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Phenolic Compositions of Grapes and Wines from Cultivar Cabernet Sauvignon Produced in Chile and Their Relationship to Commercial Value

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ABSTRACT: The phenolic composition of wine depends on, among other factors, the grapes used to make it. In this sense, knowledge of the chemical composition of grapes and its association with the resulting wines is an important tool to determine if there is a relationship between the phenolic composition of grapes and the price that these wines obtain in the market. For this purpose, grape skins and seeds from the cultivar Cabernet Sauvignon from the central region of Chile, in 2009 and 2010 vintages from two ripening points, were subjected to chemical and phenolic analyses, as were the wines made from these grapes. Grapes and the corresponding wines from three retail price wine categories, U.S. $6−8, U.S. $28−30, and U.S. $150−160, were evaluated. No differences were found across the price categories in the chemical analysis of grapes. Berry skins and wines from the higher price categories presented a higher concentration only of total tannins, and the differences in their concentrations were only among the different fractions of proanthocyanidins in the skins, seeds, and wines; there were no differences in their proportions. A seasonal effect influenced the concentrations of certain compounds in grapes and led to a decrease in the concentration of total phenols, total tannins, and total anthocyanins between sampling dates as harvesting moved toward the common commercial grape harvest in Chilean viticulture.

KEYWORDS: *Retail price, proanthocyanidins, ripening*

INTRODUCTION

The quality of a wine can be defined by several criteria, including its delicacy and complexity, potential for aging, stylistic purity, and/or varietal expression; however, these assessments are governed by the criteria of wine experts along with consumer acceptance. Ripening of the grapes is one of the most influential factors in wine quality.[1] The development of the ripening process is a result of complex physiological and biochemical phenomena that are intrinsically linked to environmental conditions (grape variety, soil, climate).[2] During ripening, a compositional change occurs in the berry that affects the concentration and extraction of enological compounds, such as sugars, acids, and phenolic compounds.[3] The proanthocyanidins and anthocyanins are the most abundant class of phenolic compounds found in grape berries and wines, and these compounds are important qualitative factors in red wine due to their role in astringency, bitterness, and color.[4−7] The concentration and composition of phenolic compounds in the berry at harvest time is often considered to be an indicator of the quality of the fruit. Commercial winemakers typically consider the relationship between the chemical composition of grapes, especially in the phenolic composition, and the potential retail price that a red wine bottle can reach. It is important to note that for the production of commercial wines in different price categories, grapes are typically used from vineyards that differ in agronomical management (e.g., cluster thinning and yield, irrigation). In addition, the viticultural management and winemaking practices and the concentration of compounds at the time of harvest, and their subsequent expression in the wine, lead to different grades or categories of wine, which is then reflected in the price of the final product. There is a lack of studies on Chilean Cabernet Sauvignon that relate the physical and chemical parameters, specifically the composition of proanthocyanidins from grape skins and seeds, with the retail price that these wines reach in the market. To clarify this relationship, the aim of this study was to examine the phenolic composition in Cabernet Sauvignon grapes from three commercial vineyards corresponding to three retail price categories from the Aconcagua Valley (Chile).

MATERIALS AND METHODS

Chemical Reagents. Standards of (+)-catechin, (−)-epicatechin, and (−)-epicatechin 3-*O*-gallate and 0.45 μm pore size membranes were purchased from Sigma Chemical Co. (St. Louis, MO). Vanillin 99%, ethyl acetate, high-performance liquid chromatography (HPLC)

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-grade acetonitrile, and analytical reagent-grade solvents were purchased from Merck (Darmstadt, Germany). A Sep-Pak Plus tC_{18} environmental cartridge and a Sep-Pak Plus Short tC_{18} cartridge were obtained from Waters (Milford, MA).

Instrumentation. The Agilent Technologies 1100 series HPLC system (Agilent Technologies, Santa Clara, CA) consisted of a photodiode array detector (DAD), model G1315B; a quaternary pump, model QuatPump G1311A; a degasser, model G1379A; and an autosampler, model G1329A. A reversed-phase Nova Pack C_{18} column (4 μm, 3.9 mm i.d. × 300 mm; Waters Corp.) was used for the HPLC-DAD analysis of individual compounds. Absorbances were measured on a Shimadzu UV−vis spectrophotometer, model UV/vis 1700 Pharmaspec (Kyoto, Japan).

Description of Trial Site and Experimental Treatment. This study was conducted with two vintages: 2008−2009 (2009) and 2009−2010 (2010) from February to April. The sites for this study were three commercial vineyards of cv. Cabernet Sauvignon from the wine company "Viña Errázuriz" located in the Aconcagua Valley, central region of Chile, approximately 100 km north of Santiago. The grapes for this study were harvested in vineyards that belong to the company "Viña Errázuriz" and that are used for the production of three retail price categories of wine: low (U.S. $6−8 per bottle), medium (U.S. $28−30 per bottle), and high (U.S. $150−160 per bottle), commercialized in the domestic and international market. The vineyard average yields were as follows: low category, 9.8 ton/ha; medium category, 8.5 ton/ha; and high category, 7.7 ton/ha. The agroclimatic parameters during the growing season (February to April) for the geographical region where the vineyards are located are presented in Table 1. Diverse productive situations for each vineyard were considered, as the vineyards are specialized in producing commercial wines. The three vineyards maintain vertically trained vines with drip irrigation, and the vines are spur and cane pruned. The differences between the vineyards are in the type of soil from each site. The low and medium price categories have deep alluvial soils with a loam texture, while the high price category has deep colluvial soil with a loam to sandy-loam texture. The three vineyards have 30−40% stone, which provides good drainage and produces well-balanced plants with moderate vigor. The sampling dates for each commercial vineyard correspond to the first sample harvested 30 days after *veraison* (DAV) and a second sample corresponding to the commercial harvest (CH). The sampling dates for each vineyard in every season are as follows. For the 2009 season, in the low category, 30 DAV was March 2 and CH was March 27; in the medium category, 30 DAV was March 6 and CH was April 3; in the high category, 30 DAV was March 6 and CH was April 21. For the 2010 season, in the low category, 30 DAV was March 18 and CH was April 7; in the medium category, 30 DAV was March 17 and CH was April 16; in the high category, 30 DAV was March 20 and CH was April 27. The low temperatures in the 2010 season may have caused a delay in the phenological stages of the grapevines, as *veraison* occurred 6−14 days later than in the 2009 season. The 2010 delay set back the dates of the first sample (30 DAV) and the commercial harvest in each commercial vineyard. The commercial harvest date was determined by the company winemakers based on grape parameters, such as total soluble solids, titratable acidity, berry flavor, and the mouthfeel characteristics of the whole berries. Three replicates, each from 100 consecutive plants in different rows (300 plants in total), were sampled for every price category.

