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ARTICLE

Phenolic Characterization of Malbec Wines from Mendoza Province (Argentina)

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Malbec is a wine grape variety that is now mainly produced in Mendoza and considered to be the emblematic cultivar of Argentina. Forty-four phenolic compounds, including hydroxybenzoic and hydroxycinnamic acids and different flavonoids, were identified and quantified in 61 monovarietal Malbec wines from 11 geographical zones of Mendoza province, using a reversed phase high-performance liquid chromatography system coupled to a diode array detector (HPLC-DAD). Among non-flavonoids, gallic, *cis*-caftaric, *trans*-coutaric, and caffeic acids presented the higher concentrations in all of the samples, whereas *trans*-resveratrol glucoside was present at concentrations from 0.6 to 1.3 mg/L. For the flavonoids, (+)-catechin and (−)-epicatechin presented the higher concentrations among flavan-3-ols with a ratio (+)-catechin/(−)-epicatechin from 1.3 to 2.1. An astilbin derivative and quercetin presented the higher concentrations for flavonols, whereas malvidin-3-glucoside and its derivatives were the major anthocyanins. For the first time the phenolic composition of Malbec wines from Mendoza province has been characterized.

KEYWORDS: Phenolic compound; Malbec; Mendoza; high-performance liquid chromatography; Argentina; wine

INTRODUCTION

Argentina is a New World wine producer and consumer country in the southern hemisphere, with 225846 ha of vineyards representing ∼3% of the global winegrape cultivation area. Mendoza province has ∼70% of all Argentinean vineyards, with 158833 ha. In Mendoza, there are around 22000 ha of Malbec (*Vitis vinifera* L.) vines, which account for 80% of the cultivated area for that variety in the country and ∼28% of total red wine grape production in Mendoza (*1*, *2*). This middle-maturing grape variety, of French origin, is well adapted to the soil and dry climate of Mendoza and produces wines with very deep color and high tannin concentration, with a fruity aroma and a particularly plum-like flavor. Today, Malbec is considered to be the emblematic cultivar of Argentina (*3*).

Phenolic compounds are one of the most important quality parameters of wines, and they contribute to organoleptic characteristics such as color, astringency, and bitterness. These compounds are also active in biochemical processes and have nutraceutical effects on human health, including antimicrobial, anticarcinogenic, and antioxidant properties (*4*−*6*). Additionally, phenolic compounds have been suggested as chemical markers to confirm cultivar authenticity and geographical origin in grapes and wines. In past years, the cultivar-characteristic profiles of monomeric anthocyanins have been widely used for the classification and differentiation of grape cultivars and monovarietal wines (*7*−*9*).

The phenolic profile of a wine depends on the grape variety, the geographical location of the vineyard, factors that affect the berry development (e.g., soil, weather, viticultural practices, etc.), grape maturity (*10*, *11*), and the winemaking techniques (*12*−*14*). The variation in phenolic composition among cultivation areas can be explained by the fact that the phenylpropanoid pathway enzymes are highly influenced by temperature and light, factors that also affect the photosynthetic process, which provides the biosynthetic precursors (mainly sugars) necessary for synthesis of phenolic compounds (*15*−*17*).

To our knowledge, there is to date no published information on the phenolic composition of Argentinean Malbec wines. Considering this, the aim of this work was to study the non-flavonoid and flavonoid compositions of commercial wines of this cultivar from different zones of Mendoza province.

MATERIALS AND METHODS

Wine Samples. Sixty-one Malbec wines produced at commercial scale were collected in bottles (750 mL), at the end of malolactic fermentation, directly from the 23 collaborating wineries to ensure the varietal purity of the samples. The wine samples belonged to 11 different zones of Mendoza (**Table 1**): 5 samples of zone 1 (East (Santa Rosa, Rivadavia, San Martín,

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Table 1. Geographical Characteristics of Different Zones of Mendoza

zone	description	altitude (m asl[a])	latitude	longitude
1	East	650	33° 05′ S	68° 28′ W
2	East Maipú	750	32° 58′ S	68° 45′ W
3	Maipú-Luján	910	33° 00′ S	68° 52′ W
4	West Luján	1000	33° 01′ S	68° 58′ W
5	Agrelo	970	33° 07′ S	68° 52′ W
6	Alto Agrelo	1100	33° 06′ S	68° 57′ W
7	Perdriel	940	33° 04′ S	68° 52′ W
8	Ugarteche	900	33° 13′ S	68° 52′ W
9	West Valle de Uco	1450	33° 24′ S	69° 17′ W
10	Center Valle de Uco	1050	33° 22′ S	69° 08′ W
11	San Carlos	1100	33° 43′ S	69° 07′ W

[a] m asl, meters above sea level.

and Junín)), 5 samples of zone 2 (East Maipú), 7 samples of zone 3 (Maipú-Luján), 5 samples of zone 4 (West Luján), 6 samples of zone 5 (Agrelo), 4 samples of zone 6 (Alto Agrelo), 5 samples of zone 7 (Perdriel), 6 samples of zone 8 (Ugarteche), 8 samples of zone 9 (West Valle de Uco), 5 samples of zone 10 (Center Valle de Uco), and 5 samples of zone 11 (San Carlos). All wines were pure monovarietals from the 2007 vintage. They were stored in darkness at 12−15 °C, and each wine bottle was opened immediately before the analysis.

Chemical Analyses. *Total Phenols, Anthocyanins, Tannins, and Other Chemical Parameters*. Absorbance measurements were made with a Perkin-Elmer UV−vis spectrophotometer model Lambda 25 (Perkin-Elmer Instruments, Hartford, CT).

Total phenols were determined by direct reading of the absorbance of the samples at 280 nm (*18*). Total phenols were expressed as milligrams of gallic acid equivalents per liter of sample (GAE, mg/L).

Total anthocyanins were measured by diluting wine samples with ethanol and hydrochloric acid. Briefly, two aliquots of this dilution were treated either with $NaHSO_3$ or with the same amount of water. Each aliquot was then analyzed at 520 nm (*18*). Total anthocyanins were expressed as milligrams per liter of malvidin-3-glucoside.

For total tannins, the analytical method applied was the acid butanol assay (*19*). This method is based on the acid-catalyzed oxidative cleavage of the C−C interflavanic bond of proanthocyanidins in butanol−HCl. Total tannins were expressed as milligrams per liter of catechin.

Gelatin index (GI) was measured using the methodology described by Glories (*20*). To two tubes with 10 mL of wine was added 1 mL of distilled water (total tannin) or 1 mL of 70 g/L gelatin solution (tannin precipitated with gelatin). After 3 days, the samples were centrifuged at 3500 rpm for 10 min (Rolco CM4080, Buenos Aires, Argentina). The supernatants were assayed to determine the tannin concentration (*19*). Gelatin index (%) was expressed as the relationship between tannin residual (difference among total wine tannin concentration and tannin after gelatin precipitation) and total tannin concentration.

Other chemical parameters measured in the samples were pH (by Altronix equipment TPX-1, Buenos Aires, Argentina), titratable acidity (g/L of tartaric acid) (*21*), degree of polymerization of condensed tannins (DMACH, *p*-dimethylaminocinnamaldehyde assay) (*22*), color intensity (CI), and hue values (*23*).

HPLC-DAD Analysis of Anthocyanins. The chromatographic system consisted of an HPLC equipped with a photodiode array detector model L-7455, intelligent pump model L-6200, and autosampler model L-7200 (Merck-Hitachi, Darmstadt, Germany). Separation was performed on a reverse-phase Nova-Pak C_{18} column (150 mm × 3.9 mm i.d., 4 μm) at room temperature (Waters Corp., Milford, MA). A gradient consisting of solvent A (water/formic acid, 90:10, v/v) and solvent B (acetonitrile) was applied as 0−23 min, 96−85% A and 4−15% B; 23−27 min, 85−80% A and 15−20% B; 27−43 min, 80−70% A and 20−30% B and followed by washing (methanol) and re-equilibration of the column. The flow rate was 1.1 mL/min from 0 to 23 min and 1.5 mL/min from 23 to 43 min. One hundred and fifty microliters of wine, previously filtered through a 0.45 μm pore size membrane, was injected onto the column. Photodiode array detection (DAD) was performed from 260 to 600 nm (*24*). Quantification was carried out by area measurements at 520 nm, and the anthocyanin content was expressed as malvidin-3-glucoside (Extrasynthese, Lyon, France), using a standard calibration curve.

