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Commercial enological tannins: Characterization and their relative impact on the phenolic and sensory composition of Carménère wine during bottle aging

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ABSTRACT

The effect of the addition of different commercial enological tannins (CETs) on the characteristics of Carménère red wine was evaluated. Initially, chemical characterization of eleven CETs was performed using spectrophotometric and HPLC-DAD techniques. Then, the effects of six CETs on the properties of a Carménère wine during bottle storage (90 days) were evaluated for up to 90 days. Four CETs from wood exhibited highly variable phenolic compositions and the highest values of hydrolyzable tannins and phenolic acids, whereas the CETs from grapes exhibited the highest values of the mono-, oligo- and polymer fractions of flavan-3-ol. The wines enriched with grape CETs presented the highest values of (+)-catechin, (−)-epicatechin, and monomers and polymers of flavan-3-ols, whereas some wines enriched with wood CETs exhibited the highest values of total phenols, total tannins, dihydroflavonols, proanthocyanidin gallates, syringic acid and flavan-3-ol oligomers. Analysis of temporal dominance of sensations revealed no significant differences in the astringency or bitterness perceptions by a trained panel. Altogether, CETs are highly diverse products that can differentially impact the physicochemical and sensorial characteristics of wines to which they are added. Characterization of CETs before their application in winemaking is highly recommended.

1. Introduction

Phenolic compounds are secondary metabolites of plants that affect organoleptic properties of wine, such as color, aroma, bitterness and astringency (Monagas, Bartolomé, & Gómez-Cordovés, 2005; Obreque-Slier, Peña-Neira & Lopez-Solís, 2012a). Flavonoids (flavonols, anthocyanins and flavan-3-ols) and non-flavonoids (phenolic acids and stilbenes) are the two major classes of phenolic compounds. Hydrolyzable tannins (non-flavonoids) comprise polymers of gallic and ellagic acids, whereas condensed tannins or proanthocyanidins (flavonoids) are composed of flavan-3-ol subunits [(+)-catechin, (−)-epicatechin, (−)-epigallocatechin and (+)-gallocatechin] (Monagas et al., 2005). Condensed tannins, present in skins and seeds of wine grapes, are extracted during the winemaking process (Canals, Llaudy, Valls, Canals, & Zamora, 2005), whereas hydrolyzable tannins are transferred to wine from oak wood during aging (Obreque-Slier, Peña-Neira, López-Solís, Ramírez-Escudero, & Zamora-Marín, 2009).

Different oenological supplies, such as chips, staves and commercial enological tannins (CETs), are widely used to add phenolic compounds to wine (Chira & Teissedre, 2013). CETs are natural substances obtained from several botanical species and contain a high content of proanthocyanidins (from skins and seeds of grapes) and/or hydrolyzable tannins (from oak wood) (Malacarne, Nardin, Bertoldi, Nicolini, & Larcher, 2016). Some studies have reported that CETs provide antioxidant properties to red wines, enhance their aging capacity, act as fining agents, stabilize wine color, improve wine structure and contribute a number of beneficial biological effects (Baker & Ross, 2014; Hartzfeld, Forkner, Hunter, & Hagerman, 2002; Zanchi et al., 2007). CETs can also modulate astringency, a complex sensation generally thought to be produced by the interaction of red wine tannins with the protein fraction of saliva to form tannin-protein complexes (Laghi et al., 2010; Sanz,

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Martínez, & Moreno, 2008). Previously, we performed a chemical characterization of ten commercial plant-derived tannins for enological use (Obreque-Slier et al., 2009). Important differences in the concentrations of total phenols and total tannins and gelatine index values among those commercial products were observed. Different types of commercial enological tannins (mainly hydrolyzable, condensed and blends of the two) could be recognized. Despite the widespread use of CETs in winemaking, few studies have investigated their physicochemical nature and, usually, a technical data sheet provided by the supplier is the only information available about the product (Laghi et al., 2010; Malacarne et al., 2016). Moreover, major differences between such information and the actual chemical composition of the product have been reported (Obreque-Slier et al., 2009). Certainly, those discrepancies could lead to technological problems in the wine-making process because different products are aimed at different purposes. The aims of this study were to chemically characterize eleven commercial oenological tannins that are marketed for oenological use and to evaluate their effects on the chemical and sensory characteristics of a Carménère wine during 90 days of bottle aging.

