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Wines in contact with oak wood: the impact of the variety (Carménère and Cabernet Sauvignon), format (barrels, chips and staves), and aging time on the phenolic composition

Jaime Laqui-Estaña,[a] Remigio López-Solís,[b] Álvaro Peña-Neira,[a] Marcela Medel-Marabolí[a] and Elías Obreque-Slier[a]*

Abstract

BACKGROUND: This study characterized the flavonoid and nonflavonoid phenolic composition of Carménère and Cabernet Sauvignon wines that were in contact with barrels, chips, and staves during a 12 month aging period. The wines were evaluated by spectrophotometric (for total phenols, anthocyanins and tannins, colorant intensity, hue, CIELab parameters, and fractionation into mono-, oligo-, and polymers of proanthocyanidins) and high-performance liquid chromatography diode array detection analyses (for ellagitannins, gallotannins, anthocyanins, and low molecular weight phenols).

RESULTS: Wines in contact with oak wood presented a strong enrichment with nonflavonoid compounds, such as caffeic, gallic, and ellagic acids and ellagitannins. Wines in contact with staves stood out for the increased presence of total phenols, vanillic acid, and higher color intensity, whereas wines aged in contact with chips showed large contents of proanthocyanidin gallates. Wines aged in barrels exhibited high contents of ellagitannins and ethyl gallates. The effect of wood on the phenolic composition was mostly associated with the original and intrinsic characteristics of each grape variety.

CONCLUSION: Extraction of phenolic compounds from oak wood during wine aging is closely related to the wood format, grape variety (Carménère or Cabernet Sauvignon), and aging time. The final effect of wood on wine would be related not just to the transference of polyphenols from wood, but also to structural modifications of grape polyphenols.

Keywords: oak wood; aging time; flavonoid compounds; nonflavonoid compounds

INTRODUCTION

Aging wine in wood barrels is a relevant refinement stage that occurs before bottle aging. The most important phenomena that occur during barrel aging are oxygen entry, complexation of procyanidins with proteins, peptides, and polysaccharides, and precipitation or loss of some wine compounds.[1] In addition, changes in the wine organoleptic characteristics during barrel aging have been closely associated with the contribution of aromas and phenolic compounds that improve the aromatic and gustatory profile.[2,3] Polyphenols are secondary metabolites of plants that are widely distributed in beverages and plant-derived foods. Their different structures seem to play an important role in the quality of wines and are usually divided into two groups: flavonoids and nonflavonoids.[4] The nonflavonoid wine compounds are primarily derivatives of hydroxycinnamic acid and hydroxybenzoic acid, while other types of nonflavonoid phenols correspond to hydrolyzable tannins (gallotannins and ellagitannins). Flavonoid compounds of wine are represented by groups of flavonols, flavan-3-ols, and anthocyanins.[5] Condensed tannins or proanthocyanidins correspond to molecules comprising several flavan-3-ol units. Flavonols and anthocyanins are the most abundant phenolic compounds in the skins of red grapes, whereas grape seeds are rich in flavan-3-ols and proanthocyanidins.[6,7] By contrast, hydrolyzable tannins and certain low molecular weight nonflavonoid phenols occurring in wine are extracted during aging in oak wood.[8,9]

Wine aging in oak wood barrels is a common enological practice. However, it is an onerous and organizationally cumbersome process.[10] Thus, winemakers have been looking for alternatives to speed up that process, and to obtain more-affordable wines with characteristics similar to those of wines aged in barrels for several months.[11] Thus far, several wine-producing countries (e.g. Australia, the USA, and Chile) have started marketing wines macerated in contact with oak wood pieces instead of aging wines in oak wood barrels.[12] On those grounds, research efforts have

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been focused on the effects of substitute wooden products (chips and staves) on the phenolic composition of red wines. Del Álamo *et al.*[13] observed a substantial reduction in anthocyanins and catechins during aging in the presence of oak wood chips, which could result from polymerization, condensation, precipitation, and absorption processes.[14] In addition, Del Álamo *et al.*[15] showed that the concentrations of caffeic, *p*-coumaric, and ferulic acids in wines aged in contact with staves were higher than those in barrel-aged wines. On the other hand, Jourdes *et al.*[16] reported faster extraction of ellagitannins in wines aged in contact with wood chips compared with barrel-aged wines.

In spite of previous reports pointing to a potential impact of the type of oak wood format (chips, staves, or barrels) on the chemical composition of wines aged for 1 year, understanding of the subject has been rather limited. Furthermore, most of those studies have dealt with a particular subgroup of phenolic compounds (nonflavonoids), which is clearly a limiting condition to attain a more comprehensive view of the subject. Thus, wine contact with wood does not necessarily result in an increased content of nonflavonoid polyphenols, but it may involve substantial modifications of the flavonoid polyphenols in the wine matrix, particularly proanthocyanidins. Furthermore, the magnitude of that effect may also depend closely on the grape variety. Finally, comparative studies using Carménère (an emblematic cultivar of Chilean viniculture) and Cabernet Sauvignon (a widely cultivated variety) are nonexistent. The purpose of this study was to characterize and compare for the first time the nonflavonoid and flavonoid phenolic compositions of Carménère and Cabernet Sauvignon wines during aging in contact with oak wood barrels, chips, or staves for 12 months.

MATERIALS AND METHODS

Materials

Carménère and Cabernet Sauvignon wines of the 2015 Curicó Valley (Maule Region, Chile) vintage were donated by Villaseñor Vineyards (35° 09′ 00″ S; 71° 21′ 00″ W). Agronomic, photochemical, and technical variables of these vines were determined. Grapes were harvested from 10-year-old vines trained in vertical shoot position, with north–south orientation, drip irrigation, and production of approximately 12 000 kg ha^{-1}. Barrels, chips, and staves from medium-toasted and air-dried (30 months) French *Quercus petraea* (Matt.) oak wood were acquired from Nadalie cooperage (Santiago, Chile). Phenolic calibration standards and 0.45 µm pore-size membranes (Whatman cat. number 1440-125) were acquired from Sigma Chemical Co. (St. Louis, MO, USA). Vanillin 99% (code V-8510), trifluoroacetic acid, ethyl acetate, high-performance liquid chromatography (HPLC)-grade acetonitrile, and pro-analysis solvents were purchased from Merck (Darmstadt, Germany). Sep-Pak Plus tC18 cartridge numbers WAT 036810 and WAT 036800 were obtained from Waters (Milford, MA, USA).

Instrumentation

The HPLC system (Agilent Technologies, Santa Clara, CA) consisted of G1315B photodiode array detector, G1311A Quatpump, and G1329A ALS autosampler. A reversed-phase Nova Pack C18 column (4 µm, 3.9 mm i.d. × 300 mm; Waters Corp.) was used for HPLC diode array detection (DAD) analysis of individual phenolic compounds. A reversed-phase LiChrospher100 RP-18 column (5 µm, 4 mm i.d. × 250 mm; Agilent Technologies) was used in the anthocyanin and ellagitannin studies. Absorbances were measured using a Jasco UV-Vis V-530 spectrophotometer (JASCO International Co., Ltd, Tokyo, Japan).

Procedure

Wines were obtained from Carménère and Cabernet Sauvignon grapes, which were harvested at the optimal ripening stage for commercial use (23–24 °Brix). Wines were produced under similar technological management practices. In brief, the grapes were received, destemmed–crushed, and placed into stainless steel tanks. Maceration for 3 days (skins/seeds/must at 8 °C) was followed by fermentation (10 days at 25 ± 1.0 °C) after inoculating 20 g hL^{-1} of active dry yeast (*Saccharomyces cerevisiae*, Uvaferm VRB, Lallemand, France). Three pump-overs per day were performed. Pump-overs from day 1 to day 3 lasted 40 min each (aerated), pump-overs between days 4 and 7 lasted 20 min (aerated), and pump-overs between days 8 and 10 lasted 2 min (nonaerated). Subsequently, a malolactic fermentation was performed spontaneously. Once the malolactic fermentation was finished, the wines were sulfited (adjusted to 60 mg L^{-1} of free sulfur dioxide) and placed in contact with barrels (225 L) or with stainless steel tanks (320 L) containing either 7.8 g of chips per liter (irregular form, 5.47 cm^3 average contact surface per piece) or 12 staves (100 cm × 8 cm × 1 cm). All three experimental conditions represented a contact wood surface/wine volume ratio of 2.04 m^2 per 225 L barrel.[15] Wines in stainless steel tanks without staves or chips were used as controls. All treatments were conducted in triplicate for 1 year under controlled conditions of relative humidity (65–75%) and temperature (14–16 °C). During the aging period, the wines were stirred (*bâtonnage*) for 3–5 min weekly and the molecular sulfur was adjusted to 0.8 mg L^{-1}. Several wine samples were taken over 1 year. Wine volumes in barrels and tanks were adjusted with plain (no wood) Carménère or Cabernet Sauvignon wines to compensate for losses during the aging period (300 mL week^{-1} per tank during the first 2 months followed by 150 mL week^{-1} per tank for the rest of the study). Wines were filtered and kept at 4 °C until analysis.

Basic chemical analyses

The wines under study were analyzed at days 0 (first contact with oak wood) and 347 (last sampling date) by using the following methods: (i) total acidity by alkalimetry with 0.1 mol L^{-1} NaOH and bromothymol blue indicator (end point at pH 7.0), (ii) pH by potentiometry using a combination glass electrode at 20–22 °C, (iii) ethanol content by densitometry,[17] (iv) volatile acidity by the Blarez method, (v) reducing sugar content by the Fehling–Causse–Bonnans liquor method,[17] and (vi) oxygen content (Dissolved Oxygen Meter, Model HI9146, Hanna Instruments, Woonsocket, Rhode Island, USA).