HPLC-DAD Analysis of Low Molecular Weight Phenolic Compounds. An aliquot (50 mL) of wine from each bottle was extracted three times with 20 mL of ethyl ether and three times with 20 mL of ethyl acetate. The organic fractions were combined. The extracts were evaporated to dryness under vacuum at 30 °C. The residue was dissolved in 2 mL of methanol/water (1:1, v/v) and then filtered through a 0.45 μm pore size membrane, and 30 μL was injected into the HPLC-DAD system. The chromatographic system consisted of an HPLC equipped with a photodiode array detector model G1315B, quaternary pump model G1311A, and autosampler model G1329A (Agilent Technologies, Palo Alto, CA). A reverse-phase Nova-Pack C_{18} column (300 mm × 3.9 mm i.d., 4 μm) at 20 °C (Waters Corp.) was used for separation of the compounds. 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; 57−90 min, 10% A and 90% B isocratic, followed by washing (methanol) and re-equilibration of the column. The flow rate was 1.0 mL/min from 0 to 55 min and 1.2 mL/min from 55 to 90 min. Detection was performed by scanning from 210 to 360 nm with an acquisition speed of 1 s (*15*).

Qualitative and Quantitative Analysis. The identification of specific compounds was carried out by comparison of their spectra and retention time with those of standards. The standards were purchased from Sigma (St. Louis, MO): gallic, protocatechuic, syringic, *p*-coumaric, and caffeic acids; tyrosol, (+)-catechin, (−)-epicatechin, *trans*-resveratrol, myricetin, and quercetin. The flavonol glycosides, myricetin glycosides, *trans*-resveratrol glucoside (piceid), hydroxycinnamic acid esters, and the procyanidins for which no standards were available were identified by their retention time and spectral parameters, as reported by Peña-Neira et al. (*15*, *24*).

Quantitative determinations were made by using the external standard method with the 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. The compounds for which no standards were available were quantified with the curves of quercetin (flavonol glycosides, myricetin glycosides, and dihydroflavonols), *trans*-resveratrol (*trans*-resveratrol glucoside), caffeic acid (hydroxycinnamic acid esters and unknown compound), and (+)-catechin (procyanidins). All of the solvents were of HPLC grade and purchased from Merck (Darmstadt, Germany). All of the analyses were performed in duplicate.

Statistical Analysis. Means comparisons were analyzed by one-way analysis of variance (ANOVA) and Tukey's multiple-range tests (TMRT). A $p < 0.05$ was considered to be statistically significant. Canonical discriminant analyses (CDA) were performed to examine geographical differences in Malbec wines from Mendoza, using the chemical determinations, in which new variables, called canonical discriminant functions, were created to separate the zones. Statistical analysis was evaluated with Statgraphics Plus version 4.0 software (Copyright 1994−1999, Statistical Graphics Corp., Warrenton, VA).

RESULTS AND DISCUSSION

General Chemical Parameters. Table 2 presents the results of the general chemical parameters of the Malbec wines studied. Among all of the samples studied, titratable acidity varied from 5.1 to 6.1 g/L and pH from 3.5 to 3.8. These results show a low dispersion for these important parameters that influence not only the sensorial quality of wine but also the color intensity expression and the microbiology stability (*21*).

For all samples, total phenols ranged between 1932.0 and 3506.8 mg/L. These results are in agreement with those determined by Minussi et al. (*25*) for red wines from South America.

The total anthocyanins, color intensity, and hue values of the samples ranged from 261.1 to 802.8 mg/L, from 8.7 to 25.1, and from 48.4 to 65.4, respectively. The high dispersion of these results might be due to the influence of different factors (e.g., origin of wine samples or effect of agronomical and enological practices)

Table 2. Chemical Parameters (Mean ± SD) of Commercial Malbec Wines[a]

parameter	geographical zones of Mendoza (Argentina)										
	1 ($n = 5$)	2 ($n = 5$)	3 ($n = 7$)	4 ($n = 5$)	5 ($n = 6$)	6 ($n = 4$)	7 ($n = 5$)	8 ($n = 6$)	9 ($n = 8$)	10 ($n = 5$)	11 ($n = 5$)
titratable acidity (tartaric acid, g/L)	5.8 ± 0.5 a	5.4 ± 1.2 a	5.6 ± 0.6 a	6.1 ± 0.3 a	5.3 ± 1.3 a	5.6 ± 0.5 a	6.1 ± 0.8 a	5.1 ± 1.1 a	6.1 ± 1.1 a	5.6 ± 1.7 a	5.7 ± 1.5 a
pH	3.7 ± 0.2 a	3.6 ± 0.1 a	3.6 ± 0.2 a	3.5 ± 0.1 a	3.7 ± 0.2 a	3.8 ± 0.1 a	3.5 ± 0.1 a	3.7 ± 0.1 a	3.6 ± 0.1 a	3.7 ± 0.2 a	3.5 ± 0.1 a
TA (malvidin-3-glucoside, mg/L)	261.1 ± 61.1 a	462.8 ± 94.2 ab	575.6 ± 130.1 bc	631.3 ± 96.1 bc	566.8 ± 123.6 bc	656.9 ± 201.3 bc	534.5 ± 165.2 abc	619.8 ± 99.4 bc	802.8 ± 213.6 c	608.8 ± 58.0 bc	614.1 ± 185.0 bc
CI ($A_{420\ nm} + A_{520\ nm} + A_{620\ nm}$) × 10	8.7 ± 2.0 a	11.8 ± 2.5 a	14.9 ± 3.6 ab	19.5 ± 4.4 ab	14.4 ± 2.1 ab	19.5 ± 9.2 ab	17.6 ± 8.0 ab	16.2 ± 3.2 ab	25.1 ± 13.0 b	17.2 ± 5.7 ab	17.3 ± 7.8 ab
hue values ($A_{420\ nm}/A_{520\ nm}$) × 100	65.4 ± 10.7 b	54.6 ± 4.9 ab	54.8 ± 6.2 ab	50.6 ± 4.2 a	54.1 ± 4.5 ab	56.5 ± 9.7 ab	48.4 ± 3.6 a	57.7 ± 4.3 ab	53.8 ± 4.5 ab	54.1 ± 6.6 ab	50.4 ± 8.3 a
TP (GAE, mg/L)	1932.0 ± 357.3 a	2170.8 ± 404.5 a	2801.2 ± 438.3 ab	2924.5 ± 232.1 ab	2430.0 ± 355.5 a	3175.3 ± 539.1 ab	2722.9 ± 744.6 ab	2797.8 ± 411.3 ab	3506.8 ± 1080.1 b	2947.9 ± 481.2 ab	2787.8 ± 528.4 ab
TT (catechin, mg/L)	3169.3 ± 780.3 ab	2782.9 ± 298.6 a	3821.1 ± 697.7 ab	3990.1 ± 1315.5 ab	3139.7 ± 581.6 ab	4431.4 ± 1339.2 ab	4067.7 ± 1145.7 ab	4162.6 ± 1036.6 ab	4943.3 ± 1525.1 b	4346.9 ± 982.8 ab	4291.4 ± 1046.9 ab
DMACH	10.6 ± 1.0 a	11.6 ± 1.3 a	11.4 ± 1.0 a	12.4 ± 6.7 a	11.9 ± 3.2 a	12.4 ± 2.2 a	10.7 ± 0.4 a	10.7 ± 2.0 a	10.4 ± 2.7 a	9.9 ± 2.4 a	11.3 ± 3.8 a
GI (%)	79.8 ± 6.4 ab	77.9 ± 5.6 ab	86.6 ± 4.4 b	72.9 ± 10.9 a	79.3 ± 3.4 ab	77.4 ± 8.4 ab	84.4 ± 3.7 b	84.3 ± 2.5 b	82.7 ± 3.8 ab	80.5 ± 3.9 ab	84.0 ± 2.4 ab

[a] Results of the analytical methods used to determine the phenolic characteristics of young red wines cv. Malbec from different zones of Mendoza. TA, total anthocyanins; CI, color intensity; TP, total phenols; TT, total tannins; DMACH, degree of polymerization of condensed tannins; GI, gelatin index; SD, standard deviation. Different letters within the same row indicate significant differences ($p < 0.05$) according to a Tukey HSD test.

on the phenolic compounds, responsible for the color of the wines and related parameters.