2. Materials and methods

2.1. Materials

Eleven CETs were purchased in Chile from different companies that supply oenological products. According to the commercial tannin labels (Table 1), two CETs came from grape skins or seeds (CET3 and CET4, respectively), whereas nine CETs came from oak (CET1, CET2 and CET5-CET11). The Carménère wine vintage 2015 was donated by Villaseñor Wines (D.O. Lontué Valley, VII Region of Chile). Phenolic compound standards were purchased from Sigma Chemical Company (Saint Louis, Missouri, USA). All reagents (pro-analysis grade) and solvents (HPLC grade) were supplied by Merck (Darmstadt, Germany).

2.2. Instrumentation

The HPLC system (Agilent Technologies Santa Clara, CA, USA) consisted of a Model G1315B photodiode array detector, a Model Quat G1311A pump and a Model ALS G1329A autosampler. A reversed-phase Nova Pack C_{18} column (4 μm, 3.9 mm ID × 300 mm; Waters Corporation, Milford, MA, USA) was used for HPLC-DAD analysis of individual phenolic compounds. A reversed-phase LiChro Cart 100 RP-18 column (5 μm, 4 mm ID × 250 mm (Agilent Technologies, Santa Clara, CA, USA) was used in the anthocyanin studies. Absorbances were measured using a Jasco UV-Vis spectrophotometer Model V-530 (JASCO International Co., Ltd., Tokyo, Japan).

2.3. Preparation and phenolic characterization of CETs

The commercial oenological tannins (3 g/L) were dissolved with mechanical stirring in a hydroalcoholic solution (10% v/v ethanol, 0.5% w/v tartaric acid, pH adjusted to 3.5) at 20 °C for 20 min (Obreque-Slier et al., 2009). Then, the CET extracts were filtered through a 0.45 μm pore size membrane and were analyzed via spectrophotometry (fractionation of proanthocyanidins into monomers, oligomers and polymers) and HPLC–DAD chromatography (low-molecular-weight phenolic compounds) as described below.

2.4. Phenolic characterization of wines enriched with CETs

Before corking, representative CETs displaying differences in origin (grape versus wood) or phenolic composition among those of a single origin (CET1, CET3, CET4, CET6, CET9 and CET11) were added (2 g/L) to individual wine bottles (named as WT1, WT3, WT4, WT6, WT9 and WT11, respectively). Wine with no addition of CET (WT0) was used as control. All wine bottles were stored vertically at 20 °C and analyzed at 5, 45 and 90 days after the addition of CETs by using the following methods.

2.4.1. Spectrophotometric characterization

Total phenol content was determined via ultraviolet (UV) absorption at 280 nm using gallic acid as standard (Glories, 1984). Total anthocyanins were measured by serially diluting the extract with acidified ethanol and by comparing the spectrophotometric readings of aliquots of individual dilutions previously treated with either sodium metabisulfite or water, as described in detail by Ribéreau-Gayon and Stonestreet (1965). Color intensity and hue ($h°$) were estimated using the method described by Glories (1984), whereas the total proanthocyanidin content was determined by the methylcelullose method (Mercurio, Dambergs, Herderich, & Smith, 2007).

2.4.2. Total ellagitannins

These compounds were evaluated basically according to Chira and Teissedre (2013). Briefly, 20 mL of wine were vacuum-evaporated to dryness at 30 °C and re-dissolved in 10 mL of methanol/2 N HCl 4/1 (v/v). Two millilitres of the extract was membrane-filtered (0.45 μm pore size), and 8 mL of the same extract was held at 95 °C for 2.5 h and then membrane-filtered. For quantification, a 20-μL aliquot was injected into the HPLC equipment. Detection was performed by measuring absorbance at 254 nm. Mobile phases were water/phosphoric acid (99.9/0.1, v/v) (A) and methanol/phosphoric acid (99.9/1) (B). The gradient profile consisted of 0–35% B for 5 min, 45% B for 25 min and 100% B for 5 min. The flow rate was 1 mL/min.

Table 1
Technical information for the eleven commercial enological tannins (CETs) as given by the commercial suppliers.