Table 1. Climate Data (February to April) for the Period of Grape Ripening[a]

vintage	mean daily max temp (°C)	mean daily min temp (°C)	day degrees, base 10 °C	rainfall (mm)
2009	29.2	10.8	1668	0
2010	25.6	9.7	1551	0

[a]Data are from the Agroclimatic System FDF-INIA-DMC in Aconcagua Valley, V Region, Chile.

Grape Sampling and Berry Chemical Analysis. Three replicates of 200 berries per vineyard were selected from 3−4 clusters per plant from a total of 300 plants on two sampling dates in each commercial vineyard. Berries were randomly collected from different positions in the clusters. Sampled berries were immediately weighed, frozen, and stored at −20 °C until processing. The following physical and chemical variables were assessed—weight of 100 berries, skin weight of 100 berries, seed weight of 100 berries, and total soluble solids in berry juice—by use of a temperature-compensated refractometer (Atago, ATC-1, Japan).

Winemaking Procedure. Winemaking was conducted for two seasons, 2009 and 2010. A total of 120 kg of grapes was harvested for each retail price category at the commercial harvest. They were then destemmed and crushed with a semiautomatic crusher machine (Magusa, Eno 3, Spain) and placed in 100 L stainless steel tanks. Three replicates were used in this experiment. Each replicate consisted of the grapes harvested from 100 plants. In the fermentation tanks, SO_2, pH, titratable acidity, and yeast-assimilable nitrogen (YAN) were checked and adjusted in the juice as necessary. The YAN level was adjusted to a final concentration of approximately 300 mg/L. The pH was adjusted to approximately 3.5. Diammonium phosphate (DAP) additions were made on the basis of the YAN assessment according to company specifications. All tanks were inoculated with a yeast inoculum of 20 g/hL (Uvaferm VRB, Lallemand, France). All the vinifications were controlled daily by measuring the temperature and density of the must. The fermentation process was maintained at a temperature of 25−28 °C with punchdown twice per day. If required, further DAP additions were made during fermentation. After 8−9 days, all wines were dry (<2 g/L fermentable sugar). The individual replicates were then pressed separately by use of a single basket press (Magusa, PV 50, Spain). Free-run fractions were racked into individual tanks and inoculated with malolactic bacteria (*Oenococcus oeni* VP41, Lallemand, France) according to the manufacturer's instructions. Once the malolactic fermentation was complete (malic acid <0.2 g/L), the SO_2 levels were adjusted to 30 mg/L, and the wines were racked, cold-stabilized, and bottled. The free-run wines were used for the chemical analysis described in this work. All chemical analyses were performed after 1 month of storage.

Extraction of Phenolic Compounds from Grape Berries. Phenolic compounds were extracted as described in previous works.[8] The skins and seeds were separated by hand from 100 berries, weighed, and ground with 30 mL of distilled water. Forty milliliters of hydroalcoholic solution (1:9 v/v ethanol/distilled water) containing 5 g/L tartaric acid was added to the ground material (skins or grapes), and the weight of the resulting suspension was adjusted to 200 g with the same hydroalcoholic solution. The extracts were macerated for 2 h at 30 °C under mechanical stirring (Barnstead model MaxQ 2000) and were then filtered through a 0.45 μm pore size membrane (Millipore).

Spectrophotometric Characterization. The total phenol content was determined by UV absorptiometry at 280 nm with gallic acid as a standard.[9] The total tannin content was measured by the method of Ribéreau-Gayon and Stonestreet.[10] The total anthocyanins were measured by diluting the extract with 2% hydrochloric acid in ethanol and comparing spectrophotometric readings of single aliquots treated with either sodium metabisulfite or water.[11] Color intensity (CI), tonality (To), percentage of yellow (% yellow), percentage of red (% red), and percentage of blue (% blue) were estimated by the method described by Glories.[9]

Fractionation of Proanthocyanidins by C_{18} Sep-Pak Cartridges. Skin and seed extracts and wine samples were fractionated on Waters tC_{18} Sep-Pak cartridges according to the method described by Sun et al.[12] In brief, 7 mL of skin or seed extract or wine was concentrated to dryness in a rotary evaporator at <30 °C. The residue was dissolved in 20 mL of phosphate buffer, pH 7.0. The pH of the resulting solution was adjusted to 7.0 with NaOH or HCl under nitrogen atmosphere. Two tC_{18} Sep-Pak cartridges were assembled (top, Waters Sep-Pak Plus tC_{18} environmental cartridge; bottom, Waters Sep-Pak Plus Short tC_{18} cartridge) and conditioned sequentially with methanol (10 mL), distilled water (2 × 10 mL), and a phosphate buffer, pH 7.0 (10 mL). Samples were passed through