Total tannin contents ranged between 2782.9 and 4943.3 mg/L. These concentrations are similar to those observed by González-Neves et al. (*26*) for Cabernet Sauvignon, Merlot, and Tannat wines from Uruguay.

The degree of polymerization of condensed tannins is the ratio between catechin and proanthocyanidin contents and is mainly dependent upon the cultivar and the chemical age of the wine (*22*). For all samples, the values for this parameter ranged from 9.9 to 12.4, indicating high degrees of condensation for the proanthocyanidins contained in these wines.

The GI is an analytical parameter for estimating astringency in red wine. For Malbec samples, the values for this index ranged between 72.9 and 86.6%. These values are higher than those described by Llaudy et al. (*27*) for wines from different Spanish Origin Denominations and show high tannin reactivities for all of the wines studied. These results could be because the samples were of young wines, without any fining treatment.

Anthocyanins and Pyranoanthocyanins. Anthocyanins are water-soluble pigments present in red grape skins, which partition into the wine during vinification. The monomeric forms are responsible for most of the red color of young wines, and they contribute to the development of red polymeric pigments during wine aging (*28*).

Glycosylated and acylated (acetyl and *p*-coumaroyl derivatives) anthocyanins, as well as pyranoanthocyanins, were identified by HPLC-DAD. **Table 3** summarizes the individual anthocyanin and pyranoanthocyanin concentrations in Malbec wines. **Figure 1** shows a chromatographic profile of these compounds in the wines analyzed.

Concentrations of monoglucosylated anthocyanins in Malbec samples ranged from 12.0 to 67.8 mg/L for delphinidin-3-glucoside, from 1.6 to 15.5 mg/L for cyanidin-3-glucoside, from 17.7 to 83.5 mg/L for petunidin-3-glucoside, from 3.5 to 23.5 mg/L for peonidin-3-glucoside, and from 189.9 to 408.8 mg/L for malvidin-3-glucoside.

The concentrations for acetylated anthocyanins found in the wine samples ranged from 2.9 to 11.0 mg/L for delphinidin-3-(6-acetyl)glucoside, from 2.7 to 19.2 mg/L for cyanidin-3-(6-acetyl)glucoside, from 1.9 to 7.7 mg/L for petunidin-3-(6-acetyl)glucoside, from 6.4 to 10.8 mg/L for peonidin-3-(6-acetyl)glucoside, and from 32.9 to 68.7 mg/L for malvidin-3-(6-acetyl)glucoside.

In the case of coumaroyl derivatives, the concentrations ranged from 0.7 to 5.3 mg/L for delphinidin-3-(6-*p*-coumaroyl)glucoside, from 0.6 to 5.2 mg/L for cyanidin-3-(6-*p*-coumaroyl)glucoside, from 0.4 and 2.0 mg/L for petunidin-3-(6-*p*-coumaroyl)glucoside, from 1.3 to 4.8 mg/L for peonidin-3-(6-*p*-coumaroyl)glucoside, and from 19.3 to 31.8 mg/L for the malvidin-3-(6-*p*-coumaroyl)glucoside.

Anthocyanin-derived pigments, such as vitisins, are of interest for winemakers because they have high stability during the aging of red wines. These pyranoanthocyanins are more resistant to elevated pH values and bisulfite bleaching than anthocyanins, and they present an orange-red color; these compounds are responsible for deeper colors than other pigments at the typical pH of wine (*29*). **Table 3** shows that all wines contained vitisin B (6.9−37.1 mg/L), but only the wines from zones 4, 5, 6, 10, and 11 contained vitisin A (9.8−16.1 mg/L). The differences observed in the vitisin concentrations could be related with the winemaking conditions (*9*), which could influence mainly the formation of vitisin B and in some cases of vitisin A.

Low Molecular Weight Phenolic Composition. Table 4 shows the individual concentrations of the different non-flavonoids (hydroxybenzoic and hydroxycinnamic acids, *trans*-resveratrol

Table 3. Anthocyanins Quantified [Mean (mg/L) ± SD] in Commercial Malbec Wines from Different Geographical Origins of Mendoza[a]