General polyphenol analyses

Wines were analyzed at days 0, 14, 32, 77, 122, 167, 212, 257, 302, and 347 of aging by using the following methods: (i) total phenols by absorptiometry at 280 nm,[18] (ii) total tannins by the methyl cellulose procedure,[19] (iii) total anthocyanins by the bisulfite decoloration method,[18] (iv) color intensity by adding wine absorbances at wavelengths 420, 520, and 620 nm, (v) hue (420 nm/520 nm absorbance ratio),[20] and (vi) CIELab parameters.[21]

Fractionation of proanthocyanidins into monomers, oligomers, and polymers

The wines under study were fractionated at days 0, 14, 32, 122, 212, 302, and 347 of aging by using Waters C18 Sep-Pak cartridges according to the method described by Sun *et al.*[22] In brief, 10 mL

of each wine was concentrated to dryness in a rotary evaporator at <30 °C. The residue was dissolved in 20 mL of 67 mmol L^{-1} phosphate buffer pH 7.0. The pH of the resulting solution was adjusted to 7.0 with NaOH or HCl. Two C18 Sep-Pak cartridges were assembled (WAT 36800 on top and WAT 36810 at the bottom) and conditioned sequentially with methanol (10 mL), distilled water (2 × 10 mL), and phosphate buffer pH 7.0 (10 mL). The samples were passed through cartridges at a flow rate not higher than 2 mL min^{-1}, and the phenolic acids were then eliminated by elution with 10 mL of 67 mmol L^{-1} phosphate buffer at pH 7.0. The cartridges were dried with nitrogen gas and eluted sequentially with 25 mL of ethyl acetate to produce fraction FI + FII, which contains monomeric and oligomeric flavan-3-ols, and with 15 mL of methanol to produce fraction FIII, which contains polymeric proanthocyanidins. The ethyl acetate eluate was evaporated to dryness under vacuum, redissolved in 3 mL of 67 mmol L^{-1} phosphate buffer, pH 7.0, and reloaded onto the same series of cartridges that had been conditioned again as already described. The cartridges were dried under nitrogen and eluted sequentially with 25 mL of diethyl ether (monomer-containing fraction FI) and 15 mL of methanol (oligomer-containing fraction FII). Fractions FI, FII, and FIII were vacuum evaporated to dryness and redissolved in 3 mL of methanol. The total flavan-3-ol contents in each fraction was determined by the vanillin assay.[23] Thus, 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 sample. The assay tubes were incubated at 30 °C for either 15 min (FI fractions) or for a period of time that was long enough to allow for a maximal reaction (FII and FIII fractions). Absorbance was read at 500 nm. A blank was prepared by substituting the vanillin solution in the reaction mix with methanol.

HPLC-DAD analysis of anthocyanins and individual phenolic compounds

Anthocyanins were evaluated at days 0, 14, 32, 77, 167, 257 and 347 of aging. For that purpose, 100 mL of each wine was passed through a filter with a 0.45 mm pore size and then subjected to reversed-phase chromatographic separation at 20 °C under conditions reported in previous studies.[6] Individual phenolic compounds were evaluated at days 0, 14, 32, 77, 257, and 347 of aging. Thus, 50 mL of wine was extracted with ethyl ether (3 × 20 mL) and then with ethyl acetate (3 × 20 mL). The total extract was evaporated to dryness at 30 °C. The residue was collected in 2 mL of methanol–H_2O (50 : 50; v/v) and filtered with a 0.45 µm membrane. HPLC fractionation was undertaken using 20 µL of the solution. Identification and quantification of individual phenolics were performed as recently reported elsewhere.[6]

Ellagitannin content

Ellagitannins were evaluated at days 0, 14, 32, 77, 167, 257, and 347 of aging according to the method of Chira and Teissedre.[24] In brief, 20 mL of wine was vacuum evaporated to dryness at 30 °C and redissolved in 10 mL of 4 : 1 (v/v) methanol–2 mol L^{-1} HCl. A 2 mL extract was membrane filtered (0.45 mm pore size), and 8 mL of the same extract was incubated at 95 °C for 2.5 h and then membrane filtered. For quantification, a 20 mL aliquot was injected into the HPLC equipment according to conditions published elsewhere.[25]

Statistical analysis

The results were analyzed by general linear and mixed models with a significance level of 95% ($P < 0.05$). When P values were significant ($P < 0.05$), the Di Rienzo, Guzman and Casanoves test (was employed. This test is a cluster-based method for identifying groups of nonhomogeneous means. The Infostat version 2016 software package was used.

RESULTS

General analytical parameters

The basic parameters of wines in contact with different wood formats (barrels, chips, or staves) were evaluated during the study. In most cases, the values for the different chemical variables of the Carménère and Cabernet Sauvignon wines remained unchanged at days 0 and 347 of aging (Table 1).

Phenolic composition

Figure 1 presents the concentrations of total phenols, tannins, and anthocyanins of Carménère and Cabernet Sauvignon wines over 347 days of wood aging. Both wine varieties showed a slight increase in total phenols, while the control wines (that had no contact with wood) exhibited a decreasing behavior up to reaching the lowest levels from day 77 onwards. The Carménère and Cabernet Sauvignon wines aged in contact with oak staves displayed the highest concentration of those compounds during most of the time, from days 122 and 32 onwards respectively. By contrast, the anthocyanin contents decreased continuously from the beginning to the end of the study period in both wine varieties. During that period, the Carménère and Cabernet Sauvignon control wines (aged with no contact with wood) displayed significantly higher anthocyanin concentrations than the corresponding wood-aged wines from days 32 and 122 respectively. In this regard, the Cabernet Sauvignon wines aged in contact with oak staves displayed the lowest anthocyanin contents from the sixth sampling date (day 167) (Fig. 1). Contrarily, total tannin contents remained unchanged during most of the study, except for the Cabernet Sauvignon wines, which exhibited lower levels at the last sampling dates. No statistically significant differences between the total tannin contents of wines aged in contact with different wood formats were observed.

Color intensity and hue

An increase in color intensity was observed in the first part of the aging period (until day 77), both in presence and absence of oak wood in each wine variety. From that time on, color intensity decreased markedly up to minimal values during the last sampling (day 347). On the other hand, the Carménère and Cabernet Sauvignon wines aged for at least 167 days in contact with either barrels or staves showed higher color values than the other wines in the study (Fig. 2). By contrast, the hue values of both wine varieties increased continuously and significantly since day 77 of aging and until the last sampling dates. Both control wines presented the highest hue values during most of the aging period, whereas Carménère wines aged in contact with oak barrels and Cabernet Sauvignon wines aged in contact with oak staves showed the lowest hue values around the end of the aging period (Fig. 2).

CIELab parameters

Figure 3 shows clarity L^*, chroma C^*, hue h^*, and a^* and b^* values for both wine varieties during aging in contact with either barrels, staves, or chips. Control Carménère and Cabernet Sauvignon wines showed higher L^*, h^*, and b^* values with respect to the wood-aged wines. The Carménère wines aged in contact with

Table 1. General chemical parameters of Carménère and Cabernet Sauvignon wines during aging

		347 days			
	0 days	Control	Staves	Chips	Barrels
Carménère					
Titratable acidity (g H_2SO_4 L^{-1})	2.9 ± 0.1 a	2.8 ± 0.1 b	2.8 ± 0.1 b	2.7 ± 0.1 c	2.8 ± 0.0 b
pH	3.7 ± 0.0 a	3.7 ± 0.0 a	3.7 ± 0.0 a	3.7 ± 0.0 a	3.7 ± 0.0 a
Alcoholic content (%, v/v)	13.8 ± 0.2 a	13.7 ± 0.2 a	13.6 ± 0.2 a	13.6 ± 0.1 a	13.7 ± 0.1 a
Reducing sugars (g glucose L^{-1})	1.9 ± 0.2 a	1.9 ± 0.1 a	1.9 ± 0.1 a	1.8 ± 0.1 a	2.0 ± 0.0 a
Volatile acidity (g acetic acid L^{-1})	0.5 ± 0.0 b	0.6 ± 0.0 a	0.6 ± 0.0 a	0.6 ± 0.1 a	0.62 ± 0.0 a
Dissolved oxygen (mg oxygen L^{-1})	3.2 ± 0.0 a	0.3 ± 0.0 b	0.3 ± 0.1 b	0.3 ± 0.0 b	0.3 ± 0.0 b
Cabernet Sauvignon					
Titratable acidity (g H_2SO_4 L^{-1})	3.1 ± 0.1 a	2.9 ± 0.1 b	3.0 ± 0.1 a	2.8 ± 0.0 b	3.1 ± 0.1 a
pH	3.6 ± 0.0 a	3.6 ± 0.0 a	3.6 ± 0.0 a	3.6 ± 0.0 a	3.6 ± 0.0 a
Alcoholic content (%, v/v)	13.6 ± 0.2 a	13.6 ± 0.2 a	13.4 ± 0.2 a	13.6 ± 0.1 a	13.5 ± 0.1 a
Reducing sugars (g glucose L^{-1})	2.1 ± 0.1 a	2.0 ± 0.1 a	2.1 ± 0.0 a	2.1 ± 0.0 a	2.0 ± 0.2 a
Volatile acidity (g acetic acid L^{-1})	0.5 ± 0.0 b	0.6 ± 0.0 a	0.6 ± 0.0 a	0.6 ± 0.0 a	0.6 ± 0.0 a
Dissolved oxygen (mg oxygen L^{-1})	3.0 ± 0.0 a	0.3 ± 0.1 b	0.3 ± 0.0 b	0.2 ± 0.0 b	0.3 ± 0.0 b

Values represent means plus/minus standard deviation (triplicate). Different lower-case letters in single rows stand for statistically significant differences (DGS test; $P < 0.05$). Alcoholic content is at 20 °C.

different wood formats showed no significant differences from each other, excepting those aged in oak barrels, which presented high C^* and a^* values at the end of the aging period. However, the Cabernet Sauvignon wines in contact with staves presented low values for L^* at day 32 and for h^* and b^* at day 122. Furthermore, some treatments (barrels or staves) presented the highest C^* values, while those wines in contact with staves showed highest a^* parameters during all the study.