CETs	Commercial name	Supplier	Origin	Chemical composition
CET1	Premium Limousin	Enológica Vason	Oak	Hydrolysable Tannin (ellagic and gallic) from French oak
CET2	Premium Whiskey Lattone	Enológica Vason	Oak	Hydrolysable Tannin (ellagic and gallic) from American oak
CET3	Premium Uva	Enológica Vason	Grape skins	Condensed tannin (catechin)
CET4	Premium Vinacciolo	Enológica Vason	Grape seeds	Condensed tannin (catechin)
CET5	Trŭ/Tan Vb	Oak solutions	Oak	Mix of gallic and ellagic tannins from French toasted oak
CET6	QuerPlus Natural oak extract	Laffort	Oak	Ellagic tannin from oak stave
CET7	Trŭ/Tan Fi	Oak solutions	Oak	Mix of gallic and ellagic tannins from French toasted oak
CET8	Trŭ/Tan F2	Oak solutions	Oak	Mix of gallic and ellagic tannins from French toasted oak
CET9	Ambrosia French complex	Tonelería Nacional	Oak	Aqueous extraction from oak toasted chip
CET10	Trŭ/Tan Rf	Oak solutions	Oak	Mix of gallic and ellagic tannins from French toasted oak
CET11	Ambrosia American complex	Tonelería Nacional	Oak	Aqueous extraction from oak toasted chip

2.4.3. Antioxidant capacity

One hundred 50 μL of each wine sample was mixed with 2850 μL of 2,2-diphenyl-1-picrylhydrazyl (DPPH) solution (53.28 mg/L). Methanol instead of a wine sample served as a control. After placing the tubes in the dark for 30 min, absorbance was measured at 515 nm. Discoloration in each experimental tube was calculated by subtracting the absorbance in the experimental tube from that in the control. Trolox (6-hydroxy-2,5,7,8-tetramethyl chroman-2-carboxylic acid) was used as standard. Results are expressed in μmol of TEAC (Trolox equivalent antioxidant capacity)/L of wine (Brand-Williams, Cuvelier, & Berset, 1995).

2.4.4. Fractionation of proanthocyanidins into monomers, oligomers and polymers

Ten millilitres of each CET extract or wine was vacuum-dried at 30 °C, re-suspended in 20 mL of phosphate-buffered solution (pH 7), filtered and loaded onto C-18 and tC-18 cartridges (Sep-Pak Plus tC18 cartridges WAT 036810 and WAT 036800, Waters, Milford, MA), containing 10 mL of methanol, 20 mL of distilled water and 10 mL of phosphate-buffered saline solution (pH 7). Next, 10 mL of phosphate-buffered saline solution diluted in water (1:8) was added to each cartridge. The mixture was dried for 2 h with gaseous nitrogen, and the monomeric (FI) + oligomeric fractions (FII) were eluted by adding 25 mL of ethyl acetate. The polymeric fraction (FIII) was then eluted with 15 mL of methanol. The FI + FII fractions were vacuum-dried at 30 °C, re-dissolved in 10 mL of phosphate-buffered saline solution (pH 7) and loaded again into reconditioned cartridges, which were then dried with gaseous nitrogen. Finally, F1 was eluted with 25 mL of ether, and FII was eluted with 15 mL of methanol. Each fraction was quantified by the vanillin assay (Sun, Ricardo Da Silva, & Spranger, 1998). A 2.5-mL aliquot of methanol/sulfuric acid 3:1 (v/v) solution and a 2.5-mL aliquot of vanillin solution (10 mg/mL in methanol) were mixed with 1 mL of sample. The tubes were incubated at 30 °C for either 15 min (FI fraction) or for a period of time sufficiently long to allow maximal reaction (FII and FIII fractions). Absorbance was measured at 500 nm. A blank was prepared by replacing the vanillin solution by methanol in the reaction mix. The results are expressed as mg of monomer, oligomer or polymer per g of CET or per L of wine, as used by Sun et al. (1998).