		geographical zones of Mendoza										
peak	compound	1 (*n* = 5)	2 (*n* = 5)	3 (*n* = 7)	4 (*n* = 5)	5 (*n* = 6)	6 (*n* = 4)	7 (*n* = 5)	8 (*n* = 6)	9 (*n* = 8)	10 (*n* = 5)	11 (*n* = 5)
1	delphinidin-3-glucoside	12.0 ± 7.0 a	17.3 ± 14.6 a	25.1 ± 6.8 a	61.5 ± 39.5 a	29.1 ± 14.8 a	46.6 ± 23.0 a	31.4 ± 25.0 a	27.2 ± 14.3 a	67.8 ± 62.3 a	52.9 ± 22.4 a	50.0 ± 32.9 a
2	cyanidin-3-glucoside	11.5 ± 9.9 a	6.8 ± 4.1 a	7.9 ± 7.4 a	4.2 ± 3.3 a	7.2 ± 6.3 a	14.1 ± 12.1 a	13.1 ± 8.5 a	7.8 ± 7.4 a	15.5 ± 20.9 a	10.1 ± 12.6 a	1.6 ± 1.7 a
3	petunidin-3-glucoside	17.7 ± 16.5 a	37.9 ± 12.5 a	50.4 ± 14.9 a	71.1 ± 26.9 a	50.9 ± 18.5 a	83.5 ± 45.4 a	53.0 ± 33.4 a	34.5 ± 26.9 a	82.1 ± 67.4 a	58.4 ± 17.2 a	61.7 ± 37.8 a
4	peonidin-3-glucoside	3.5 ± 2.7 a	8.0 ± 7.2 a	19.0 ± 10.2 a	16.5 ± 5.6 a	14.7 ± 5.3 a	22.7 ± 22.2 a	15.9 ± 11.6 a	7.9 ± 6.2 a	23.5 ± 23.7 a	10.8 ± 2.7 a	10.4 ± 8.2 a
5	malvidin-3-glucoside	189.9 ± 42.9 a	265.9 ± 74.7 a	320.5 ± 95.9 a	349.9 ± 131.2 a	369.4 ± 47.1 a	408.8 ± 149.5 a	308.9 ± 155.0 a	283.0 ± 148.0 a	340.8 ± 171.0 a	384.4 ± 42.2 a	315.6 ± 131.3 a
	total glucosylated	234.6 (73.3[b])	335.9 (72.7)	422.9 (77.5)	503.2 (75.0)	471.3 (73.6)	575.7 (75.4)	422.3 (77.0)	360.4 (77.3)	529.7 (76.8)	516.6 (74.4)	439.3 (73.6)
VA	vitisin A	nd	nd	nd	13.5	9.8	16.1	nd	nd	nd	15.1	13.7
VB	vitisin B	6.9 ± 4.0 a	10.6 ± 5.3 a	14,1 ± 5.0 a	33.2 ± 22.6 a	24.6 ± 9.1 a	35.3 ± 3.9 a	18.3 ± 18.5 a	9.7 ± 7.6 a	27.7 ± 18.1 a	28.6 ± 23.9 a	37.1 ± 20.3 a
6	delphinidin-3-(6-acetyl)glucoside	6.1 ± 4.1 a	2.9 ± 3.4 a	8.9 ± 6.2 a	10.6 ± 6.7 a	7.3 ± 7.6 a	4.3 ± 2.5 a	11.0 ± 9.4 a	6.9 ± 5.8 a	11.0 ± 10.2 a	7.6 ± 5.8 a	6.6 ± 4.6 a
7	cyanidin-3-(6-acetyl)glucoside	2.9 ± 3.2 a	6.7 ± 7.3 a	7.3 ± 3.5 a	11.0 ± 9.5 a	6.5 ± 4.1 a	6.6 ± 2.8 a	6.2 ± 5.0 a	2.7 ± 1.8 a	19.2 ± 28.6 a	7.6 ± 8.8 a	4.8 ± 7.1 a
8	petunidin-3-(6-acetyl)glucoside	4.5 ± 6.4 a	7.7 ± 13.6 a	1.9 ± 2.4 a	2.4 ± 1.7 a	7.7 ± 14.8 a	2.1 ± 1.2 a	2.5 ± 2.5 a	2.6 ± 2.6 a	5.0 ± 7.1 a	4.6 ± 5.6 a	4.0 ± 4.0 a
9	peonidin-3-(6-acetyl)glucoside	6.5 ± 5.6 a	7.0 ± 3.9 a	7.9 ± 4.0 a	7.6 ± 3.7 a	8.8 ± 4.3 a	10.8 ± 6.3 a	10.3 ± 7.1 a	6.4 ± 4.2 a	9.2 ± 7.3 a	6.9 ± 1.5 a	7.3 ± 3.9 a
10	malvidin-3-(6-acetyl)glucoside	32.9 ± 9.4 a	53.8 ± 24.8 a	52.3 ± 21.0 a	51.6 ± 21.1 a	64.8 ± 10.8 a	68.7 ± 23.4 a	46.2 ± 25.1 a	47.4 ± 27.5 a	53.6 ± 27.6 a	68.1 ± 12.7 a	50.5 ± 22.6 a
	total acetylated	52.9 (16.5)	78.1 (16.9)	78.3 (14.3)	83.2 (12.4)	95.1 (14.8)	92.5 (12.1)	76.2 (13.9)	66.0 (14.2)	98.0 (14.2)	94.8 (13.7)	73.2 (12.3)
11	delphinidin-3-(6-*p*-coumaroyl)glucoside	2.9 ± 3.0 a	4.2 ± 4.4 a	0.7 ± 0.6 a	5.0 ± 4.2 a	2.0 ± 1.6 a	5.3 ± 8.4 a	0.7 ± 0.7 a	1.2 ± 1.7 a	2.7 ± 4.9 a	2.3 ± 0.1 a	1.1 ± 1.0 a
12	cyanidin-3-(6-*p*-coumaroyl)glucoside	0.6 ± 0.8 a	2.0 ± 1.1 a	2.1 ± 2.0 a	5.0 ± 6.5 a	5.2 ± 6.1 a	1.0 ± 0.5 a	1.8 ± 2.8 a	3.0 ± 1.8 a	2.4 ± 2.4 a	1.9 ± 2.2 a	5.2 ± 3.6 a
13	petunidin-3-(6-*p*-coumaroyl)glucoside	1.4 ± 1.0 a	1.2 ± 0.4 a	1.9 ± 1.6 a	1.0	0.6 ± 0.5 a	0.7 ± 0.7 a	2.0 ± 1.7 a	1.5 ± 2.4 a	0.9 ± 0.6 a	0.5 ± 0.2 a	0.4 ± 0.4 a
14	peonidin-3-(6-*p*-coumaroyl)glucoside	1.3 ± 0.9 a	2.3 ± 1.7 a	3.0 ± 1.5 a	3.7 ± 1.8 a	3.7 ± 0.7 a	4.8 ± 1.6 a	3.5 ± 2.5 a	3.6 ± 1.6 a	4.2 ± 4.0 a	3.3 ± 0.7 a	2.7 ± 1.9 a
15	malvidin-3-(6-*p*-coumaroyl)glucoside	19.3 ± 8.5 a	27.7 ± 12.6 a	22.7 ± 7.7 a	23.4 ± 7.9 a	28.4 ± 8.4 a	31.8 ± 14.6 a	23.9 ± 12.5 a	20.8 ± 10.9 a	23.8 ± 14.1 a	31.0 ± 2.3 a	24.5 ± 13.6 a
	total coumaroylated	25.5 (8.0)	37.4 (8.1)	30.4 (5.6)	38.1 (5.7)	39.9 (6.2)	43.6 (5.7)	31.9 (5.8)	30.1 (6.5)	34.0 (4.9)	39.0 (5.6)	33.9 (5.7)
	total anthocyanins	319.9	462.0	545.7	671.2	640.7	763.2	548.7	466.2	689.4	694.1	597.2
	Σ glucosylated/Σ acetylated	4.4	4.3	5.4	6.0	5.0	6.2	5.5	5.5	5.4	5.4	6.0
	Σ glucosylated/Σ coumaroylated	9.2	9.0	13.9	13.2	11.8	13.2	13.2	12.0	15.6	13.2	13.0
	Σ coumaroylated/Σ acetylated	0.5	0.5	0.4	0.5	0.4	0.5	0.4	0.5	0.3	0.4	0.5
	Σ acetylated/Σ coumaroylated	2,1	2,1	2,6	2,2	2,4	2,1	2,4	2,2	2,9	2,4	2,2

[a] Different letters within the same row indicate significant differences ($p < 0.05$) according to a Tukey HSD test. nd, not detected. [b] Relationship (%) between anthocyanin derivatives by acylation and total anthocyanins.

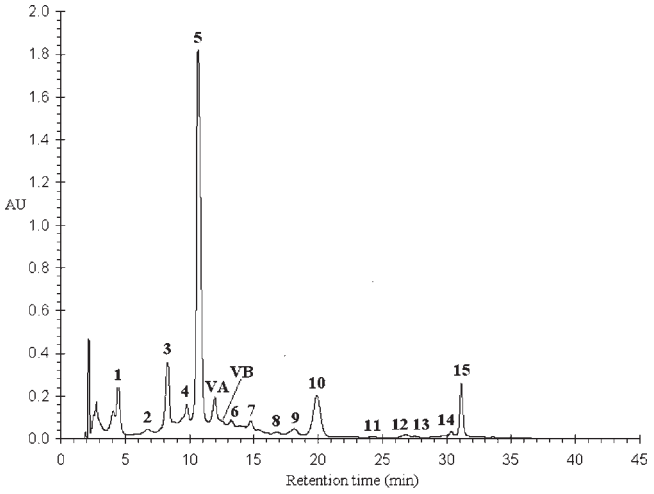

Figure 1. Chromatographic profile of anthocyanins in Malbec wine. For peak identification, see **Table 3**.

glucoside, and tyrosol) and flavonoids (flavanols, flavanonols, and flavonols). **Figure 2** shows a chromatographic profile of low molecular weight phenolic compounds in Malbec wine samples.

An unknown compound (peak 23) was found in all of the wines studied. The peak eluted at 46 min and has a UV spectrum with an absorption maximum at 279 nm, shown in **Figure 3**.

The phenolic acids (gallic, protocatechuic, syringic, *cis*-caftaric, *trans*-caftaric, caffeic, *cis*-coutaric, *trans*-coutaric, *cis*-*p*-coumaric, and *trans*-*p*-coumaric) and tyrosol were identified and quantified in all of the wines analyzed. By comparison of the average concentrations for the hydroxybenzoic acids, it was observed that gallic acid was the most abundant, representing 72−77% of all benzoic acids in the wines studied. These values are in accordance with some young Spanish red wines (*30*); however, the values are higher than those found by Peña-Neira et al. (*15*) in Spanish red wines.

For the different hydroxycinnamic acids identified in the Malbec wines, their total contents were lower than those found by other authors in Spanish wines (*31*). Therein, different relationships were observed between the trans and cis isomers of caftaric, coutaric, and coumaric acids; on average, for all wines, the trans/cis ratios were 4.8, 2.2, and 0.2 for coumaric, coutaric, and caftaric acid, respectively.

Among non-flavonoids, stilbenes are the important compounds due to their putative protective effects against cardiovascular diseases (*32*). Some authors (*33*) have suggested that the concentrations of these compounds in wines vary from values of <1 to 30.0 mg/L, depending on multiple factors such as grape variety, fungal infections, winemaking procedures, and weather conditions. In this study, *trans*-resveratrol glucoside was the only stilbene identified, with concentrations ranging from 0.6 to 1.3 mg/L. These values are in agreement with those previously reported by other authors in Tempranillo, Cabernet Sauvignon, and Merlot wines (*12*). Finally, the levels of tyrosol, formed during yeast fermentation from tyrosine (*15*), were lower in the Malbec wines than those found in Tempranillo and Cabernet Sauvignon (*34*).