Degree of polymerization of wine proanthocyanidins during wood aging

Figure 4 shows the mono-, oligo-, and polymeric fractions of wine flavan-3-ols during aging. Monomeric flavan-3-ols represented the far less abundant fraction and polymeric flavan-3-ols the most abundant fraction in the Carménère and Cabernet Sauvignon wines throughout the entire study period. Additionally, the monomeric fraction decreased and the oligomeric fraction increased towards the end of the aging period. The Carménère and Cabernet Sauvignon wines aged in contact with oak barrels, chips, or staves displayed low contents of the monomeric and oligomeric flavan-3-ols fractions at the two last sampling dates. For both fractions and dates, the control wines (aging without wood) presented the highest values. Contents of the polymeric flavan-3-ol fraction in both varieties subjected to the various wood aging treatments remained unchanged throughout the 1 year aging period.

Wine anthocyanins during oak wood aging

Figure 5 shows anthocyanin contents of wines from the Carménère and Cabernet Sauvignon varieties during aging in contact with different wood formats. By using HPLC-DAD analysis, we identified delphinidin-3-glucoside, cyanidin-3-glucoside, petunidin-3-glucoside, peonidin-3-glucoside, malvidin-3-glucoside, delphinidin-3-acetyl glucoside, cyanidin-3-acetyl glucoside, petunidin-3-acetyl glucoside, peonidin-3-acetyl glucoside, malvidin-3-acetyl glucoside, delphinidin-3-*p*-cumarilglucoside, cyanidin-3-*p*-cumarilglucoside, petunidin-3-*p*-cumarilglucoside, peonidin-3-*p*-cumarilglucoside, and malvidin-3-*p*-cumarilglucoside. All these compounds were grouped into anthocyanin monoglucosides (A), acetylated anthocyanins (B), and coumarilated glucosides (C). In wines aged in contact with any wood forms, concentrations of all the anthocyanin groups displayed a fall at the end of the assay. By contrast, the Carménère and Cabernet Sauvignon wines aged with no wood contact (control wines) presented higher contents of monoglucosides and acetylated and coumarilated anthocyanins. In general, wines aged in contact with either barrels, chips, or staves displayed similar concentrations to the three anthocyanin groups, with the exception of the Cabernet Sauvignon wines aged in contact with staves, which exhibited the lowest concentrations of anthocyanins from day 167 onwards.

Low molecular weight phenolic compounds in aging wines

Table 2 shows the contents of flavonoid and nonflavonoid compounds in Carménère and Cabernet Sauvignon wines during aging in contact with oak wood. HPLC-DAD analysis showed five flavonoids: (+)-catechin (C), (−)-epicatechin (EC), astilbins (AS), procyanidingallates (GP), and total flavonols (FS). Overall, those compounds showed a decreasing behavior throughout aging, excepting GP, which increased progressively towards the end of the study. The Carménère wines aged in contact with staves exhibited significantly lower contents of FS and C at three time points. By contrast, the Cabernet Sauvignon wines aged in barrels presented lower contents of FS at the last sampling, while the wines aged in contact with chips displayed higher AS and GP contents. Control wines displayed the highest contents of FS in both wine varieties compared with wines aged in barrels. Table 2 also shows the contents of various phenolic acids detected by HPLC-DAD. Thus, concerning the hydroxycinnamic acids, *trans-p*-coumaric acid (APC), caffeic acid (AC), and ferulic acid (AF) were identified. All the wines aged in contact with wood showed significantly reduced contents of APC at the last sampling, while the AF content remained unchanged. As to Carménère, the wines aged in contact with wood showed higher AC than the control wines, while the latter ones displayed significantly higher APC and AF contents at three time points. The Cabernet Sauvignon wines aged in contact with chips showed higher AC contents at the last sampling dates with respect

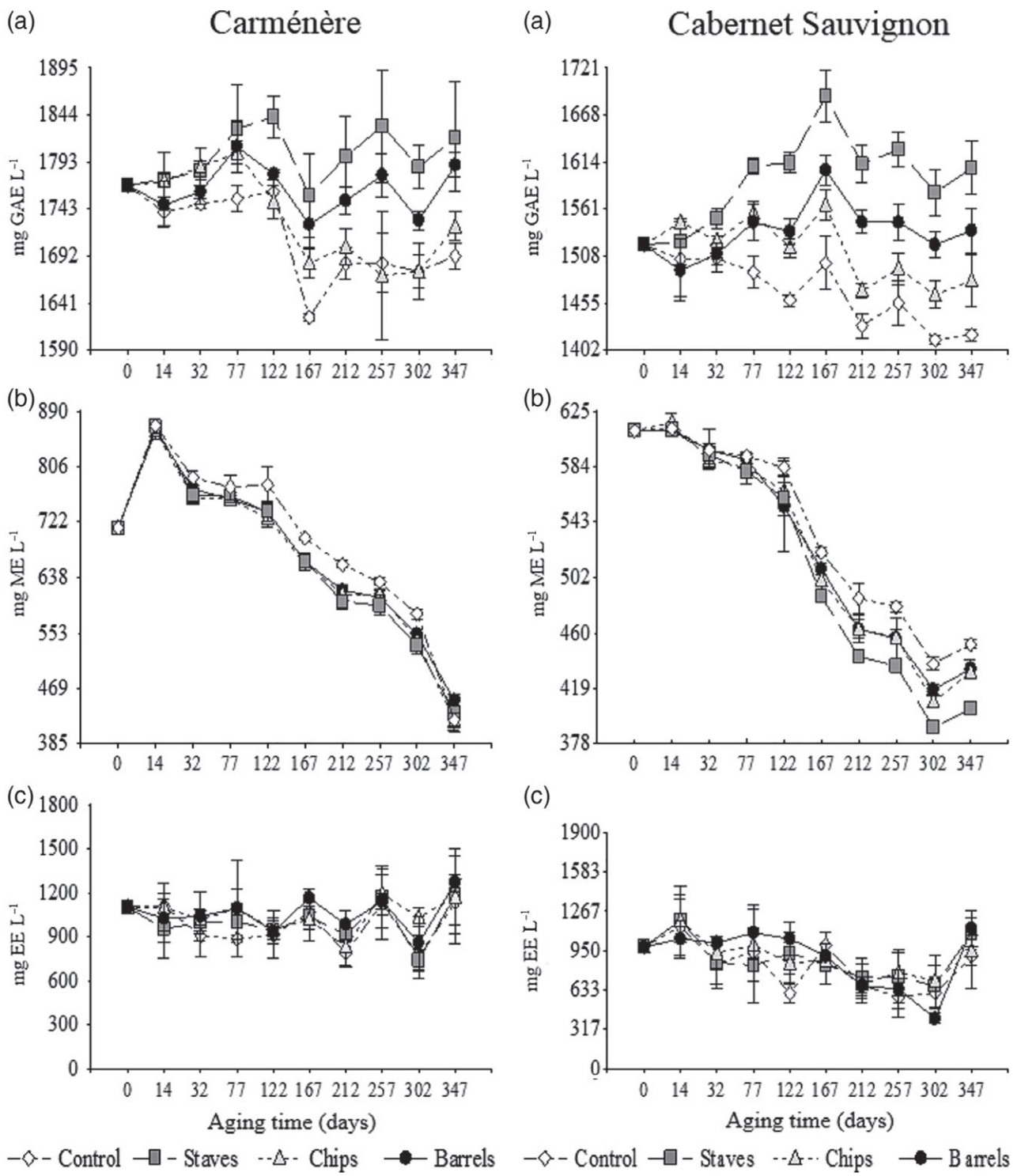

Figure 1. Total phenols (A), total anthocyanins (B) and total tannins (C) of Carménère and Cabernet Sauvignon wines during aging in contact with different wood formats (corresponding symbols indicated at the bottom of the figure). GAE, gallic acid equivalent; ME, malvidin-3-glucoside equivalent; EE, (−)-epicatechin equivalent.

to the other treatments. There were no differences in the wine AF concentrations between the various treatments in the study. The contents of six hydroxybenzoic acids were determined: gallic acid (AG), protocatechuic acid (AP), syringic acid (ASG), vanillic acid (AV), ethyl gallate (EG), and ellagic acid (AE) (Table 2). Thus, the concentrations of AG, AV, EG, and AE were found to increase gradually during aging in contact with oak wood. A similar behavior was observed for the ASG content in wines aged in contact with chips or staves. In regard to Carménère, wines aged in contact with oak barrels exhibited higher concentrations of AG, EG, AE, and AP by the end of the study. A similar trend was observed regarding the AV, AP, and ASG contents in wines aged in contact with staves and regarding the ASG content in wines aged in contact with chips. As for Cabernet Sauvignon, by the end of the assay