Table 2. General Physical and Chemical Analyses of Cabernet Sauvignon Grape Berries from Different Enological Categories[a]

	low price		medium price		high price	
	30 DAV	CH	30 DAV	CH	30 DAV	CH
			Vintage 2009			
soluble solids (g/100 g)	22.4 ± 0.5 aA	23.2 ± 0.9 aA	23.1 ± 0.6 aAB	23.1 ± 0.1 aA	23.8 ± 0.3 aB	24.2 ± 1.1 aA
skin weight (g)	17.5 ± 1.1 aAB	20.2 ± 1.2 bA	16.1 ± 1.9 aA	22.7 ± 1.2 bA	20.2 ± 1.2 aB	20.6 ± 3.0 aA
seed weight (g)	5.0 ± 0.2 bA	4.4 ± 0.1 aA	4.5 ± 0.3 aA	4.4 ± 0.1 aA	5.2 ± 0.5 aA	4.7 ± 0.3 aA
berry weight (g/100 berries)	109.8 ± 2.0 bB	97.5 ± 1.2 aA	102.5 ± 3.0 aA	97.5 ± 2.1 aA	112.4 ± 0.8 bB	95.0 ± 1.8 aA
			Vintage 2010			
soluble solids (g/100 g)	22.2 ± 0.6 aA	23.3 ± 0.5 aA	25.2 ± 0.7 aB	26.0 ± 1.0 aB	23.7 ± 0.8 aAB	24.4 ± 0.3 aAB
skin weight (g)	20.3 ± 0.6 bB	16.0 ± 0.8 aA	18.3 ± 2.4 aB	16.8 ± 2.5 aA	14.2 ± 0.1 aA	17.8 ± 1.7 bA
seed weight (g)	4.9 ± 0.5 aB	4.2 ± 0.4 aA	4.0 ± 0.2 aA	4.9 ± 1.4 aA	4.6 ± 0.1 aAB	4.7 ± 0.8 aA
berry weight (g/100 berries)	109.9 ± 5.7 aA	104.8 ± 1.9 aA	107.4 ± 1.1 aA	110.4 ± 1.8 aA	124.4 ± 4.9 bB	107.2 ± 4.2 aA

[a]All data are expressed as the mean ± standard deviation ($n = 3$). Different lowercase letters indicate significant differences ($p < 0.05$) between the dates sampled for each price category according to Tukey's HSD test. Different uppercase letters within a row indicate significant differences ($p < 0.05$) between the price categories for each date sampling according to Tukey's HSD test. 30 DAV, 30 days after *veraison*; CH, commercial harvest.

Table 3. Phenolic Composition of Cabernet Sauvignon Berry Skins from Different Price Categories[a]

	total phenols (mg of GAE/g of skins)		total tannins (mg of CE/g of skins)		total anthocyanins (mg of ME/g of skins)	
price category	30 DAV	CH	30 DAV	CH	30 DAV	CH
			Vintage 2009			
low	5.4 ± 0.9 bA	3.6 ± 0.3 aA	11.7 ± 0.6 bA	6.7 ± 0.3 aA	4.5 ± 0.3 bB	3.1 ± 0.4 aA
medium	6.9 ± 0.4 bB	4.3 ± 0.6 aA	18.1 ± 1.1 bB	10.9 ± 0.8 aB	4.2 ± 0.5 bAB	2.7 ± 0.3 aA
high	5.0 ± 0.3 bA	3.9 ± 0.2 aA	9.6 ± 1.2 aA	9.9 ± 0.4 aB	3.5 ± 0.1 bA	3.0 ± 0.1 aA
			Vintage 2010			
low	4.1 ± 0.8 bB	2.1 ± 0.3 aA	7.5 ± 0.3 bA	5.6 ± 0.8 aA	3.5 ± 0.8 aA	3.5 ± 0.9 aA
medium	2.5 ± 0.6 aA	2.9 ± 0.9 aB	7.1 ± 0.8 aA	7.7 ± 1.0 aB	4.7 ± 0.2 bB	2.4 ± 0.7 aA
high	4.4 ± 0.6 bB	3.1 ± 0.0 aB	7.3 ± 0.3 aA	6.9 ± 0.7 aAB	3.2 ± 0.7 aA	3.5 ± 0.9 aA

[a]All data are expressed as the mean ± standard deviation ($n = 3$). Different lowercase letters within a row indicate significant differences ($p < 0.05$) between the dates sampled according to Tukey's HSD test. Different uppercase letters within a column indicate significant differences ($p < 0.05$) between the price categories according to Tukey's HSD test. 30 DAV, 30 days after *veraison*; CH, commercial harvest; GAE, gallic acid equivalents; CE, (+)-catechin equivalents; ME, malvidin equivalents.

the cartridges at a flow rate no faster than 2 mL/min, and phenolic acids were then eliminated by elution with 10 mL of 67 mM phosphate buffer solution at pH 7.0. The cartridges were dried with nitrogen gas and eluted sequentially with 25 mL of ethyl acetate (fractions FI + FII, containing monomeric and oligomeric flavan-3-ols, respectively) and 15 mL of methanol (fraction FIII, containing polymeric proanthocyanidins). The ethyl acetate elute was taken to dryness under vacuum, redissolved in 3 mL of 67 mM phosphate buffer, pH 7.0, and reloaded onto the same series of cartridges that had been conditioned again as described previously. The cartridges were dried with nitrogen and eluted sequentially with 25 mL of diethyl ether (fraction FI, containing monomers) and 15 mL of methanol (fraction FII, containing oligomers). Fractions FI, FII, and FIII were evaporated to dryness under vacuum and redissolved in 3 mL of methanol. The total content of flavan-3-ols in each fraction was determined by a vanillin assay.[13]

Determination of Total Content of Flavan-3-ols. The vanillin assay was performed as described by Sun et al.[13] A 2.5 mL aliquot of 1:3 (v/v) sulfuric acid/methanol solution and a 2.5 mL aliquot of 1% (w/v) vanillin in methanol were mixed with 1 mL of the sample. The tubes were incubated at 30 °C for either 15 min (FI fraction) or for a period of time long enough to allow maximal reaction (FII and FIII fractions). The absorbance was read at 500 nm. A blank was prepared by substituting the vanillin solution in the reaction mix with methanol. The absorbance of the blank is subtracted from the absorbance of the corresponding vanillin-containing sample. The value obtained is compared to standard curves. Quantification was performed by means of standard curves prepared from monomers (for FI), oligomers (for FII), and polymers of flavan-3-ol (for FIII) isolated from grape seeds, as previously described.[13]