Flavonoids have been shown to inhibit low-density lipoprotein oxidation, both in vitro and in vivo, and reduce platelet aggregation (*35*). Flavan-3-ols (catechins) are some of the most widely occurring flavonoids, and the most important sources of these compounds in the diet are grapes and wines, at least in the Mediterranean region (*36*). Flavan-3-ols were the major class of phenolic compounds present in the samples studied. In all of the Malbec wines, the (+)-catechin contents were higher than those of (−)-epicatechin, with concentrations ranging from 24.4 to 47.0 mg/L and from 14.5 to 23.6 mg/L, respectively.

Flavonols accumulate in the skins of red grapes during ripening (*37*). The time of harvest and the vinification conditions have noticeable influences on flavonol content. The wines obtained from very ripe grapes with longer sun exposure contain higher concentrations of flavonols. In the Mendoza region, with a dry period during the harvest time and especially with high sunlight intensity, the grapes are allowed to ripen to a much greater extent than elsewhere, and this appears to be associated with an increased accumulation of flavonols (*38*, *39*). In the Malbec wines studied, the content of total flavonols was between 11.2 and 16.7 mg/L. These results are in agreement with those obtained by other authors in red wines of different geographical origins (*30*, *39*).

Another important 2-phenylbenzopyran subclass found commonly in fruit-based beverages is the dihydroflavonols (flavanonols). These compounds contribute to a smaller fraction of total wine flavonoids, and they play functional roles in grape berries. Flavanonols such as astilbin most likely function in plants to fight botrytis infection. Astilbin (dihydroquercetin-3-*O*-rhamnoside) is a bioactive flavanonol thought to provide antimicrobial, antibacterial, cardiopreventive, and possibly chemopreventive effects in humans (*40*). From the UV characteristics (λ_{max} 290 nm; $\lambda_{shoulder}$ 327 nm) (*40*), astilbin was tentatively identified in all of the Malbec wines, with concentrations ranging from 9.1 to 16.3 mg/L. These values are in agreement with those found by Vitrac et al. (*33*) in commercial red wines from southwestern France. Using the UV spectral information, it was possible to detect three astilbin derivatives (1, 2, and 3, **Table 4**) by comparison with the astilbin spectrum. The retention times of these compounds were 19, 31, and 33 min, respectively, and they presented a UV spectrum with an absorption maximum at 290 nm (**Figure 4**).

Considering that to our knowledge there is not any information in the literature about the chemical composition of Malbec wines, our discussion will consider a comparison of Malbec wines with those of other international red varieties.

It is irrefutable that the amounts as well as the several types of phenolic compounds that occur in wines depend on a wide range of factors, including cultural practices, local climate conditions, vinification techniques, storage, and aging (*10*−*12*, *14*). These factors make it difficult to compare different wines. The examination of the polyphenolic composition has in some instances provided evidence of the potential of certain cultivars for polyphenol biosynthesis (*41*). The phenolic profile and the range of the data obtained in the Malbec samples analyzed in this work are in agreement with the available international literature for other red varieties. Their phenolic content was comparable to, and in some cases richer than, the content of the most well-known varieties used for producing quality wines (*12*, *15*, *16*, *25*, *30*, *31*, *33*, *36*, *39*, *41*). The results obtained confirm a variation in phenolic content among wine samples tested and are indicative of the polyphenolic richness of the Malbec samples analyzed.

The critical assessment of the data from the wine samples analyzed clearly indicates some areas from Mendoza province to be distinctive for their exceptional polyphenolic potential. Considering total phenols, tannins, and anthocyanins, as well as the total anthocyanins determined by HPLC-DAD, zones 9 and 6 were particularly rich in these phenolic groups. In addition, all Malbec wine samples were exceptionally high in total tannin content, which could be possibly used in mixtures with other varieties poor in tannins to produce balanced, in both mouth structure and body, wines.

Table 4. Phenolic Compounds Quantified [Mean (mg/L) ± SD] in Commercial Malbec Wines from Different Geographical Origins of Mendoza[a]