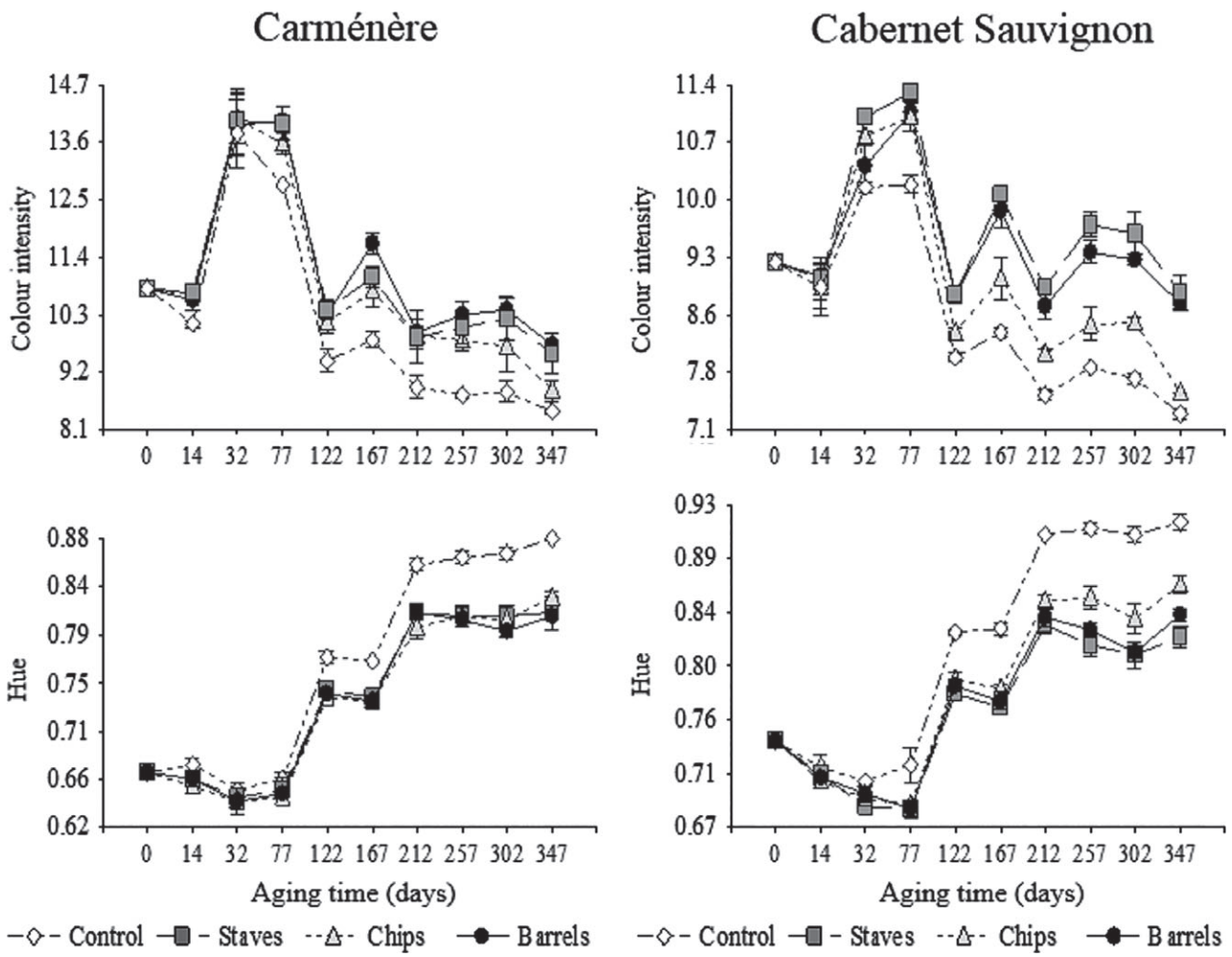

Figure 2. Color intensity and hue of Carménère and Cabernet Sauvignon wines during aging in contact with different wood formats (corresponding symbols indicated at the bottom of the figure).

we observed significantly higher concentrations of AP, ET, and AE in barrel-aged wines and higher ASG contents in wines aged in contact with either chips or staves. Under these latter conditions, wines showed higher AV contents. Similar AG concentrations were observed in all the Cabernet Sauvignon wines in the study.

Ellagitannin and gallotannin concentrations

Figure 6 shows the evolution of ellagitannin and gallotannin contents during wine aging in contact with different oak wood formats. Regarding Carménère, barrel-aged wines presented a significantly higher ellagitannin concentration from day 167 onwards. Likewise, Carménère wines aged in contact with either barrels or staves stood out for their higher gallotannin contents by the end of the aging period. With regard to the Cabernet Sauvignon wines, these exhibited higher concentrations of both gallotannins and ellagitannins after 167 days in contact with either staves and barrels respectively.

DISCUSSION

In this study we have characterized the phenolic composition of wine throughout oak wood aging. At variance with other studies determining the effect on wine aging of various factors, such as the amount of wood and the amount of oxygen,[1] in this study we assessed the influence of time, wine variety, and wood format on the phenolic profile during wine aging. The evolution of the Carménère and Cabernet Sauvignon wine varieties were compared throughout a 1 year aging period in contact with any of three wood formats; namely, barrels, staves, and chips. Control conditions consisted of wines aged in the absence of wood. HPLC-DAD and spectrophotometric analyses of total phenols, total tannins, anthocyanin profiles, proanthocyanidin fractions (degree of polymerization), color intensity, and hue and CIELab indexes were conducted. Overall, we observed that the phenolic profile of wood-aged wines is markedly influenced by wood format, wine grape variety, and aging time.

In regard to aging time, the wines aged in contact with oak wood presented a marked increase in the contents of several nonflavonoid compounds, in accordance with several previous reports.[13,15,26–28] By contrast, color intensity showed a significant increase only during the first half of the aging period and then experienced a gradual reduction. A similar trend was observed for the CIELab color parameters C^* and a^*, whereas the L^*, h^*, and b^* parameters displayed gradual increases mostly in the second half of the aging period. Other researchers have observed similar trends in wines under wood aging conditions.[13,29,30] The notable decline in color intensity is according with a decreased contribution of red color (a^*) to the total color, which would result in more luminous wines (L^*), with a high tone (h^*) and a

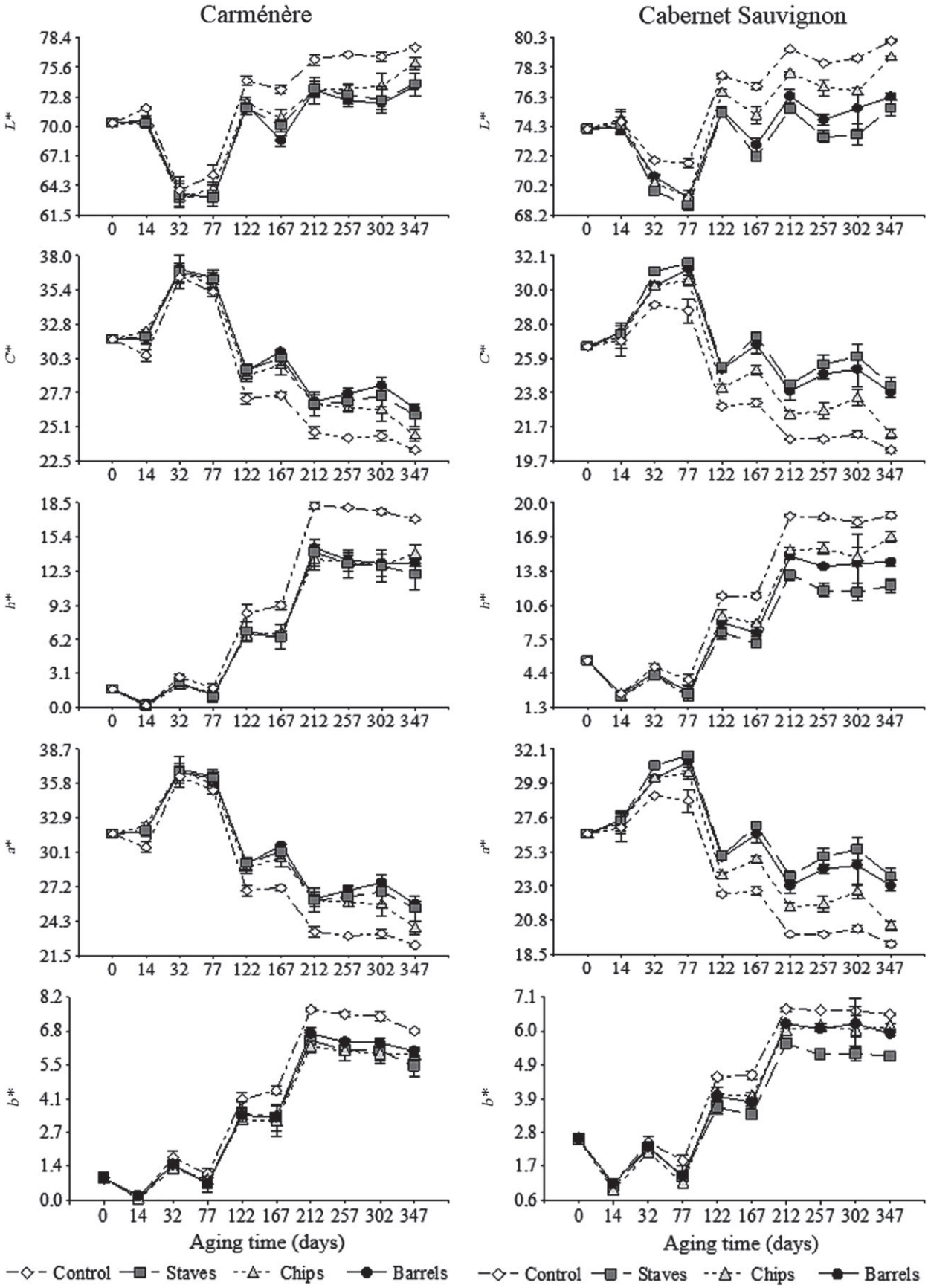

Figure 3. CIELab color space values of Carménère and Cabernet Sauvignon wines during aging in contact with different wood formats (corresponding symbols indicated at the bottom of the figure). L^*, lightness; C^*, saturation; h^*, hue.