HPLC-DAD Analysis of Flavan-3-ol Compounds. Red wines (50 mL) were extracted with diethyl ether (3 × 20 mL) and ethyl acetate (3 × 20 mL). The resulting extracts were evaporated to dryness at 30 °C, redissolved in 2 mL of 50% (v/v) methanol/water, and membrane-filtered (0.45 μm pore size).[8] Aliquots (25 μL) of the final solution were subjected to reversed-phase chromatographic separation at 20 °C on a Nova Pack C_{18} column. A photodiode array detector was set from 210 to 360 nm. Two mobile phases were used as follows: A, water/acetic acid (98:2 v/v), and B, water/acetonitrile/acetic acid (78:20:2 v/v/v). A gradient was applied at a flow rate of 1.0 mL/min from 0 to 55 min and 1.2 mL/min from 55 to 90 min as follows: 100−20% A from 0 to 55 min, 20−10% A from 55 to 57 min, 10−10% A from 57 to 90 min. Each major peak in the HPLC chromatograms of the extracts was characterized by both the retention time and the absorption spectrum (from 210 to 360 nm). Identification of specific compounds was achieved by comparison of the UV spectra and retention times against those of pure standards. Quantitative determinations were performed by the external standard method and commercial standards. All of the qualitative and quantitative analyses of phenolic composition (including extraction) were performed in triplicate.[8,14]

Statistical Analyses. The statistical methods used for the berry chemical analyses and the phenolic composition of the grape skins and seeds were two-way analysis of variance (ANOVA) and Tukey's honestly significant difference (HSD) test, which, after ANOVA was performed on the averages of the treatments examined, was used to establish which categories differed significantly from each other with a significance level of 95% ($p < 0.05$). For the global phenolic content in wines and the proanthocyanidin proportion of the grapes and wines, one-way ANOVA and Tukey's HSD test with a significance level of 95% ($p < 0.05$) were used. All statistical analyses were conducted with

Statgraphics Centurion, version 15 (Statpoint Technologies, Inc. 2009).

RESULTS AND DISCUSSION

Chemical and Physical Characterization of the Berries. Table 2 displays the parameters for the soluble solids (grams/100 g), skin weights (grams), seed weights (grams), and berry weights (grams/100 berries) for the two seasons. The parameters for the soluble solids from both seasons were within the normal ranges for cv. Cabernet Sauvignon grapes in the central region of Chile.[14] The berry skin weights from the 2009 season were slightly higher, although without great variations across the price categories. The seed weights from both seasons were similar. The berry weights from the 2009 season varied from 95.0 ± 1.8 to 112.4 ± 0.8 g/100 berries. In the 2010 season, the berry weights varied from 104.8 ± 1.9 to 124.4 ± 4.9 g/100 berries. It is interesting to note that, in both seasons, there were no significant differences across the price categories in terms of skin weight, seed weight, or berry weight from the commercial harvest. Differences in certain parameters of the chemical and physical compositions of the berries from the 30 DAV sample date tended to decrease with grape ripening and proximity to the commercial harvest date across the enological categories. It is important to consider that because the three harvesting sites are commercial vineyards, they harvested on different dates for technical reasons or due to the phenolic maturity of the grapes. There were no differences in the physical parameters across the three price categories.

Global Phenolic Composition of Grape Berries Extracts. *Global Phenolic Composition of Grape Skin Extracts.* Table 3 displays the results of the analyses of total phenols, total tannins, and total anthocyanins conducted on the berry skin extracts in different categories. Total phenols from both seasons indicated a decrease in concentration from 30 DAV to the harvest across all categories. At the harvest in the 2009 season, all treatments revealed the same total phenol content, while in the 2010 season, the medium and high categories presented a greater total phenol content. The decrease in total phenols for some enological categories is in agreement with results previously reported by others for Cabernet Sauvignon berry skins.[14,15]

The concentration of total tannins decreased or remained constant between sampling dates in both seasons, which is in agreement with previous studies.[16−18] It is interesting that in both seasons at commercial harvest, the medium and high categories had a higher tannin content than the low category. A higher content is beneficial to the wine made from those grapes because the wines could present a better color stability.[19,20] Skin tasting is used as a criterion of technological maturity by some winemakers; a higher content of extractable total tannins in the grape skins from higher categories may influence certain sensorial characteristics, such as astringency and bitterness, which could influence the time of harvest.[21]

There was a decrease in the total anthocyanin content in the berry skins from 30 DAV to commercial harvest in both seasons. The decrease in anthocyanin content is in agreement with previous studies that indicated a similar decrease found in Cabernet Sauvignon grapes during ripening.[14,15] Interestingly, there were no differences in the concentration of total anthocyanins in the grape skins at commercial harvest across price categories in both seasons. The total phenol and tannin concentrations were higher in the 2009 season than in the 2010 season, while the total anthocyanin concentrations were similar in both seasons. Because the cultural practices in each of the vineyards were in some ways the same in the two years of study, such as pruning, irrigation, and fertilization, the differences in concentrations between seasons could be due to differences in humidity and temperature (Table 1) that affected the concentrations of phenolic compounds, particularly tannins in the berry skins.[22,23]

Global Phenolic Composition of Grape Seed Extracts. Table 4 displays the analyses of total phenols and total tannins for the berry seed extracts in the different categories. In both seasons, the concentrations of seed phenols decreased or remained constant between the sampling dates. The contents were similar across the categories, although there were differences depending on the season, but the higher price categories demonstrated a trend toward higher phenol contents. The total tannin concentrations decreased in the medium category between the sampling dates, with similar concentrations across the categories at commercial harvest in both seasons. The decrease in seed polyphenols during fruit ripening could be due to oxidation phenomena, although this decrease was significant only in the medium category.[24,25] Compared with the concentration of total tannins in the grape skins, which revealed higher concentrations in the medium and high categories (Table 3), the grape seeds in both seasons did not exhibit significant differences in the tannin contents across the categories (Table 4). According to the polyphenol concentration results for the grape skins and seeds in this study, there were no clear differences across the categories, with the exception of the tannin contents from the skins, which was increased in the highest price categories. It is also important to note that the differences in the concentrations of certain secondary metabolites at the 30 DAV sampling tended to disappear closer to the commercial harvest date. Because the geographical area of study is characterized by no rain during the ripening of the grapes (November to May), red grape varieties for reserve wines are harvested very late to attain the correct phenolic maturity. The significance of this condition is that if red grapes are left on the vine, the longer duration could produce a decrease in the content of certain metabolites, such