		geographical zones of Mendoza										
peak	compound	1 (n = 5)	2 (n = 5)	3 (n = 7)	4 (n = 5)	5 (n = 6)	6 (n = 4)	7 (n = 5)	8 (n = 6)	9 (n = 8)	10 (n = 5)	11 (n = 5)
	hydroxybenzoic acids											
1	gallic	17.7 ± 6.6 a	13.8 ± 3.1 a	20.1 ± 5.1 a	18.5 ± 4.7 a	15.1 ± 3.8 a	21.7 ± 6.0 a	18.8 ± 5.2 a	17.5 ± 3.5 a	18.2 ± 4.2 a	18.6 ± 7.0 a	18.6 ± 6.7 a
2	protocatechuic	2.7 ± 0.8 a	2.3 ± 0.7 a	3.6 ± 0.7 a	2.3 ± 0.5 a	2.6 ± 0.8 a	4.1 ± 1.9 a	2.7 ± 0.7 a	2.4 ± 0.6 a	3.2 ± 0.9 a	2.5 ± 1.3 a	2.6 ± 0.9 a
13	syringic	3.3 ± 0.4 a	2.3 ± 1.0 a	4.1 ± 1.5 a	3.3 ± 1.1 a	3.0 ± 0.8 a	4.2 ± 1.1 a	3.5 ± 1.1 a	3.1 ± 0.6 a	2.9 ± 0.7 a	3.8 ± 2.2 a	2.9 ± 1.8 a
	total	23.7	18.4	27.8	24.1	20.7	30.0	25.0	23.0	24.3	24.9	24.1
	hydroxycinnamic acids											
3	*cis*-caftaric	2.8 ± 2.1 a	4.5 ± 2.3 a	2.4 ± 1.7 a	4.4 ± 2.4 a	3.5 ± 2.2 a	5.6 ± 6.5 a	5.0 ± 3.0 a	3.1 ± 1.3 a	3.0 ± 0.8 a	3.4 ± 1.4 a	5.1 ± 3.1 a
4	*trans*-caftaric	0.9 ± 0.4 b	0.6 ± 0.2 ab	0.4 ± 0.1 ab	0.7 ± 0.2 ab	0.6 ± 0.3 ab	0.6 ± 0.3 ab	0.7 ± 0.2 ab	0.4 ± 0.1 a	0.4 ± 0.1 a	0.6 ± 0.1 ab	0.8 ± 0.4 ab
10	caffeic	2.4 ± 1.4 a	1.8 ± 2.0 a	2.0 ± 1.1 a	2.1 ± 1.1 a	1.7 ± 0.5 a	3.4 ± 2.9 a	1.9 ± 1.1 a	1.5 ± 0.7 a	1.8 ± 1.1 a	2.1 ± 2.5 a	1.3 ± 0.5 a
6	*cis*-coutaric	2.0 ± 1.5 a	2.2 ± 1.7 a	1.2 ± 1.1 a	3.1 ± 1.6 a	1.8 ± 1.0 a	2.4 ± 2.7 a	2.3 ± 1.9 a	2.1 ± 1.0 a	1.5 ± 0.7 a	2.0 ± 1.1 a	3.2 ± 1.7 a
12	*trans*-coutaric	3.0 ± 0.9 a	4.1 ± 1.9 a	5.1 ± 0.9 a	4.7 ± 1.7 a	4.1 ± 1.1 a	4.7 ± 1.2 a	6.0 ± 3.4 a	6.0 ± 3.4 a	5.4 ± 1.2 a	5.8 ± 3.3 a	3.6 ± 0.7 a
15	*cis*-*p*-coumaric	0.3 ± 0.1 a	0.4 ± 0.1 a	0.3 ± 0.2 a	0.4 ± 0.2 a	0.4 ± 0.1 a	0.6 ± 0.4 a	0.5 ± 0.2 a	0.5 ± 0.2 a	0.4 ± 0.2 a	0.4 ± 0.1 a	0.4 ± 0.2 a
16	*trans*-*p*-coumaric	2.7 ± 1.7 a	3.0 ± 2.1 a	2.2 ± 1.0 a	1.9 ± 0.8 a	1.9 ± 0.8 a	3.0 ± 2.0 a	1.4 ± 0.2 a	1.5 ± 1.2 a	1.6 ± 1.0 a	2.0 ± 2.3 a	2.0 ± 2.0 a
	total	14.1	16.6	13.6	17.3	14.0	20.3	17.8	15.1	14.1	16.3	16.4
	stilbene											
20	*trans*-resveratrol glucoside	1.1 ± 0.6 a	0.9 ± 0.5 a	0.8 ± 0.4 a	1.2 ± 0.7 a	0.7 ± 0.4 a	1.3 ± 1.1 a	1.1 ± 0.5 a	0.6 ± 0.5 a	1.3 ± 0.5 a	1.0 ± 0.4 a	0.7 ± 0.4 a
	flavanols											
7	procyanidin B3	3.6 ± 1.3 a	nd	2.1	3.4 ± 1.4 a	2.3 ± 0.4 a	2.6 ± 0.6 a	nd	5.9	3.1 ± 1.1 a	3.0 ± 1.8 a	2.7
8	procyanidin B1	7.3 ± 5.7 a	4.1 ± 3.8 a	7.5 ± 5.4 a	11.7 ± 3.5 a	5.6 ± 3.8 a	9.9 ± 7.0 a	2.5 ± 0.7 a	7.4 ± 6.8 a	10.0 ± 5.3 a	6.0 ± 4.2 a	5.2 ± 4.3 a
14	procyanidin dimer	5.4 ± 2.3 a	2.2	7.1 ± 5.9 a	3.7 ± 2.1 a	3.1 ± 1.5 a	2.3 ± 0.6 a	2.5 ± 0.4 a	3.1 ± 2.5 a	2.9 ± 1.4 a	3.5 ± 2.3 a	3.0 ± 0.5 a
9	(+)-catechin	26.0 ± 7.9 a	25.2 ± 5.9 a	33.6 ± 13.5 a	24.4 ± 8.9 a	28.1 ± 10.7 a	47.0 ± 9.9 a	39.3 ± 12.1 a	42.1 ± 25.1 a	33.6 ± 15.0 a	33.4 ± 22.2 a	29.3 ± 16.3 a
17	(−)-epicatechin	20.1 ± 6.8 a	14.5 ± 2.1 a	17.9 ± 5.6 a	14.6 ± 4.7 a	17.2 ± 5.3 a	23.6 ± 9.9 a	18.7 ± 5.2 a	20.2 ± 7.1 a	17.4 ± 5.5 a	18.4 ± 6.9 a	17.6 ± 9.3 a
	total	62.4	46.0	68.2	57.8	56.3	85.4	63.0	78.7	67.0	64.3	57.8
	(+)-catechin/(−)-epicatechin	1.3	1.7	1.9	1.7	1.6	2.0	2.1	2.1	1.9	1.8	1.7
	flavanonols											
22	astilbin	9.1 ± 3.8 a	16.0 ± 3.5 ab	15.0 ± 3.4 ab	16.3 ± 1.7 b	12.2 ± 2.1 ab	14.8 ± 5.5 ab	14.7 ± 5.1 ab	16.0 ± 3.9 b	13.8 ± 2.3 ab	13.6 ± 1.8 ab	12.9 ± 2.9 ab
11	astilbin derivative 1	1.5 ± 0.4 a	1.9 ± 0.6 a	2.9 ± 1.4 a	2.8 ± 0.6 a	2.0 ± 0.7 a	2.7 ± 0.5 a	2.3 ± 0.7 a	2.2 ± 0.4 a	2.1 ± 0.5 a	2.6 ± 2.1 a	3.6 ± 1.2 a
18	astilbin derivative 2	28.3 ± 14.1 a	42.6 ± 2.5 ab	37.8 ± 5.4 ab	41.8 ± 5.9 ab	34.8 ± 3.6 ab	40.9 ± 12.6 ab	37.9 ± 7.9 ab	47.4 ± 14.2 b	39.9 ± 5.9 ab	47.9 ± 7.6 b	38.1 ± 6.5 ab
19	astilbin derivative 3	2.0 ± 1.1 a	2.0 ± 0.7 a	1.7 ± 0.5 a	1.6 ± 0.6 a	1.9 ± 0.9 a	1.6 ± 0.4 a	1.5 ± 0.2 a	2.4 ± 1.2 a	1.7 ± 0.7 a	2.5 ± 1.0 a	2.0 ± 1.5 a
	total	40.9	62.5	57,4	62.5	50.9	60.0	56.4	68.0	57.5	66.6	56.6
	flavonols											
21	flavonol-glycoside 1	2.1	2.6 ± 1.7 a	3.8 ± 2.1 a	3.1 ± 2.2 a	3.1 ± 1.4 a	3.3 ± 4.2 a	3.3 ± 1.9 a	5.4 ± 3.3 a	3.8 ± 1.4 a	1.5 ± 0.6 a	0.8 ± 0.3 a
26	flavonol-glycoside 2	4.1 ± 1.3 a	2.7 ± 1.5 a	3.7 ± 1.0 a	4.3 ± 1.5 a	3.8 ± 2.0 a	3.0 ± 2.0 a	3.3 ± 2.3 a	2.8 ± 1.7 a	4.2 ± 1.8 a	2.9 ± 0.7 a	4.3 ± 1.9 a
24	myricetin-3-*O*-glucoside	1.6 ± 0.9 a	1.3 ± 0.1 a	1.3 ± 0.5 a	2.5 ± 0.6 a	1.7 ± 0.8 a	2.9 ± 1.7 a	1.9 ± 0.4 a	1.4 ± 0.9 a	1.7 ± 1.1 a	1.8 ± 0.9 a	1.8 ± 1.6 a
25	myricetin-3-*O*-galactoside	0.8 ± 0.3 a	1.0 ± 0.3 a	1.4 ± 1.0 a	0.9 ± 0.1 a	1.0 ± 0.1 a	0.9	0.9 ± 0.3 a	1.7 ± 1.1 a	0.9 ± 0.2 a	0.9 ± 0.2 a	0.7 ± 0.1 a
27	quercetin	4.3 ± 2.4 a	4.1 ± 1.9 a	3.2 ± 2.1 a	5.0 ± 1.5 a	4.4 ± 3.1 a	5.0 ± 2.0 a	4.9 ± 2.7 a	5.4 ± 2.5 a	4.7 ± 2.5 a	4.1 ± 1.7 a	4.5 ± 1.6 a
	total	12.9	11.7	13.4	15.8	14.0	15.1	14.3	16.7	15.3	11.2	12.1
	other compounds											
5	tyrosol	5.0 ± 2.8 a	5.0 ± 1.4 a	5.8 ± 1.0 a	6.2 ± 1.3 a	5.7 ± 1.0 a	7.5 ± 0.9 a	5.7 ± 1.2 a	5.4 ± 1.1 a	6.7 ± 1.1 a	6.7 ± 1.8 a	5.5 ± 1.3 a
23	unknown compound	1.1 ± 0.4 a	2.1 ± 1.1 a	1.3 ± 0.3 a	1.9 ± 0.9 a	1.7 ± 0.7 a	2.2 ± 1.5 a	1.9 ± 1.8 a	2.6 ± 1.1 a	2.0 ± 0.5 a	1.8 ± 0.5 a	1.6 ± 0.7 a
	total	6.1	7.1	7.1	8.1	7.4	9.7	7.6	8.0	8.7	8.5	7.1
	total phenolic compounds	161.2	163.2	188.3	186.8	164.0	221.8	185.2	210.1	188.2	192.8	174.8

[a] Different letters within the same row indicate significant differences ($p < 0.05$) according to a Tukey HSD test. nd, not detected.