2.4.5. HPLC-DAD analysis of anthocyanins and low-molecular-weight phenolics

For anthocyanin analysis via HPLC-DAD, one hundred millilitres of each wine were filtered through a 0.45 μm pore size and then subjected to reversed-phase chromatographic separation at 20 °C, according to conditions described previously (Obreque-Slier et al., 2013). Additionally, low molecular weight phenolic compounds were extracted with ethyl ether (3 × 20 mL) and ethyl acetate (3 × 20 mL) from 50 mL of wine. The total extracts were evaporated to dryness at 30 °C, re-dissolved in 2 mL of 50% (v/v) methanol/water and membrane-filtered (0.45 μm pore size). Aliquots of 100 μL were subjected to reversed-phase fractionations at 20 °C using a Nova Pack C_{18} column, according to conditions described previously (Obreque-Slier, López-Solís, Castro-Ulloa, Romero-Díaz,

Table 2
Concentration of low molecular weight phenols (mg/g) in eleven commercial enological tannins.

CETs	PhA	HT	P	F
CET1	4.7 ± 0.5 c	2.0 ± 0.3 a	0.9 ± 0.5 ab	0.5 ± 0.1 ab
CET2	5.0 ± 0.5 c	2.7 ± 0.3 a	0.8 ± 0.4 ab	3.3 ± 0.1 cd
CET3	1.7 ± 0.2 a	0.5 ± 0.1 a	5.5 ± 1.1 c	0.4 ± 0.1 a
CET4	1.4 ± 0.1 ab	0.8 ± 0.2 a	12.4 ± 0.5 d	0.4 ± 0.1 a
CET5	12.1 ± 1.7 e	195.9 ± 5.5 b	0.0 ± 0.0 a	4.1 ± 0.6 d
CET6	4.2 ± 0.6 c	1.8 ± 0.3 a	1.2 ± 0.2 ab	0.2 ± 0.0 a
CET7	8.4 ± 0.3 d	325.8 ± 92.0 c	0.0 ± 0.0 a	0.0 ± 0.0 a
CET8	10.4 ± 0.2 de	122.4 ± 7.6 b	1.7 ± 0.9 b	0.0 ± 0.0 a
CET9	3.6 ± 0.2 bc	1.6 ± 0.1 a	0.7 ± 0.1 ab	2.0 ± 0.2 bc
CET10	8.4 ± 1.6 d	178.6 ± 21.6 b	0.0 ± 0.0 a	6.5 ± 1.6 e
CET11	4.1 ± 0.3 c	2.1 ± 0.3 a	0.8 ± 0.1 ab	0.3 ± 0.0 a

Values represent means ± standard deviations (triplicates). Values with different letters in single column are significantly different (Tukey test. $p \leq 0.05$). PhA, phenolic acids; HT, hydrolysable tannins; P, proanthocyanidins; F, flavonols.