Table 4. Phenolic Composition of Cabernet Sauvignon Berry Seeds from Different Price Categories[a]

	total phenols (mg of GAE/g of seeds)		total tannins (mg of CE/g of seeds)	
price category	30 DAV	CH	30 DAV	CH
	Vintage 2009			
low	31.7 ± 2.8 bA	21.9 ± 1.7 aA	41.8 ± 3.7 aA	40.8 ± 3.4 aA
medium	37.7 ± 2.1 bB	27.2 ± 1.5 aB	51.9 ± 5.4 bB	39.2 ± 5.7 aA
high	29.0 ± 1.7 aA	25.9 ± 1.5 aB	45.5 ± 1.6 aAB	43.4 ± 3.7 aA
	Vintage 2010			
low	17.3 ± 2.8 aA	17.8 ± 3.7 aA	32.6 ± 3.5 aA	35.8 ± 2.8 aA
medium	21.1 ± 2.5 aA	18.7 ± 1.8 aA	37.4 ± 1.9 bA	28.1 ± 4.2 aA
high	19.9 ± 0.7 aA	18.5 ± 3.6 aA	32.3 ± 3.5 aA	31.5 ± 4.2 aA

[a]All data are expressed as the mean ± standard deviation (n = 3). Different lowercase letters within a row indicate significant differences ($p < 0.05$) between the dates sampled according to Tukey's HSD test. Different uppercase letters withinin a column indicate significant differences ($p < 0.05$) between the price categories according to Tukey's HSD test. 30 DAV, 30 days after *veraison*; CH, commercial harvest; GAE, gallic acid equivalents; CE, (+)-catechin equivalents.

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as phenolic compounds, due to overripening and degradation phenomena.[2] An increase in the berry temperature, which occurs in warm growing regions such as the Aconcagua Valley,[26] may have affected the concentrations of tannins and anthocyanins[27] in this study; warming especially affects the berry skins and could explain the concentration differences found between the two sampling dates.

Proanthocyanidin Composition According to the Polymerization Degree in Grape Berries. *Extractable Proanthocyanidins According to the Polymerization Degree in Grape Skins.* Figure 1 displays the monomeric, oligomeric, and polymeric fractions in Cabernet Sauvignon berry skins from the commercial harvest. In both seasons, the extractable polymeric fraction (2009, 97.1%; 2010, 95.3%) was far more predominant than the oligomeric (2009, 2.2%; 2010, 2.9%) and monomeric (2009, 0.7%; 2010, 1.8%) fractions in the skins at commercial harvest. It is interesting that in both seasons the monomeric, oligomeric, and polymeric fractions of flavan-3-ols did not differ in concentration between the low and high categories. In addition, the medium category had a higher concentration of flavan-3-ol polymers in both seasons (2009, 1855 ± 335 mg/L; 2010, 1563 ± 431 mg/L), compared with the low category (2009, 685 ± 152 mg/L; 2010, 236 ± 113 mg/L) and the high category (2009, 917 ± 169 mg/L; 2010, 205 ± 93 mg/L). The concentrations of polymeric proanthocyanidins were higher in the 2009 season than the 2010 season, but there was a change only in the concentrations of the different fractions, with the proportions remaining the same among the different fractions. The contents of the flavan-3-ol fractions observed in this study are lower than those reported by Sun et al.[28] and higher than those reported by other authors for Cabernet Sauvignon grapes.[14,29]

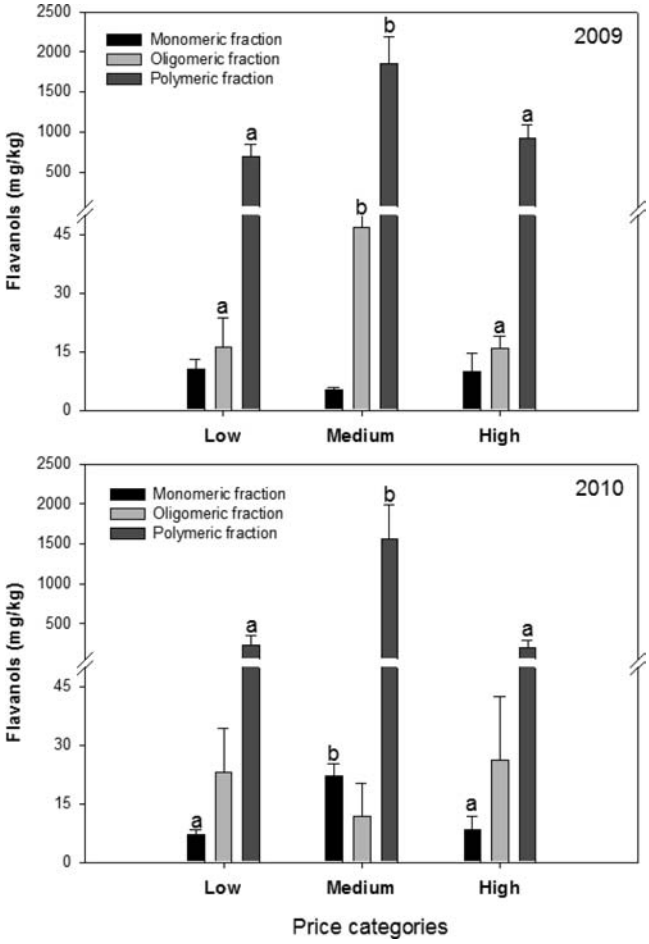

Figure 1. Monomeric, oligomeric, and polymeric fractions of proanthocyanidins in berry skins from cv. Cabernet Sauvignon from different price categories. Different letters within the same fraction indicate significant differences ($p < 0.05$) among the price categories according to Tukey's HSD test.