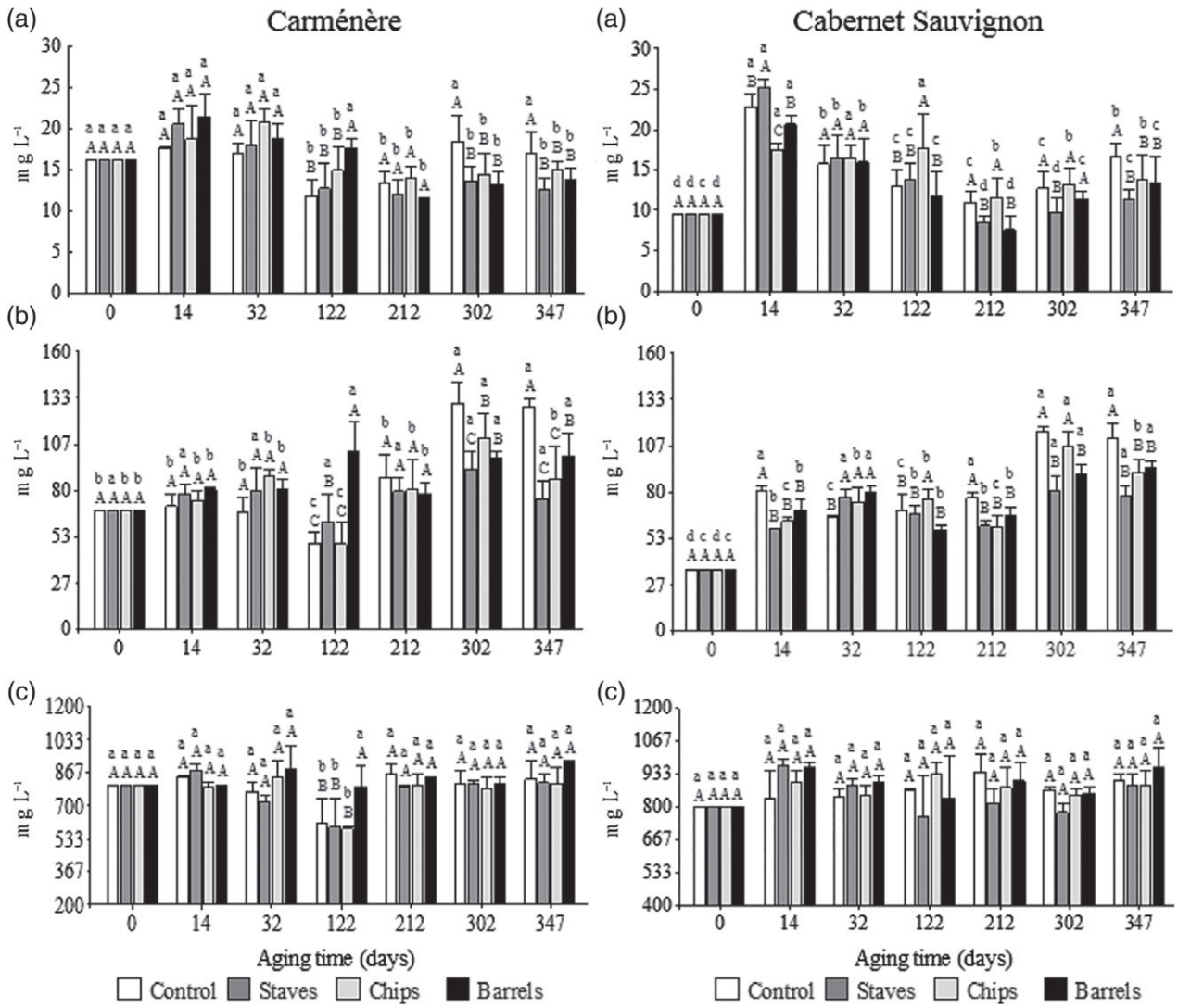

Figure 4. Flavan-3-ols content of monomeric (A), oligomeric (B), and polymeric (C) fractions of Carménère and Cabernet Sauvignon wines aged in contact with different wood formats (corresponding symbols indicated at the bottom of the figure). Different lower-case letters on top of the bars indicate statistically significant differences between sampling dates for the same wine. Different upper-case letters on top of the bars indicate statistically significant differences between wines (control, staves, chips, and barrels) in the same sampling date (DGS test, $P < 0.05$).

high contribution of the yellow component (b^* and hue). Such behavior would be related to the continuous decrease throughout aging of both monoglucosides and acetylated, coumarilated, and total anthocyanins, which is also in agreement with independent reports from other laboratories.[29–33] It is well known that anthocyanins are responsible for the red color of wine, either through their direct contribution or by associative reactions with other wine compounds.[32,34] We have shown that the contact between wine and wood results in a continuous decrease in the anthocyanin contents, thus provoking a reduction in the red color of wine. These findings could derive from oxidation reactions during aging or from condensation reactions between anthocyanins and certain wood molecules, all of which would generate large, insoluble and precipitable polymers. Likewise, the monomeric proanthocyanidin fraction and the (+)-catechin and (−)-epicatechin monomers also showed a significant decrease throughout the aging time. By contrast, the oligomeric proanthocyanidin fraction (two to ten subunits)[29,35,36] was found to increase throughout aging. Taken together, these observations suggested that wood aging enhances associativity between proanthocyanidins, which would result in more polymerized molecules.[28,37–39] Nevertheless, aging in contact with oak wood would interfere with formation of larger (over ten subunits) proanthocyanidin polymers.[35,36] This observation fully supports the view that wood aging is related not only with the extraction of wood polyphenols (nonflavonoids), but also with substantial physicochemical changes in the original wine grape polyphenols (flavonoids).

As for the varietal effect on the presence of phenolic compounds throughout the aging time, in this study substantial and numerous differences were observed when both wine varieties under the same aging conditions were compared. For example, the content of total tannins experienced a significant decrease in the Cabernet Sauvignon wines but remained unchanged in all the Carménère wines. Also, barrel-aged Carménère wines but not barrel-aged Cabernet Sauvignon wines showed increased contents of gallotannins (among other nonflavonoids), Cabernet Sauvignon wines but not Carménère wines aged in contact with chips showed increased concentrations of ellagitannins, and Carménère wines but not Cabernet Sauvignon wines aged in contact with oak staves showed a constant decline

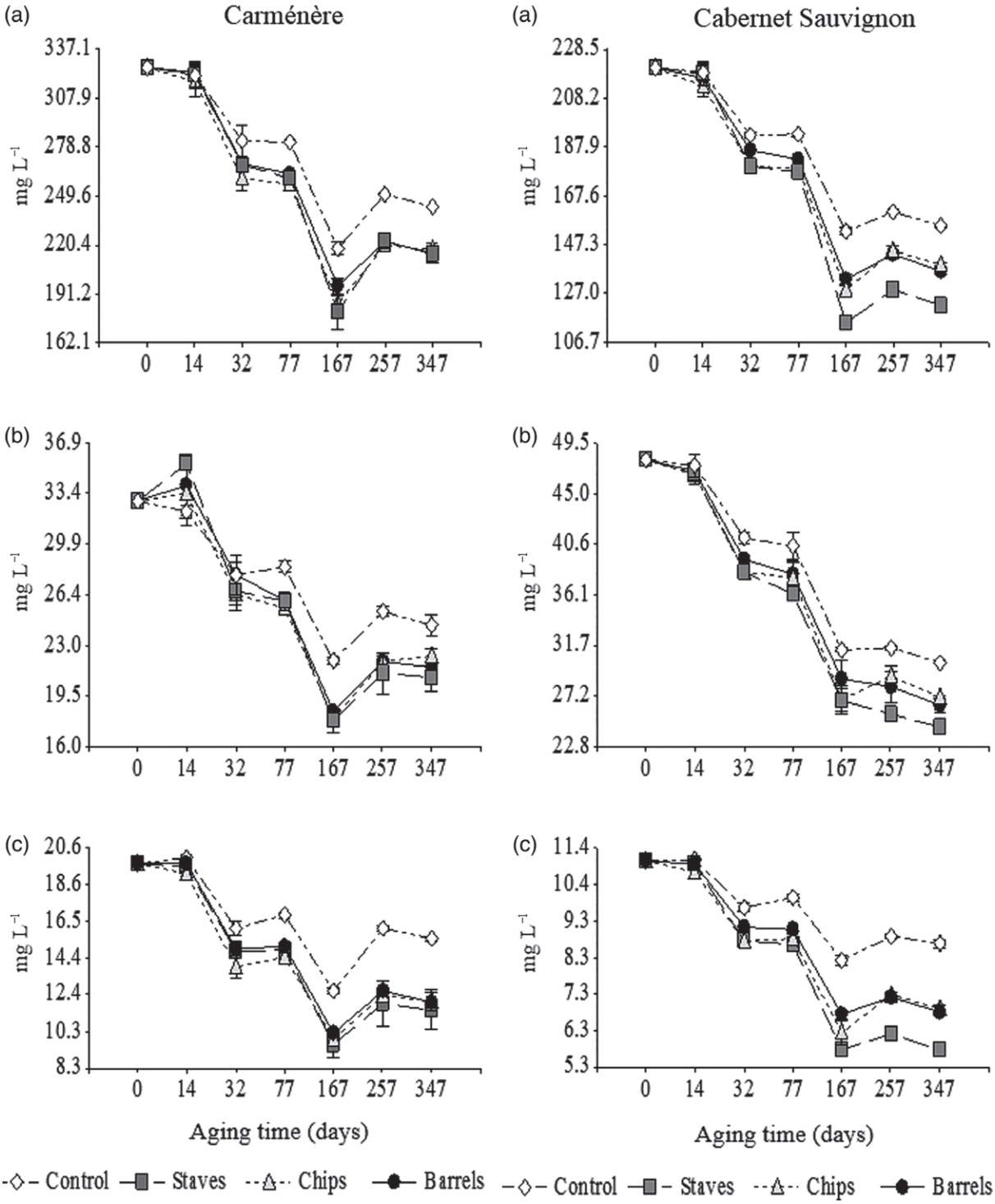

Figure 5. Anthocyanin-glucosides (A), -acetylglucosides (B), and -cumarilglucosides (C) of Carménère and Cabernet Sauvignon wines during aging in contact with different wood formats (corresponding symbols indicated at the bottom of the figure). In all panels, concentrations are expressed as milligrams malvidin-3-glucoside equivalent per liter.

in the content of flavonols. Interestingly, both wine varieties showed similar levels of pH, residual sugar, total acidity, and alcohol, whereas their initial phenolic compositions (no contact with wood) were substantially different for several major families and types of polyphenol compounds. On these grounds, our observations highly suggest that both wine evolution and extraction of certain wood polyphenols during wine aging would be dependent on the wine grape variety. Furthermore, the effect of wood on the physicochemical properties of wine would be in close relationship with the intrinsic characteristics of the corresponding grape variety.