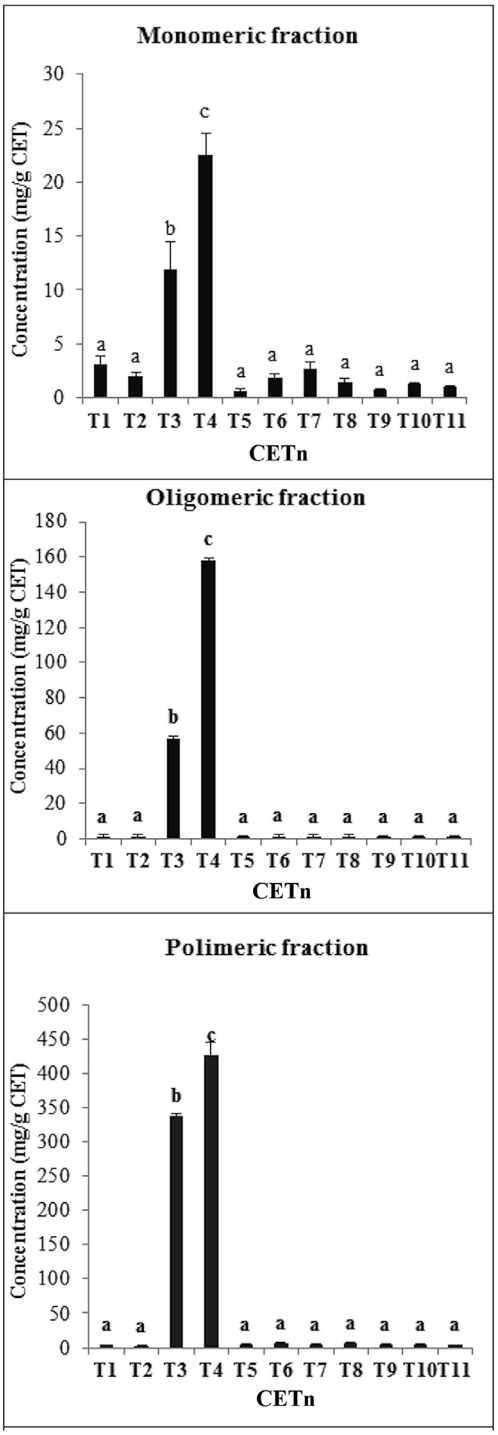

Fig. 1. Flavan-3-ols content of monomeric, oligomeric, and polymeric fractions of commercial enological tannins (CETs). Different small letters on top of the bars stand for statistically significant differences between CETs (Tukey test, $p \leq 0.05$).

& Peña-Neira, 2012b). Proanthocyanidins and proanthocyanidin gallates were quantified using (+)-catechin as standard while gallotannins were quantified with gallic acid standard. Likewise, flavonols and dihydroxyflavonols were quantified with the flavonols and astilbin curves, respectively. All quantitative analyses of phenolic composition of CETs and wines were performed in triplicate.

2.5. Sensorial analysis of wines enriched with CETs

Wine sensorial analysis was performed at 5, 45, 90 days using the temporal dominance of sensations (TDS) methodology (Meillon, Urbano, & Schlich, 2009). Fourteen trained panelists were included. The curves represented the dominance percentage, which permitted determination of the evolution of the dominant position for each attribute during time. The following temporal parameters