Extractable Proanthocyanidins According to the Polymerization Degree in Grape Seeds. Figure 2 displays the monomeric, oligomeric, and polymeric fractions in Cabernet Sauvignon berry seeds from the commercial harvest. Compared with the grape skins, the seeds revealed higher concentrations of monomers, oligomers, and polymers of flavan-3-ol. The monomeric fraction was the least abundant fraction in the seeds (2009, 3.2%; 2010, 3.1%), followed by the oligomeric fraction (2009, 18.9%; 2010, 18.5%), and the polymeric fraction was the most predominant in the seeds at commercial harvest (2009: 78.0%; 2010: 78.4%). Interestingly, the proportion of flavan-3-ol fractions remained unchanged in both seasons and experienced a drastic change only in the concentration of the polymeric fraction, which was higher in the 2009 season. The relative contents of the various fractions were lower than those

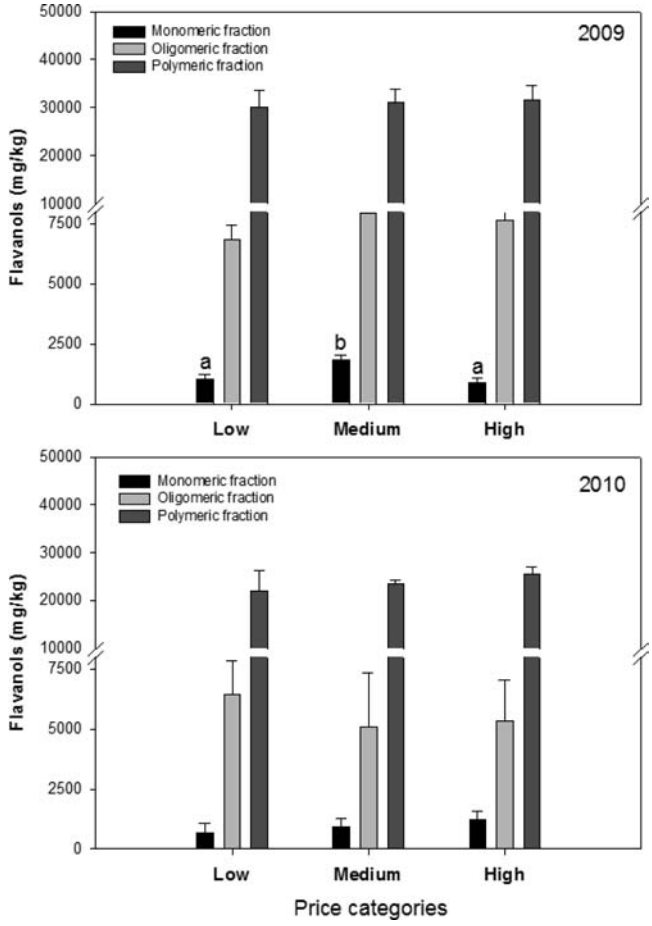

Figure 2. Monomeric, oligomeric, and polymeric fractions of proanthocyanidins in berry seeds from cv. Cabernet Sauvignon from different price categories. Different letters within the same fraction indicate significant differences ($p < 0.05$) among the price categories according to Tukey's HSD test.

Table 5. Global Phenolic and Color Composition of Cabernet Sauvignon Wines from Different Price Categories[a]

	2009			2010		
	low	medium	high	low	medium	high
total phenols (mg of GAE/L)	1421.8 ± 24.9 a	1928.8 ± 17.4 b	1933.0 ± 36.5 b	1279.5 ± 44.5 a	1865.6 ± 93.6 c	1502.7 ± 74.4 b
total tannins (mg of CE/L)	2274.5 ± 115.1 a	3947.8 ± 84.8 b	3880.2 ± 170.2 b	2366.5 ± 57.0 a	3460.7 ± 86.5 b	3501.4 ± 34.3 b
total anthocyanins (mg of ME/L)	470.6 ± 19.8 a	512.3 ± 5.3 b	565.7 ± 15.0 c	423.0 ± 22.5 a	439.7 ± 35.7 a	439.2 ± 19.3 a
CI	12.1 ± 0.1 a	13.5 ± 0.0 b	14.5 ± 0.0 c	11.2 ± 0.1 a	13.3 ± 0.2 b	14.1 ± 0.1 c
To	0.6 ± 0.0 a	0.7 ± 0.0 b	0.6 ± 0.0 a	0.6 ± 0.0 a	0.7 ± 0.0 b	0.7 ± 0.0 b
% yellow	33.4 ± 0.3 a	36.0 ± 0.7 b	33.4 ± 0.2 a	33.8 ± 0.3 a	35.8 ± 0.2 c	34.8 ± 0.3 b
% red	56.3 ± 0.2 c	52.4 ± 0.4 a	54.5 ± 0.3 b	55.5 ± 0.3 b	52.9 ± 0.2 a	53.4 ± 0.3 a
% blue	10.3 ± 0.1 a	11.6 ± 0.3 b	12.1 ± 0.2 b	10.7 ± 0.1 a	11.3 ± 0.4 ab	11.8 ± 0.4 b

[a]All data are expressed as the mean ± standard deviation ($n = 3$). Different letters within a row indicate significant differences ($p < 0.05$) between the price categories according to Tukey's HSD test in each vintage. GAE, gallic acid equivalents; CE, (+)-catechin equivalents; ME, malvidin equivalents; CI, color intensity; To, tonality.

reported by other authors;[29] however, they are higher than those reported by Obreque-Slier et al.[14] When the fractions of flavanols in this study are compared, the grape skins revealed more polymerized flavanols and fewer flavan-3-ol oligomers than the grape seeds.[23,24,30,31] There was a clear seasonal effect on the grape skins and seeds that influenced the concentration of the flavan-3-ol fractions. It is necessary to keep in mind that the vineyards differed in their agricultural management, which may explain the differences in concentrations across the price categories. The proanthocyanidin fraction concentrations were affected across the price categories, but their proportions did not change across the categories or between the seasons. Moreover, the proanthocyanidin fraction concentrations in the grape skins demonstrated differences across the price categories; however, the proanthocyanidin concentrations in the seeds did not differ. In general terms, the higher price categories did not present higher concentrations of proanthocyanidin fractions or a different proanthocyanidin proportion than the lower price category. In addition, the polymeric fraction presented the greatest concentration differences across the price categories and between seasons, which may have occurred because this fraction was greatly affected by climatic differences between the seasons and by different agricultural management practices between the price categories.