Finally, regarding the effect of the wood format (barrels, chips, and staves) on the phenolic composition of wines throughout aging, an important major observation was that aging in contact

Table 2. Low molecular weight phenols (mg L^{-1}) quantified of Carménère and Cabernet Sauvignon wines during the aging time (AT, days)

		Carménère				Cabernet Sauvignon			
	AT	Control	Staves	Chips	Barrels	Control	Staves	Chips	Barrels
FS	0	13.4 ± 0.7aA	13.4 ± 0.7aA	13.4 ± 0.7aA	13.4 ± 0.7aA	12.2 ± 0.4bA	12.2 ± 0.4aA	12.2 ± 0.4aA	12.2 ± 0.4aA
	14	6.4 ± 1.0cA	5.3 ± 0.6dB	5.1 ± 0.5cB	4.7 ± 0.5dB	13.0 ± 0.8bA	13.1 ± 0.9aA	13.0 ± 0.4aA	12.6 ± 1.5aA
	32	12.9 ± 1.9aA	10.4 ± 2.6bB	8.8 ± 1.5bC	10.6 ± 0.0bB	12.3 ± 1.7bA	11.8 ± 1.4aA	11.8 ± 2.0aA	13.9 ± 0.6aA
	167	11.3 ± 0.5bB	11.1 ± 2.3bB	12.6 ± 0.8aA	9.4 ± 2.2cC	10.2 ± 0.7cA	8.6 ± 0.1bB	8.9 ± 0.9cB	7.8 ± 0.0cC
	257	9.0 ± 1.6cA	6.8 ± 0.7cA	6.7 ± 1.0bA	7.3 ± 0.4cA	14.0 ± 0.3bA	11.9 ± 0.5aA	10.7 ± 1.1bB	9.4 ± 1.1bC
	347	10.5 ± 1.8bA	8.6 ± 1.3cB	7.7 ± 0.6bB	8.2 ± 1.3cB	17.0 ± 0.3aA	11.5 ± 0.6aB	11.5 ± 1.8aB	12.0 ± 3.3aB
AS	0	12.2 ± 0.8aA	12.2 ± 0.8aA	12.2 ± 0.8aA	12.2 ± 0.8aA	2.8 ± 0.1aA	2.8 ± 0.1aA	2.8 ± 0.1bA	2.8 ± 0.1bA
	14	9.8 ± 2.0bA	9.1 ± 0.8bA	8.9 ± 0.3bA	7.8 ± 0.4bA	2.4 ± 0.1bA	2.2 ± 0.3bA	2.2 ± 0.3cA	2.2 ± 0.2cA
	32	12.7 ± 1.4aA	12.2 ± 2.2aA	10.8 ± 1.8bA	10.8 ± 3.1bA	3.0 ± 0.4aB	2.8 ± 0.2aB	2.7 ± 0.0bB	3.3 ± 0.5aA
	167	10.3 ± 0.3bA	8.5 ± 0.2bA	9.7 ± 1.4bA	8.4 ± 0.2bA	2.7 ± 0.1aA	2.1 ± 0.3bB	2.9 ± 0.2bA	2.2 ± 0.1cB
	257	6.4 ± 0.4cA	5.7 ± 0.6cA	6.8 ± 0.5cA	6.0 ± 0.2cA	2.5 ± 0.2bB	2.1 ± 0.1bB	3.3 ± 0.3aA	2.0 ± 0.3cB
	347	5.6 ± 0.4cA	5.7 ± 0.7cA	5.5 ± 0.5cA	5.3 ± 0.7cA	1.1 ± 0.1cA	0.9 ± 0.0cB	1.1 ± 0.3dA	1.0 ± 0.0dA
C	0	12.8 ± 1.1aA	12.8 ± 1.1aA	12.8 ± 1.1aA	12.8 ± 1.1aA	11.9 ± 1.2aA	11.9 ± 1.2aA	11.9 ± 1.2aA	11.9 ± 1.2aA
	14	7.2 ± 2.9cA	7.3 ± 0.6bA	6.7 ± 0.0cA	5.7 ± 1.6bA	9.8 ± 0.5bA	9.2 ± 1.4bA	8.7 ± 0.3bA	9.5 ± 0.6bA
	32	11.1 ± 2.4bA	6.7 ± 2.2bB	7.8 ± 1.6cB	7.8 ± 2.7bB	9.7 ± 1.0bA	9.6 ± 1.1bA	9.1 ± 1.9bA	9.4 ± 0.6bA
	167	9.4 ± 0.9bA	3.8 ± 0.9cC	7.4 ± 0.5cB	6.3 ± 0.2bB	8.5 ± 0.2bA	4.8 ± 0.5cC	6.9 ± 0.7cB	5.3 ± 0.4dC
	257	8.7 ± 0.4cA	3.7 ± 0.1cB	7.4 ± 1.0cA	7.0 ± 0.4bA	9.1 ± 0.9bA	2.9 ± 0.4dD	6.8 ± 0.2cB	5.2 ± 0.4dC
	347	9.7 ± 0.2bA	6.4 ± 1.3bB	9.2 ± 0.3bA	8.2 ± 0.2bB	10.2 ± 0.8bA	5.9 ± 2.2cC	8.8 ± 0.9bA	6.9 ± 2.3cB
EC	0	7.0 ± 1.6aA	7.0 ± 1.6aA	7.0 ± 1.6aA	7.0 ± 1.6aA	6.8 ± 0.2aA	6.8 ± 0.2aA	6.8 ± 0.2aA	6.8 ± 0.2aA
	14	4.6 ± 1.5bA	3.5 ± 0.4bA	3.6 ± 0.4bA	3.6 ± 0.4bA	5.7 ± 1.3bA	4.5 ± 0.9bA	4.5 ± 1.0bA	4.9 ± 0.9bA
	32	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	167	4.4 ± 0.2bA	2.3 ± 0.4cC	3.9 ± 0.3bA	3.1 ± 0.2cB	4.6 ± 0.4bA	2.8 ± 0.2cC	4.0 ± 0.4cB	2.8 ± 0.2cC
	257	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	347	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
GP	0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	14	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	1.8 ± 0.1aA	1.7 ± 0.1aA	1.7 ± 0.1aA	1.7 ± 0.1aA
	32	1.6 ± 0.2cA	1.5 ± 0.2cA	1.4 ± 0.1cA	1.5 ± 0.3cA	1.5 ± 0.2bB	1.5 ± 0.0bB	1.6 ± 0.1aA	1.6 ± 0.0aA
	167	1.5 ± 0.2cA	1.4 ± 0.1cA	1.3 ± 0.1cA	1.3 ± 0.1cA	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	257	3.5 ± 0.1aB	3.4 ± 0.0aC	3.6 ± 0.1aA	3.4 ± 0.1aC	1.4 ± 0.1bA	1.5 ± 0.0bA	1.5 ± 0.1bA	1.3 ± 0.1cB
	347	2.9 ± 0.2bA	2.7 ± 0.1bA	2.8 ± 0.2bA	2.8 ± 0.3bA	1.6 ± 0.1aA	1.4 ± 0.0bB	1.6 ± 0.1aA	1.5 ± 0.3bB
APC	0	8.8 ± 0.6bA	8.8 ± 0.6aA	8.8 ± 0.6aA	8.8 ± 0.6aA	4.1 ± 0.1bA	4.1 ± 0.1bA	4.1 ± 0.1bA	4.1 ± 0.1bA
	14	9.1 ± 0.6bA	8.6 ± 0.3aA	8.3 ± 0.3bB	8.1 ± 0.2bB	5.3 ± 0.2aA	4.8 ± 0.7aA	4.8 ± 0.7aA	4.9 ± 0.6aA
	32	8.6 ± 0.4bA	7.9 ± 0.6bB	7.1 ± 0.9bB	7.3 ± 1.1bB	3.9 ± 0.3cA	3.8 ± 0.3cA	3.8 ± 0.3cA	3.9 ± 0.1cA
	167	9.1 ± 0.1bA	8.3 ± 0.0bB	8.0 ± 0.6bB	7.8 ± 0.1bB	4.2 ± 0.1bA	3.8 ± 0.1cB	3.9 ± 0.1cB	3.8 ± 0.0cB
	257	8.1 ± 0.7cA	7.4 ± 0.4bA	7.6 ± 0.3bA	7.4 ± 0.3bA	4.1 ± 0.3bA	3.8 ± 0.2cB	3.9 ± 0.1cB	3.5 ± 0.3cB
	347	10.0 ± 0.5aA	8.7 ± 0.3aB	8.7 ± 0.1aB	8.4 ± 0.3bC	4.6 ± 0.2aA	3.7 ± 0.2cB	3.8 ± 0.2cB	3.6 ± 0.2cB
AC	0	0.0 ± 0.0aA	0.0 ± 0.0cA	0.0 ± 0.0cA	0.0 ± 0.0cA	0.0 ± 0.0aA	0.0 ± 0.0cA	0.0 ± 0.0cA	0.0 ± 0.0cA
	14	0.0 ± 0.0aB	1.1 ± 0.3bA	0.9 ± 0.2bA	0.5 ± 0.3bA	0.0 ± 0.0aB	0.3 ± 0.1bA	0.4 ± 0.1bA	0.3 ± 0.1bA
	32	0.0 ± 0.0aB	1.3 ± 0.6bA	0.8 ± 0.7bA	1.0 ± 0.8bA	0.0 ± 0.0aB	0.1 ± 0.2cB	0.1 ± 0.2cB	0.4 ± 0.3bA
	167	0.0 ± 0.0aB	2.1 ± 0.3aA	1.9 ± 0.7aA	1.7 ± 0.2aA	0.0 ± 0.0aB	0.5 ± 0.1aA	0.6 ± 0.1aA	0.5 ± 0.2aA
	257	0.0 ± 0.0aB	0.2 ± 0.2cB	0.5 ± 0.4bA	0.2 ± 0.2cB	0.0 ± 0.0aB	0.2 ± 0.2bA	0.3 ± 0.1bA	0.1 ± 0.2cB
	347	0.0 ± 0.0aB	1.8 ± 0.3aA	2.0 ± 0.1aA	1.7 ± 0.3aA	0.0 ± 0.0aB	0.1 ± 0.2cB	0.2 ± 0.2bA	0.1 ± 0.1cB
AF	0	0.6 ± 0.1aA	0.6 ± 0.1aA	0.6 ± 0.1aA	0.6 ± 0.1aA	0.5 ± 0.0aA	0.5 ± 0.0aA	0.5 ± 0.0aA	0.5 ± 0.0aA
	14	0.6 ± 0.1aA	0.5 ± 0.0aA	0.5 ± 0.0bB	0.5 ± 0.0bB	0.5 ± 0.0aA	0.5 ± 0.0aA	0.5 ± 0.0aA	0.5 ± 0.0aA
	32	0.6 ± 0.1aA	0.6 ± 0.1aA	0.5 ± 0.0bB	0.6 ± 0.0aA	0.5 ± 0.1aA	0.5 ± 0.1aA	0.5 ± 0.1aA	0.5 ± 0.0aA
	167	0.7 ± 0.0aA	0.6 ± 0.0aA	0.6 ± 0.1aA	0.6 ± 0.0aA	0.6 ± 0.0aA	0.5 ± 0.1aA	0.6 ± 0.1aA	0.6 ± 0.1aA
	257	0.6 ± 0.0aA	0.5 ± 0.0bB	0.5 ± 0.0bB	0.5 ± 0.1bB	0.5 ± 0.0aA	0.5 ± 0.0aA	0.5 ± 0.0aA	0.4 ± 0.1aA
	347	0.7 ± 0.1aA	0.6 ± 0.1aA	0.7 ± 0.1aA	0.7 ± 0.1aA	0.6 ± 0.0aA	0.5 ± 0.0aA	0.5 ± 0.0aA	0.5 ± 0.1aA
AG	0	9.9 ± 0.4bA	9.9 ± 0.4bA	9.9 ± 0.4bA	9.9 ± 0.4cA	8.9 ± 0.2bA	8.9 ± 0.2bA	8.9 ± 0.2bA	8.9 ± 0.2bA
	14	8.5 ± 0.9cA	8.3 ± 0.5cA	8.2 ± 0.3cA	7.5 ± 0.3dA	8.8 ± 0.5bA	8.9 ± 0.0bA	8.9 ± 0.1bA	9.0 ± 0.2bA
	32	12.2 ± 1.5aA	11.7 ± 1.6aA	10.9 ± 1.6bB	10.9 ± 2.0cB	10.7 ± 0.9aA	10.8 ± 0.2aA	11.1 ± 1.0aA	11.6 ± 0.1aA
	167	11.4 ± 1.4bB	11.6 ± 0.7aA	11.1 ± 1.3bB	12.2 ± 0.5bA	11.2 ± 0.2aA	11.3 ± 0.1aA	11.3 ± 0.2aA	12.0 ± 0.6aA
	257	10.2 ± 0.7bB	9.9 ± 0.2bB	10.4 ± 0.6bB	11.9 ± 0.5bA	10.8 ± 0.8aA	11.2 ± 0.4aA	11.1 ± 0.3aA	12.3 ± 1.0aA
	347	11.9 ± 1.0aB	12.1 ± 0.6aB	12.1 ± 0.3aB	13.7 ± 1.2aA	11.8 ± 1.0aA	11.2 ± 1.3aA	11.8 ± 0.7aA	12.8 ± 1.4aA