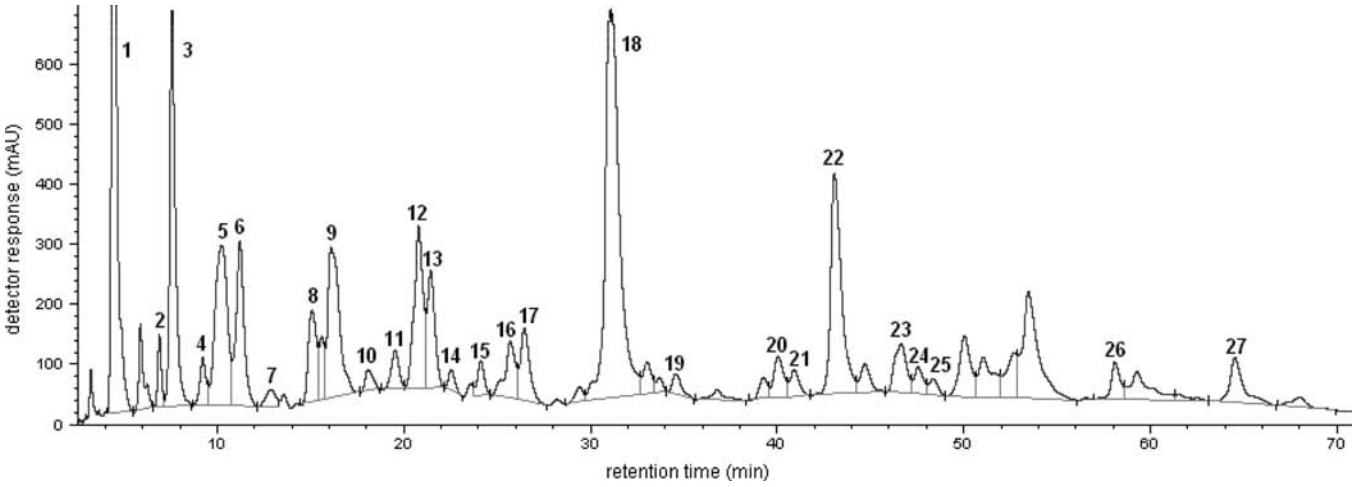

Figure 2. Chromatographic profile of low molecular weight phenolic compounds determined in Malbec wines. For peak identification, see **Table 4**.

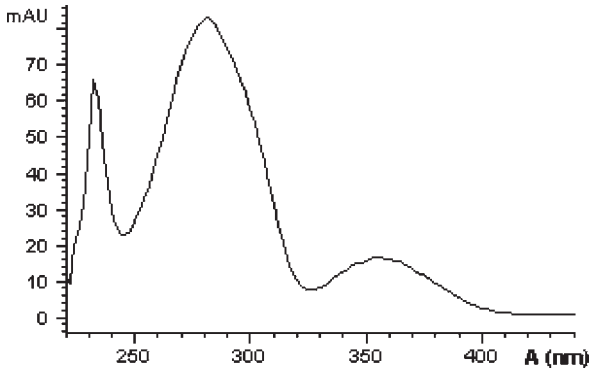

Figure 3. UV spectrum of an unidentified phenolic compound in Malbec wines.

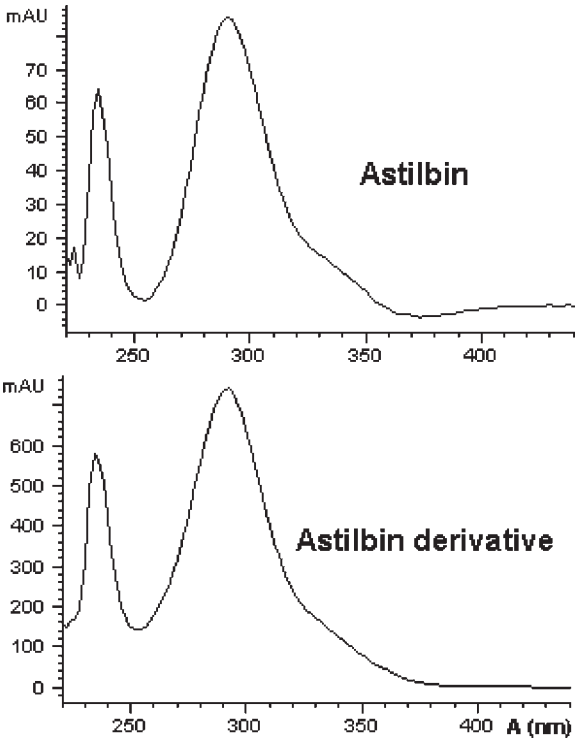

Figure 4. UV spectra of astilbin and one of the astilbin derivatives found in Malbec wines.

The composition data that have been available to date do not permit the distinction of trends related to specific phenolic metabolites and, therefore, do not allow recognition of variety-dependent patterns. With regard to other important international varieties (Syrah, Tempranillo, and Cabernet Sauvignon), a similar but not identical phenolic profile was observed compared with previous works (*9*, *12*, *15*, *26*, *41*). The compound with an UV absorption spectra similar to that of the flavanonol astilbin, showing an absorption maximum at 290 nm but a different retention time, can correspond to an astilbin derivative (**Figure 4**). It was the major compound found among the low molecular weight phenolic compounds studied in all of the samples (astilbin derivative 2, **Table 4**). We have observed the same profile behavior in skin samples from Malbec grape berries compared with those from Cabernet Sauvignon, Carménère, and Syrah (data not published). These results and the low amount of flavonols (quercetin, myricetin, and kaempferol) and their glycosylated derivatives, compared with those described for Chilean Cabernet Sauvignon and Merlot wines (mean value of 29 mg/L for both varieties) (*39*), could be a distinctive phenolic profile of grapes and wines from the Malbec variety. Considering that dihydroflavonols (flavanonols) are precursors of flavonols (*42*), the high concentration of dihydroflavonols could be related with a lower activity for flavonol synthase (FLS) in Malbec grapes.

Flavan-3-ols were the major class of phenolic compounds present in the samples studied. In all of the Malbec wines, the (+)-catechin contents were higher than those of (−)-epicatechin. These results are in agreement with those presented by other authors for other varieties (*16*, *25*, *36*). In grapes, the biosynthesis of flavanol monomers involves two enzymes: leucoanthocyanidin reductase (LAR) and anthocyanidin reductase (ANR), responsible for the synthesis of (+)-catechin and (−)-epicatechin, respectively. The expression of these enzymes is mainly related to environmental conditions in the vineyard (*42*). Considering that the ratio (+)-catechin/(−)-epicatechin varies from 1.3 to 2.1 among the samples from the different zones studied, it could be possible to confirm the variation in the LAR and ANR activity due to the effect of environmental conditions. In addition, and independent from the zone, it is possible to suppose that the LAR enzyme is more active than the ANR in the Malbec variety.

Figure 5 shows that the non-acylated glucosides were the most abundant group of pigments in Malbec wines studied (mean value = 75.1%) compared with the acylated forms. These results are in agreement with those described by Núñez et al. (*8*) for other *Vitis vinifera* L. grape varieties such as Cabernet Sauvignon,

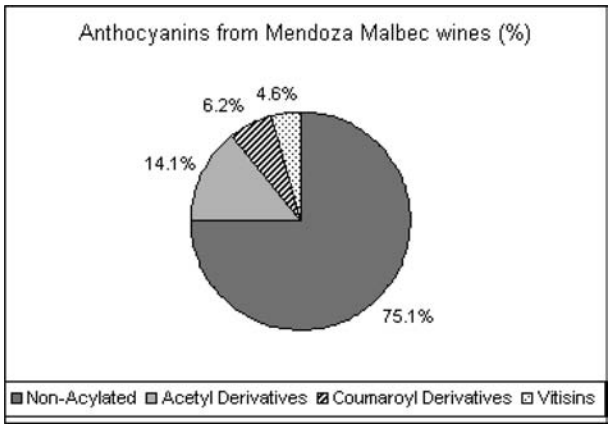

Figure 5. Anthocyanin distribution by acylation in Mendoza Malbec wines.