Phenolic Composition of the Wines. *Global Phenolic Composition of the Wines.* The vinification of grapes in commercial wineries that are used for wines with different market prices may reveal differences in the enological tasks involved in the process, such as the number of pump-overs, the use of prefermentative and/or postfermentative maceration, and the use of wood in the form of barrels, staves, or chips. These enological practices will cause a differential extraction of compounds from the different quality of grapes, which will impact the concentration and composition of phenolic compounds in the wines made from those grapes. In this study, we employed the same winemaking process to determine if there were differences in the concentrations and compositions of phenolic compounds and if the differences observed in the grapes were also observed in the wines made from these grapes.

Table 5 presents the analyses of total phenols, total tannins, and total anthocyanins in the wines produced from grapes of different enological categories. In both seasons, significant differences in the total phenols were observed across the wine categories; the samples from the low category had the lowest phenol content, which is in agreement with the results reported by other authors.[32−35] The low category presented the lowest total tannin content in both seasons, which is also in agreement with other authors.[35,36] The overall contents of total tannins in the wines studied here were much higher than those published by others.[33,34,36,37] In a normal wine fermentation a greater release of tannins is expected, especially from seeds.[38] Although the content of tannins in the seeds was much greater than in the skins (Tables 3 and 4), the subsequent concentrations in the wine were due largely to the contributions from the skins rather than the seeds, an observation that held true across all categories. The correlations between tannin concentrations in the skins and the seeds with those in the wines are as follows: skins 2009, $r = 0.9509$; skins 2010, $r = 0.7575$; seeds 2009, $r = -0.0156$; and seeds 2010, $r = -0.6642$. The higher concentrations of tannins in the skins in the medium and high categories could impact the tannin concentrations in the resulting wines, while the seed tannins did not differ significantly on the harvest date. The strong extraction of tannins from the grape skins could have been due to overripening of the grapes, leading to degradation of the cell walls by active hydrolysis of structural cell wall polysaccharides.[39] Conversely, the price categories presented similar seed tannin contents at harvest, and as discussed above, the skin tannins could produce the differences in content in the resulting wines. An interaction between the tannins and the cell walls and a hardening of the seed coat may have reduced the extraction of tannins from the seeds.[40] The greater tannin content in wines from the medium and high price categories may have been due to the higher concentration of tannins in the grape skins from these categories, which demonstrates a possible relationship between the grape tannin concentration and the projected market bottle price.[36] Furthermore, it is likely that the increased extraction of tannins produced a higher level of extraction of other compounds, such as polysaccharides,[35] which could modify the sensory properties of the wines made from these grapes.[41,42]

The total anthocyanin differences across price categories were not clear and depended on the season of study, as there were differences across the price categories in 2009 but not in 2010. No significant differences were found in the concentrations of anthocyanins between the wines from the three price categories. The total anthocyanin contents in this study were comparable to those reported by other authors.[32,43,44] The differences between the seasons and price categories may have been due to differences in the cell wall composition among the different grape categories that affected the extractability of anthocyanins from the berry skins.[45] There was a higher CI in wines from the high category, followed by the medium

category. The lowest CI was found in wines from the low category in both seasons. The wines from the medium and high categories demonstrated a higher To than the low category. The To indicates the development of a color toward orange, combining the yellow fraction with the red fraction. The higher To in the medium and high categories may have been due to the higher content of total tannins contributing to the yellow color development in the wines.[43] Changes in the phenolic composition are well-known to have a strong influence on the color composition and chromaticity of wines. Although significant differences were observed between the color components, these differences were minimal, and there was no clear relationship between the red component (% red) and total anthocyanins in the wines. Instead, there was a weak relationship between the yellow component (% yellow) and the total tannin contents of the wines, with a higher % yellow value in the medium and high categories. With regard to the blue component (% blue), there was a higher value in the medium and high categories. The higher % blue value in these wines was likely due to a strong copigmentation or condensation of the anthocyanins with flavan-3-ols, which stabilize the violet tonalities of the wine.[19] These results are in agreement with those obtained by other authors for wines of the same variety.[32,35,42] The wines produced in the 2009 season revealed higher contents of phenols, tannins, and anthocyanins, which coincides with the results for the phenolic compositions of the grape skins and seeds in the different categories (Tables 3 and 4).

Extractable Proanthocyanidins According to the Polymerization Degree in the Wines. Figure 3 displays the monomeric, oligomeric, and polymeric flavan-3-ol proportions in wines produced from grapes of different enological categories. Sun et al.[12] indicate that the monomeric fraction consists only of (+)-catechin, (−)-epicatechin, and (−)-epicatechin 3-*O*-gallate, whereas the oligomeric fraction is formed by dimers, trimers, and tetramers of proanthocyanidins and the polymeric fraction is composed of polymeric proanthocyanidins (more than 4 units). The differences between the price categories in the proportions of the monomeric fractions of flavan-3-ol did not indicate a clear trend in either season. In contrast, the oligomeric and polymeric fractions demonstrated a clear trend in both seasons, with a lower concentration of oligomeric fraction in the high category and a higher concentration of polymeric fraction in the medium category. The same concentration was observed in the low and high categories. Across both seasons and all wine price categories, the extractable polymeric fraction was far more predominant (2009, 91.6%; 2010, 89.6%) than the oligomeric (2009, 7.3%; 2010, 9.4%) and monomeric (2009, 1.1%; 2010, 1.0%) fractions. There were no differences in the proanthocyanidin proportions across the price categories and between the seasons, although the content of polymeric proanthocyanidins was similar in the low and high categories. These differences in proportions may have influenced the astringency and bitterness of these wines, which should be confirmed in further studies.[4,5,46] The higher level of the polymeric fraction coincides with that of the polymeric fraction from the berry skins in the medium category (Figure 1). Even so, it is clear that the proportions and concentrations of proanthocyanidins in the grapes and the resulting wines did not affect the price of the wine in the market, which indicates that more expensive wines do not necessarily contain a higher concentration or different proportion of proanthocyanidins than less expensive wines.