Table 2. Continued.

		Carménère				Cabernet Sauvignon			
	AT	Control	Staves	Chips	Barrels	Control	Staves	Chips	Barrels
AP	0	6.7 ± 0.1bA	6.7 ± 0.1bA	6.7 ± 0.1bA	6.7 ± 0.1bA	3.2 ± 0.1cA	3.2 ± 0.1cA	3.2 ± 0.1dA	3.2 ± 0.1dA
	14	8.2 ± 0.6aA	7.7 ± 0.3aA	7.5 ± 0.8aA	7.2 ± 0.3bB	3.9 ± 0.2bA	3.9 ± 0.2bA	3.9 ± 0.4bA	4.0 ± 0.3bA
	32	9.4 ± 0.7aA	8.4 ± 0.8aA	7.1 ± 1.1bB	7.9 ± 1.2aA	5.1 ± 0.4aA	5.1 ± 0.3aA	4.9 ± 0.5aA	5.3 ± 0.1aA
	167	8.0 ± 0.3aA	6.1 ± 1.2bB	5.3 ± 1.4cC	6.3 ± 1.1bB	4.1 ± 0.2bA	3.8 ± 0.1bA	3.6 ± 0.1cB	4.1 ± 0.2bA
	257	6.8 ± 0.6bA	5.7 ± 0.4cB	5.7 ± 0.3cB	6.5 ± 0.3bA	3.2 ± 0.2cB	3.3 ± 0.1cB	3.0 ± 0.1dB	3.5 ± 0.3cA
	347	8.1 ± 0.4aA	6.4 ± 0.4bB	5.8 ± 0.1cC	6.9 ± 0.2bB	3.7 ± 0.1bA	3.3 ± 0.3cC	3.2 ± 0.1dC	3.6 ± 0.2cB
ASG	0	5.0 ± 0.3aA	5.0 ± 0.3bA	5.0 ± 0.3bA	5.0 ± 0.3aA	3.5 ± 0.1aA	3.5 ± 0.1bA	3.5 ± 0.1bA	3.5 ± 0.1aA
	14	4.7 ± 0.5aA	4.6 ± 0.4bA	4.8 ± 0.2bA	4.1 ± 0.4aA	3.5 ± 0.3aB	3.5 ± 0.1bB	3.7 ± 0.1aA	3.4 ± 0.0aB
	32	4.8 ± 0.5aA	5.0 ± 0.7bA	4.9 ± 0.5bA	4.3 ± 0.8aA	3.1 ± 0.2bB	3.5 ± 0.3bA	3.5 ± 0.2bA	3.4 ± 0.2aA
	167	4.2 ± 0.5aA	5.1 ± 0.3bA	4.8 ± 0.6bA	4.4 ± 0.2aA	3.2 ± 0.1bB	3.8 ± 0.1aA	3.8 ± 0.2aA	3.3 ± 0.1bB
	257	3.7 ± 0.3aA	4.3 ± 0.2bA	4.5 ± 0.2bA	4.0 ± 0.2aA	2.9 ± 0.2bC	3.7 ± 0.1aA	3.6 ± 0.2bB	3.0 ± 0.3bC
	347	4.9 ± 0.6aB	5.7 ± 0.2aA	5.7 ± 0.4aA	4.9 ± 0.5aB	3.3 ± 0.2aB	3.8 ± 0.3aA	4.0 ± 0.0aA	3.2 ± 0.3bC
AV	0	2.4 ± 0.1bA	2.4 ± 0.1cA	2.4 ± 0.1bA	2.4 ± 0.1bA	2.2 ± 0.2aA	2.2 ± 0.2bA	2.2 ± 0.2aA	2.2 ± 0.2aA
	14	2.7 ± 0.2aA	2.6 ± 0.1bA	2.6 ± 0.0aA	2.4 ± 0.1bB	2.4 ± 0.1aA	2.4 ± 0.0bA	2.4 ± 0.0aA	2.3 ± 0.1aA
	32	2.9 ± 0.2aA	3.0 ± 0.2bA	2.8 ± 0.2aA	2.8 ± 0.3aA	2.3 ± 0.1aA	2.6 ± 0.1bA	2.5 ± 0.1aA	2.5 ± 0.1aA
	167	2.5 ± 0.2aA	2.8 ± 0.1bA	2.7 ± 0.2aA	2.6 ± 0.1aA	2.3 ± 0.0aA	2.4 ± 0.1bA	2.4 ± 0.1aA	2.2 ± 0.1aA
	257	2.4 ± 0.1bC	3.3 ± 0.4aA	2.6 ± 0.1aB	2.6 ± 0.1aB	2.1 ± 0.1aB	3.1 ± 0.7aA	2.3 ± 0.1aB	2.2 ± 0.1aB
	347	2.6 ± 0.1aB	3.5 ± 0.3aA	2.8 ± 0.0aB	2.8 ± 0.1aB	2.2 ± 0.1aB	2.9 ± 0.4aA	2.4 ± 0.1aB	2.3 ± 0.2aB
EG	0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	14	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	32	3.5 ± 0.6aA	3.5 ± 0.4aA	3.3 ± 0.3aA	3.6 ± 0.6bA	3.7 ± 0.2aA	3.3 ± 0.4aA	3.4 ± 0.3aA	3.5 ± 0.4aA
	167	3.4 ± 0.3aA	3.0 ± 0.1bB	2.9 ± 0.3bB	3.2 ± 0.2bA	2.9 ± 0.1bB	2.9 ± 0.0bB	2.9 ± 0.1bB	3.1 ± 0.1aA
	257	3.3 ± 0.2aA	3.0 ± 0.2bB	3.3 ± 0.2aA	3.5 ± 0.1bA	3.5 ± 0.2aA	3.1 ± 0.1aA	3.5 ± 0.1aA	3.5 ± 0.2aA
	347	3.6 ± 0.1aB	3.3 ± 0.1aB	3.5 ± 0.0aB	3.8 ± 0.2aA	3.6 ± 0.1aA	3.1 ± 0.2aA	3.5 ± 0.1aA	3.6 ± 0.3aA
AE	0	0.0 ± 0.0aA	0.0 ± 0.0cA	0.0 ± 0.0bA	0.0 ± 0.0cA	0.0 ± 0.0aA	0.0 ± 0.0dA	0.0 ± 0.0cA	0.0 ± 0.0dA
	14	0.0 ± 0.0aA	0.3 ± 0.3cA	0.9 ± 1.2bA	0.0 ± 0.0cA	0.0 ± 0.0aB	2.0 ± 0.5cA	1.2 ± 0.7bA	1.1 ± 1.1cA
	32	0.0 ± 0.0aA	0.7 ± 0.1cA	0.6 ± 0.3bA	0.3 ± 0.3cA	0.0 ± 0.0aB	0.8 ± 1.4dB	1.6 ± 0.9bA	2.0 ± 1.6cA
	167	0.0 ± 0.0aB	1.4 ± 0.2bA	1.0 ± 1.7bB	0.8 ± 0.7cB	0.0 ± 0.0aC	2.8 ± 0.5bB	0.5 ± 0.5cC	3.6 ± 0.7bA
	257	0.0 ± 0.0aB	0.8 ± 0.3cB	2.2 ± 1.9aA	1.8 ± 1.1bA	0.0 ± 0.0aC	2.3 ± 0.6cB	1.5 ± 0.4bB	3.9 ± 0.2bA
	347	0.0 ± 0.0aD	3.7 ± 1.0aB	2.9 ± 2.5aC	5.6 ± 0.3aA	0.0 ± 0.0aD	5.7 ± 0.5aB	4.7 ± 0.9aC	7.4 ± 0.3aA