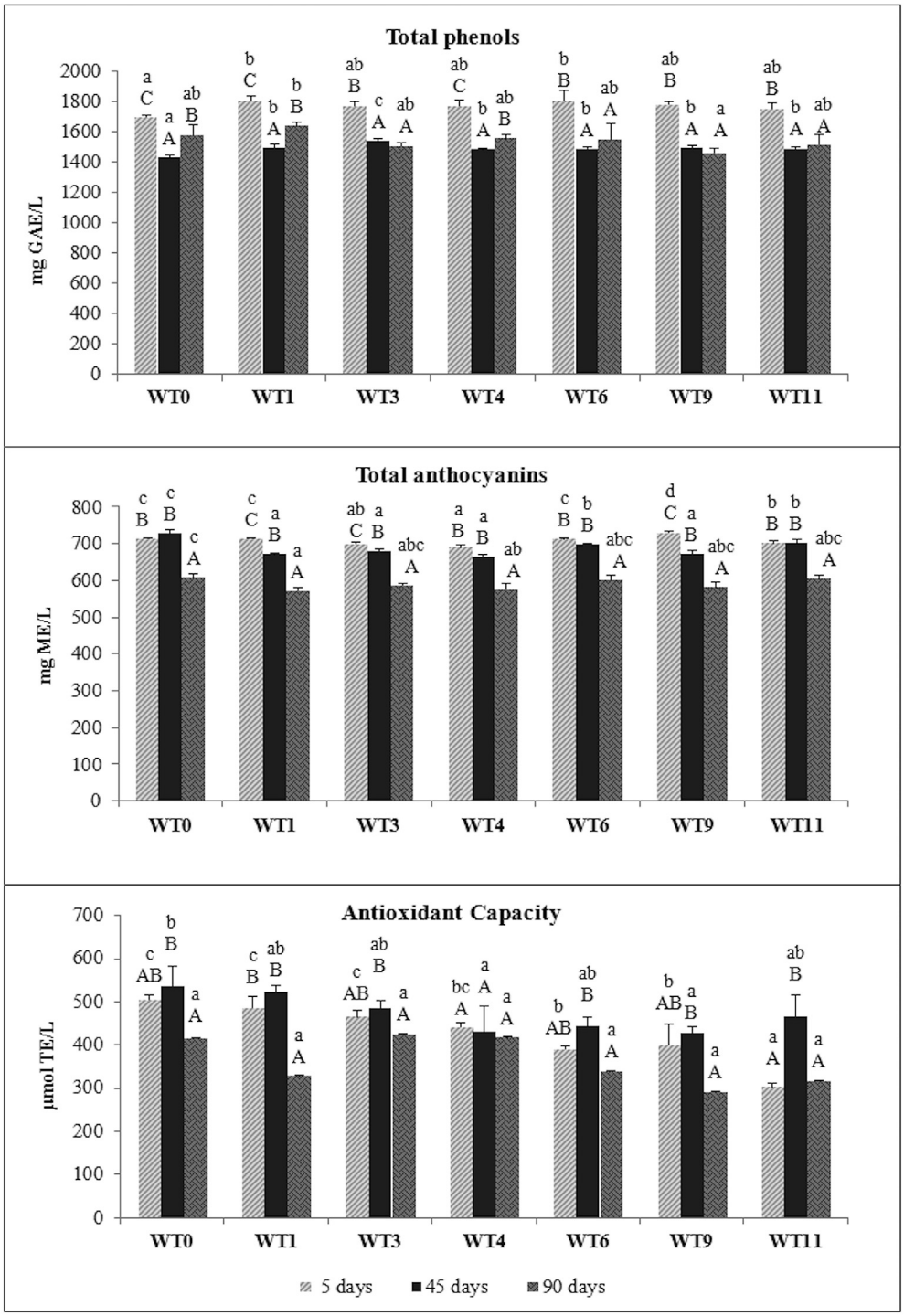

Fig. 2. Total phenols, total anthocyanins and antioxidant capacity values of Carménère wines. Different small letters on top of the bars stand for statistically significant differences between wines (WTn) in a same sampling date. Different capital letters on top of the bars stand for statistically significant differences between sampling dates (5, 45 and 90 days) for a same wine (Tukey test, $p \leq 0.05$). WT0 represents control wine (no CET addition).

were evaluated: a) the time of occurrence, which is the moment when the judge indicated the start of descriptor dominance; b) the duration of dominance, which is the span of time when the descriptor was dominant; and c) the astringency intensity at 20 s.

2.6. Statistical analysis

The Infostat version 2016 software package was used. The Tukey's *t*-test with a 95% confidence interval was applied to compare quantitative variables.

3. Results

3.1. Chemical characterization of CETs

3.1.1. Low molecular weight phenol compounds

Table 2 shows the concentration of phenols in the commercial enological tannins classified into 4 groups: phenolic acids (PhA), hydrolyzable tannins (HT), proanthocyanidins (P) and flavonols (F). CET5, CET7, CET8 and CET10 presented significantly higher concentrations of phenolic acids (sum of gallic, ellagic, syringic, vanillic and protocatechuic acids) and hydrolyzable tannins (sum of gallotannins and ellagitannins) compared with the rest of the treatments. In contrast, CET3 and CET4 stood out for their high proanthocyanidin contents [sum of (+)-catechin, (−)-epicatechin and other proanthocyanidins], whereas CET5 and CET10 exhibited significantly higher amounts of different glycosylated flavonols (quercetin, myricetin and kaempferol).

3.1.2. Monomeric, oligomeric and polymeric fractions of flavan-3-ols

Fig. 1 shows the concentrations of the mono-, oligo- and polymeric fractions of the eleven CET extracts. The polymer fraction was the most abundant whereas the monomeric fraction was the least abundant. In addition, CET3 and CET4 presented higher concentrations of the monomer, oligomer and polymer fractions than the rest of the treatments. Notwithstanding the above, CET4 presented significantly higher contents of the mono-, oligo- and polymer fractions than CET3.

3.2. Chemical characterization of wines

3.2.1. Total phenols, antioxidant capacity and total anthocyanins

Wines enriched with CETs were analyzed after 5, 45 and 90 days (Fig. 2). WT1 presented the highest values of total phenols at all sampling dates, whereas the control wine (WT0) exhibited the lowest concentration. In all wines enriched with CETs and also in the control, the concentration of these polyphenols decreased drastically between the first and second sampling dates (5 and 45 days). All wines treated with CETs exhibited