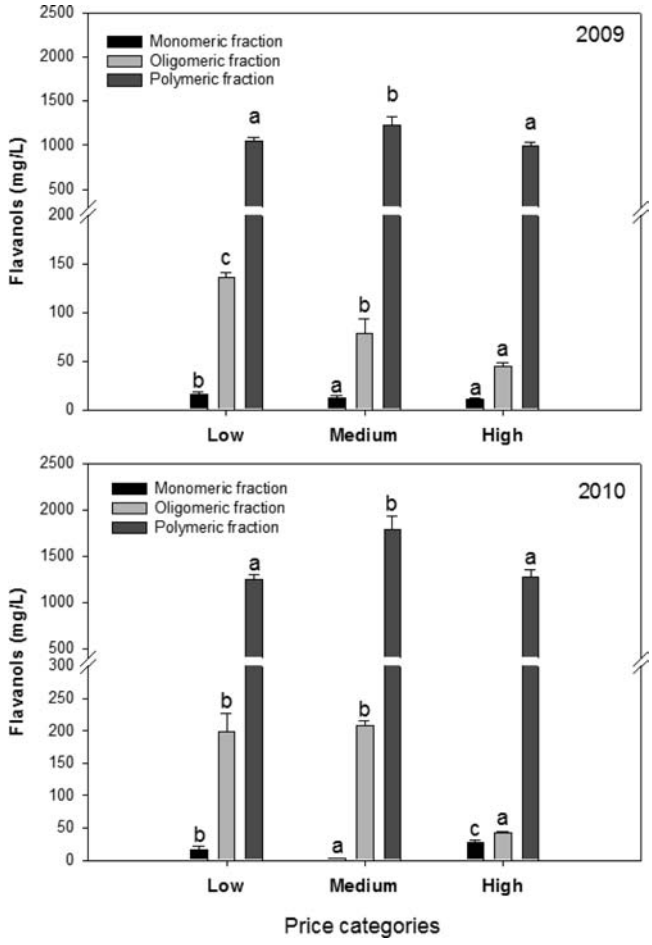

Figure 3. Monomeric, oligomeric, and polymeric fractions of proanthocyanidins in wines from cv. Cabernet Sauvignon from different price categories. Different letters within the same fraction indicate significant differences ($p < 0.05$) among the price categories according to Tukey's HSD test.

An interesting result occurred between the concentrations of proanthocyanidin fractions in grapes and wines, showing an opposite pattern between seasons. Although the winemaking was the same, the extraction could be different due to differences in cell wall composition and differences in binding between proanthocyanidins and polysaccharides.[39,40] Moreover, the study of Bindon and Kennedy[31] noted that as proanthocyanidin polymerization increased, the affinity of these compounds for the skin cell wall declined. The difference of days in the grape harvest between the seasons could produce a difference in ripening that affected the proanthocyanidins' polymerization and their affinity with cell wall that caused differences in winemaking extraction. Further studies should be done to confirm this behavior.

Flavan-3-ol Monomer and Dimer Contents in Wines. Table 6 displays the concentrations of monomers and dimers of flavan-3-ol in the three wine price categories; those identified in the wine samples were (+)-catechin, (−)-epicatechin 3-*O*-gallate, and procyanidins B1−B4. The flavan-3-ol compound contents in this study were lower than those published by others for Cabernet Sauvignon wines.[35,47] Procyanidins B1−B4 and (−)-epicatechin 3-*O*-gallate were found in higher concentrations in wines of the higher price categories, with significant differences between the categories. Procyanidin B2 was not found in the wines from the low category in either

Table 6. Monomers and Dimers of Flavan-3-ol Quantified in Cabernet Sauvignon Wines from Different Price Categories[a]

	2009			2010		
	low	medium	high	low	medium	high
procyanidin B1, mg/L	6.5 ± 0.0 a	9.2 ± 0.1 b	10.7 ± 0.1 c	12.3 ± 0.1 a	14.7 ± 0.1 b	19.2 ± 0.1 c
procyanidin B2, mg/L	nd	16.9 ± 0.1 a	20.3 ± 0.2 b	nd	9.4 ± 0.1 a	9.9 ± 0.1 a
procyanidin B3, mg/L	2.3 ± 0.1 a	8.1 ± 0.2 b	10.3 ± 0.1 c	10.5 ± 0.2 a	8.8 ± 0.1 b	12.6 ± 0.1 c
procyanidin B4, mg/L	1.8 ± 0.1 a	5.1 ± 0.0 b	4.4 ± 0.1 c	0.6 ± 0.1 a	3.2 ± 0.1 b	3.4 ± 0.3 b
(+)-catechin, mg/L	12.0 ± 0.1 a	15.2 ± 0.2 b	13.6 ± 0.1 c	8.3 ± 0.1 a	6.2 ± 0.1 b	5.8 ± 0.3 b
epicatechin-3-*O*-gallate, mg/L	2.7 ± 0.1 a	6.3 ± 0.2 b	6.6 ± 0.0 b	1.9 ± 0.1 a	6.1 ± 0.1 b	7.5 ± 0.3 c

[a]All data are expressed as the mean ± standard deviation ($n = 3$). Different letters in a row indicate significant differences ($p < 0.05$) between the price categories according to Tukey's HSD test in each vintage. nd, not detected.

season. There was no clear trend for the concentration of (+)-catechin in the different categories studied. There was a clear difference in the concentrations of flavan-3-ol monomers and dimers between the seasons. The higher level of these compounds in the higher price categories may be explained by the higher CI and To observed in the wines in the medium and high categories due to a copigmentation process (Table 5).[43]

Knowledge of the composition and concentration of phenolic compounds in grapes and their relationship with the retail price of wines in the market is important for determining if higher-priced wines have higher concentrations of phenolic compounds. Furthermore, because higher-quality wines undergo enological procedures that result in a higher level of extraction of these compounds, it is necessary to analyze whether the grapes that produce more expensive wines present different concentrations or compositions of phenolic compounds than grapes that produce less expensive wines or if the enological procedures performed with higher-quality wines are responsible for the higher levels. There was no clear relationship between the higher price categories and a greater content of phenolic compounds in this study; the only such trend was found for the higher concentration of total tannins. Moreover, the only differences between the proanthocyanidin fractions in the skins, seeds, and wines were in their concentrations and not in their proportions. Further studies in this area, including studies that take into account other compounds that may influence wine composition in conjunction with viticultural management practices, environmental conditions, winemaking procedures, and the aging process, could provide useful information to improve the quality of the final wine product.

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Notes

The authors declare no competing financial interest.

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