Values represent means plus/minus standard deviation (triplicate). Different lower-case letters in single columns indicate statistically significant differences between the different sampling dates. Different upper-case letters in single rows indicate statistically significant differences between the different aging systems (DGS test; $P < 0.05$). FS, total flavonols; AS, astilbins; C, (+)-catechin; EC, (−)-epicatechin; GP, procyanidin gallates; APC, *trans-p*-coumaric acid; AC, caffeic acid; AF, ferulic acid; AG, gallic acid; AP, protocatechic acid; ASG, syringic acid; AV, vanillic acid; EG, ethyl gallate; AE, ellagic acid.

with any of the three formats almost invariably resulted in increased contents of certain nonflavonoids (caffeic acid and ellagitannins), increased indexes of hue, L^*, h^*, and b^*, and decreased contents of most of the anthocyanin subtypes and total flavonols, among others. Another major related observation was that the continuous contact of wine with a given wood format provoked particular changes in phenolic parameters, regardless of the wine variety. Accordingly, in our study with the Cabernet Sauvignon and Carménère varieties, the oak staves contributed to an increase in total phenols, vanillic acid, gallotannins, and color intensity, the oak chips provided procyanidin gallates, and the oak barrels supplied ellagitannins and ethyl gallates. In any case, the wines aged in contact with either barrels, chips, or staves also showed some minor differences from each other.

Altogether, our present observations are consistent with the view that wine aging in contact with wood is a highly complex and dynamic process comprising numerous and diverse wood and grape components. As such, a number of factors, including wine grape variety, wood format, and aging time, may affect in different ways and to different extents the aging process as a whole and, therefore, the properties of the aged beverage. Quite often, those factors have been studied by different authors as single isolated or partially integrated variables.[1] Furthermore, this study has also provided evidence that the modifying influence of wood on wine phenolic composition would not be dependent solely on the passive transference of phenolics from wood to wine but also on physicochemical modifications of grape polyphenols by the wood polyphenols. In the same regard, the physicochemical composition of wine at the start of aging plays an important role in the extraction of wood components, and in this way on the subsequent evolution of its aging (varietal effect). Likewise, the study has also shown that the contents of different phenolic wine compounds change in a nonparallel manner all along the aging process in contact with wood. This was a common observation in the study in which the aging process was conducted under three different controlled conditions (wood format, wine

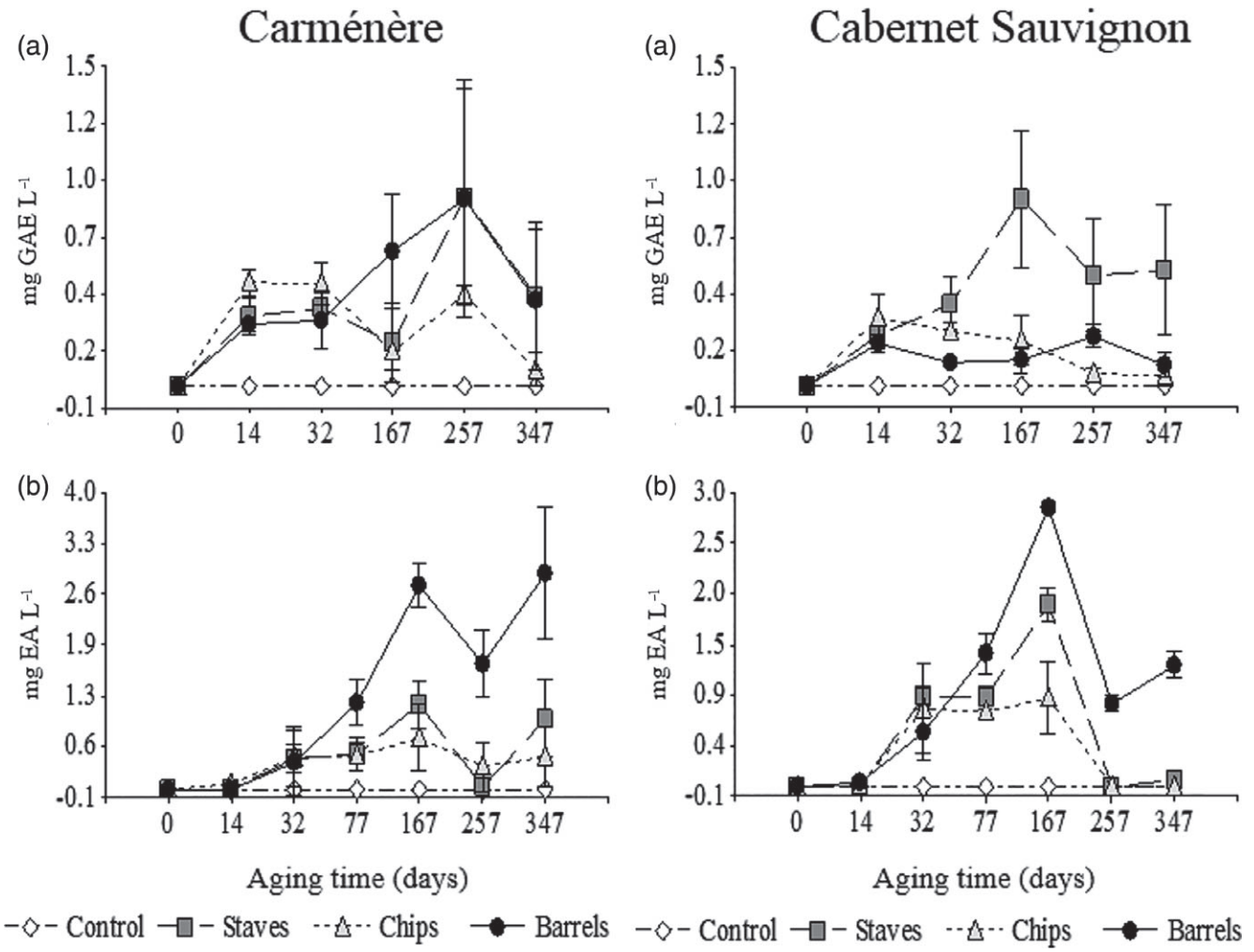

Figure 6. Gallotannins (A) and ellagitannins (B) contents of Carménère and Cabernet Sauvignon wines during aging in contact with different wood formats (corresponding symbols indicated at the bottom of the figure). GAE, gallic acid equivalent; EA, ellagic acid.

grape variety, and aging time), each of them representing a putatively influential factor during wine maturation. In addition, this observation is in full agreement with reports from different laboratories pointing to the aging time as the main factor affecting the physicochemical features of wines aged in contact with oak wood.[13,16,24,27] This factor would allow to meet the conditions that are necessary for a number of diverse wine aging reactions to occur, including polyphenol extraction and oxidation and condensation reactions. Certainly, for all these wine aging reactions, wood is highly relevant, and its widely diverse contribution to wine aging observed in this study seems to be largely dominant over those of the wood format and the wine grape variety. Last but not least, considering the uppermost importance of phenolic compounds for the most relevant sensory properties of wines (astringency, bitterness, color, and aroma), on the one hand, and the differential transference of wood compounds to wine during the extractive processes of wine aging, on the other hand, may provide new insights into physicochemical determinants of wine sensoriality.

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