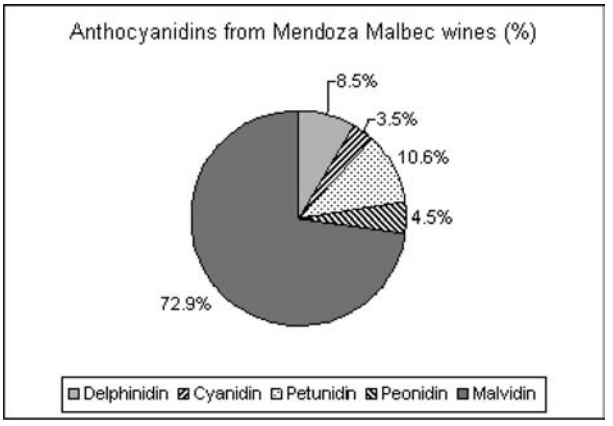

Figure 6. Anthocyanin distribution by anthocyanidin in Mendoza Malbec wines.

Tempranillo, and Graciano. Considering the acylated derivatives, Malbec wines presented a pattern, similar to that of Cabernet Sauvignon, that usually has a higher proportion of acetylglucosides than of coumaroylglucosides (mean values = 14.1 and 6.2%, respectively), whereas other varieties such as Tempranillo are characteristic for presenting the opposite values (*9*). With regard to the monomeric anthocyanins determined by HPLC-DAD, the total concentration of these compounds was higher than that described by Pérez-Lamela et al. (*43*) for wines from Sousón, Mencía, and Brancellao, three different *V. vinifera* red grape varieties grown in northwestern Spain.

For the verification of varietal authenticity in red wines, the use of the ratio of acetylated and coumaroylated anthocyanins (Σ acetylated/Σ coumaroylated) has been proposed (*44*). The values of this ratio obtained in this study ranged between 2.1 and 2.9 and are in the same range as those described for Carménère and Merlot wines (*45*). This implies that only with this parameter it is not possible to differentiate between wines of these three varieties. Additionally, the mean values obtained for the ratios Σ glucosylated/Σ acetylated and Σ glucosylated/Σ coumaroylated in the different Malbec wines were 4.3−6.2 and 9.0−15.6, respectively (**Table 3**).

As shown in **Figure 6**, the amounts of malvidin-3-glucoside were highest among all of the anthocyanins. This result could indicate that the methyltransferase enzyme involved in the biosynthesis of this anthocyanin is as active as it is in other *V. vinifera* varieties such as Syrah, Cabernet Sauvignon, and Pinot noir (*46*). The second most abundant anthocyanidin was petunidin, followed by delphinidin. This profile is different from those of other wine varieties such as Cabernet Sauvignon, Tempranillo, and Graciano (*8*). The low concentrations found for cyanidin derivatives could be explained by the fact that this anthocyanin is the biosynthetic precursor of all the others (*47*) and the synthetic pathway could be more active in this variety.

Discriminant Analysis. A canonical discriminant analysis (CDA) was applied to the data of the wines to obtain any differentiation based on their phenolic composition. This analysis was carried out by comparing the wines from the different geographical zones studied. This analysis included only the variables that presented normal distributions with a 90% or higher confidence level (gallic, protocatechuic, syringic, *cis*-caftaric, and *trans*-caftaric acids, tyrosol, (+)-catechin, (−)-epicatechin, astilbin derivatives 1 and 2, unknown compound (peak 23), malvidin-3-glucoside, malvidin-3-(6-acetyl)glucoside, peonidin-3-(6-*p*-coumaroyl)glucoside, malvidin-3-(6-*p*-coumaroyl)glucoside, total anthocyanins, color intensity, and hue values). Using a stepwise forward selection algorithm, two discriminating functions were determined ($p < 0.05$, 95%), which allowed the correct prediction of origin for 84% of the 61 wine samples studied. The variables gallic and protocatechuic acids, total anthocyanins, malvidin-3-glucoside, peonidin-3-(6-*p*-coumaroyl)glucoside, and astilbin derivatives were the most important variables for the classification of the samples analyzed.

Figure 7 depicts the distribution of Malbec samples in the plane defined by the two discriminating functions. A good discrimination was observed between wines from two extremely different zones: 1 (eastern Mendoza) and 9 (West Valle de Uco). They are principally differentiated by their altitudes above sea level (asl); zone 1 varies from 600 to 700 m asl, and zone 9 presented the highest altitudes in the whole region, between 1200 and 1500 m asl. For that reason, zone 9 is colder than zone 1 and the average day/night temperature during the ripening period reaches 20 °C (*49*). Samples from zone 9 presented a higher concentration of total phenols, tannins, and anthocyanins, which could indicate high tannin reactivity, as well as a greater potential for the formation of polymeric pigments and for color stability. These results are in agreement with those presented by Miguel-Tabares et al. (*48*), who found that the cultivation altitude had a favorable effect on anthocyanin biosynthesis in red grapes, because higher concentrations of these compounds were reported at higher altitude. Conversely, Mateus et al. (*50*) demonstrated that low altitude (higher temperature and humidity), especially at the end of maturity, appears to be advantageous for producing higher concentrations of total flavanols and tannins. In the Malbec wines from eastern Mendoza (the low-altitude zone) similar results were not obtained, perhaps explained by the dry climate of the region. In addition, the high temperatures of this zone, above 32−35 °C during the ripening, strongly decrease the anthocyanin accumulation in grapes and are accompanied by poorer wine color, according to other authors (*51*). On the other hand, the close proximity of the wines from the remaining zones reflects the similar behavior among samples, in relation with the variables used for this discriminat analysis.

The results presented in this paper show variations in some total phenolic variables analyzed and in the individual nonflavonoid and flavonoid contents of the Malbec wines from different geographical zones of Mendoza province. As a conclusion and considering the results presented above, the phenolic composition of Malbec wines from Mendoza is reported for the first time. Considering the individual phenolic composition analyzed by HPLC-DAD, the compound described as an astilbin derivative seems to be characteristic of Malbec wines, which differ from the phenolic profile of other wines from red varieties (e.g., Cabernet Sauvignon, Carménère, and Syrah). With regard to

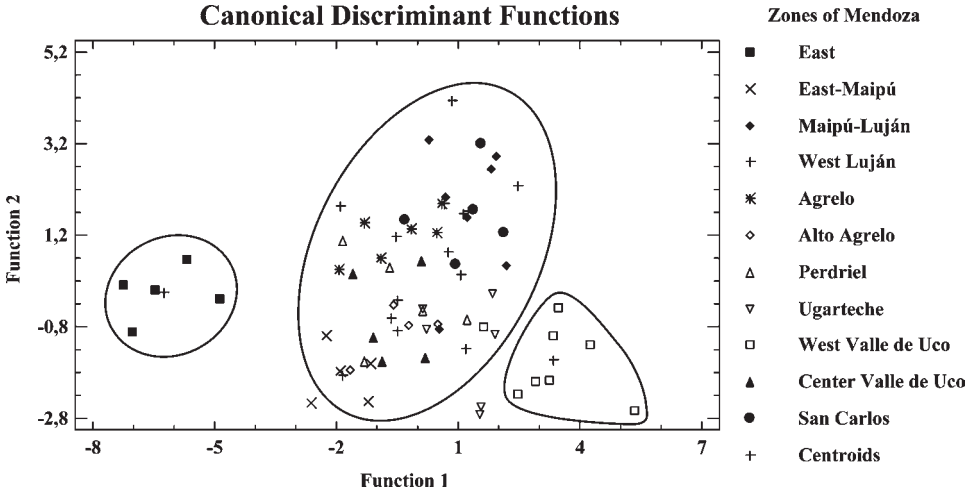

Figure 7. Canonical discriminant analysis of Malbec commercial wines from Mendoza, according to geographical zone (n = 61).

individual anthocyanins, wines of this cultivar are characterized by having a high concentration of simple glucosides, principally the malvidin derivatives, as is observed in other red varieties.

The discriminant analysis applied allowed the differentiation of wines from three origins: eastern Mendoza, West Valle de Uco, and the remaining zones. The wines of West Valle de Uco presented higher concentrations of phenolic compounds that were reputed to possess greater potential to develop polymeric pigments and color stability, suitable for long aging.

The results are indicative of the polyphenolic richness of the Malbec variety from different origins of Mendoza and their potential to produce quality wines. More studies in grapes from specific zones with controlled viticultural conditions and in wines obtained by applying different winemaking practices should be carried out to confirm these observations and to improve the polyphenolic quality of the products.

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