of the total variance, with $p<0.05$ and statistical significance at 95% confidence level. The first function, assigned as DF1, accounted for 71.8% of total variability, while DF2 for 28.2%. Both functions showed Wilks' lambda values of 1.9×10^{-3} and 6.8×10^{-2}, respectively, indicating a

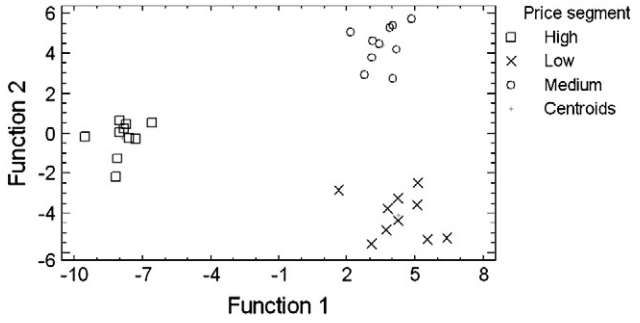

Fig. 3. Discriminant plot of anthocyanins for Malbec and Cabernet Sauvignon wines from Mendoza, according to price segment (n = 30).

satisfactory discrimination. The variables with higher incidence on DF1 were malvidin-3-glucoside, Vitisin A and cyanidin-3-glucoside, in a positive way, and Vitisin B, petunidin-3-(6″-acetyl)glucoside and peonidin-3-glucoside, in a negative way; while DF2 was strongly influenced by malvidin-3-glucoside and cyanidin-3-glucoside, in a positive way, and by Vitisin B and peonidin-3-glucoside, in a negative way. Fig. 3 depicts the distribution of wines samples in the plane defined by DF1 and DF2. Both functions allowed the classification of 100% of the wines studied according to commercial value. MB and CS wines of low and medium segments showed positive score of DF1, while high segments wines presented negative score. While regarding the DF2, MB and CS wines of medium segment showed positive score, low segment wines presented opposite behavior, and high segment wines exhibited intermediate values.

In the same framework described for anthocyanins, a second CDA, with low molecular weight phenolics as predictor variables, also resulted in two discriminant functions containing 20 variables, with only DF1 statistically significant. DF1 accounted for 99.1% of total variability, while DF2 for 0.9%. A scatter plot of the wines in the plane defined by these two functions is presented in Fig. 4, where there was a perfect prediction (100%) of the samples and a clear differentiation of wines by the commercial value. The main axis of differentiation (DF1) was strongly influenced by phenolic acids/derivatives (syringic, *trans*- and *cis*-coutaric, *p*-coumaric and gallic acids, methyl and ethyl gallates), *cis*-resveratrol-3-glucoside, flavanols ((+)-catechin, (−)-epicatechin, procyanidin dimers and trimers) and dihydroflavonols (dihydroquercetin-3-glucoside and dihydroquercetin-3-rhamnoside). All the samples were discriminated with this function, showing a negative score for MB and CS of high segment, and a positive score for the other segments. Additionally, DF2 was principally associated with flavanols and phenolic acids allowing the classification of low and high segment wines, in a positive way; and medium segment wines, in a negative way.

The discriminant analysis revealed that cyanidin, peonidin and malvidin non-acylated, and pyranoanthocyanins, as well as the phenolic acids, flavanols and dihydroflavonols, exerted a significant

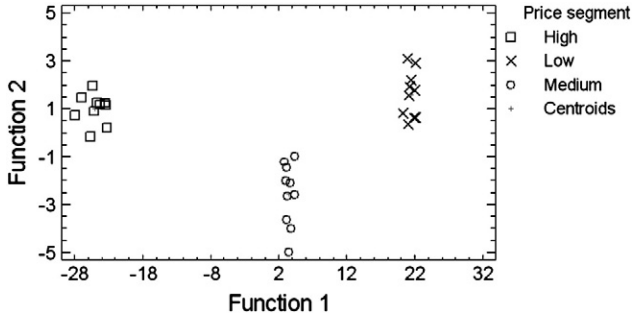

Fig. 4. Discriminant plot of non-anthocyanin phenolics for Malbec and Cabernet Sauvignon wines from Mendoza, according to price segment (n = 30).

influence in wine differentiation based on commercial value. However, the other phenolic groups had a rather minor impact. Given these results, we can select the phenolic variables for categorizing future samples, taking into account the complexity, time and cost of appropriate analytical technique.

4. Conclusions

A comprehensive study of chemical composition and sensory properties was conducted for Argentinean Malbec and Cabernet Sauvignon wines of different price segments. The data obtained provide an interesting insight, no reported so far, on the impact of phenolic and polysaccharidic composition in the final quality of the products and therefore in its market value. In general, there was a trend towards greater concentration of these with increasing the commercial value of wines. Particularly, we found that general phenolic composition, color-related compounds, main flavonoid groups and polysaccharides appear as relevant variables differing among segments and showing some differences between varieties. Additionally, the sensory wine description was in good agreement with the analytical results. The wines of greater commercial value, with the best visual and gustatory scores, coinciding with higher levels of the phenolic parameters determined.

Moreover, the successful classification of wine samples using polyphenolic data and multivariate methods has been demonstrated. We must be emphasized that, in spite of the low number of samples, discriminant analysis demonstrated the high potential of some compounds (anthocyanins, phenolic acids, flavanols and dihydroflavonols) for unambiguous differentiation and classification of wines according to the commercial value.

Therefore, the knowledge of chemical indices of quality in grapes and its expression in the wine is of great interest for wine producers, providing useful information to improve the final product. Further studies of this topic and of their relationship with viticultural management, environmental conditions, winemaking and aging process are necessary to produce wines of consistent styles for different consumers.

Acknowledgments

The authors are grateful to the Instituto Nacional de Tecnología Agropecuaria (INTA), projects AETA282831, AETA282821 and PTRMZASJ510071 for the economical support of this work, and to all nine wineries for providing the samples of this study. Special thanks are due to Bastián Bravo, and to the members of the sensory panel (INTA) for their technical assistance.

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