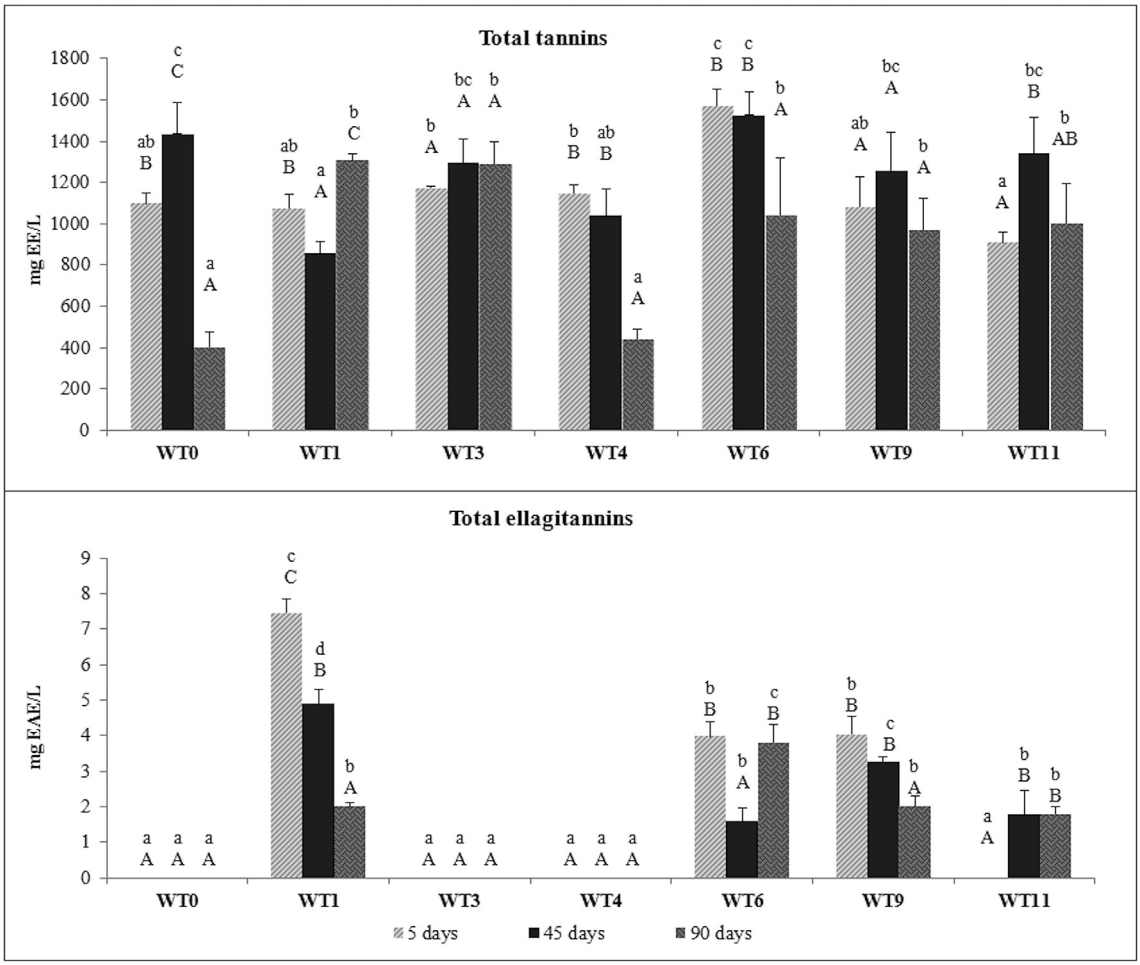

Fig. 3. Total tannin and ellagitannin contents of Carménère wines. Different small letters on top of the bars stand for statistically significant differences between wines (WTn) in the same sampling date. Different capital letters on top of the bars stand for statistically significant differences between sampling dates (5, 45 and 90 days) for the same wine (Tukey test, $p \leq 0.05$).

higher values of total phenols at 45 days compared with the control wine. Similarly, all wines mixed with CETs were found to exhibit lower anthocyanin values than the control at the first two sampling dates. Moreover, the wines WT0, WT1, WT3 and WT4 presented the highest values of antioxidant capacity at 5 days, whereas in the final sampling, there were no significant differences among treatments.

3.2.2. Total tannins and ellagitannins

Wines enriched with CETs exhibited a lower tannin concentration at the end of the study (Fig. 3). The exception was WT1, which presented a significantly higher content of total tannins after 90 days. In addition, after 90 days, most wines enriched with CETs (except WT4) exhibited significantly higher concentrations of total tannins than the control. As to the ellagitannin content, WT0, WT3 and WT4 showed no presence of these compounds. In addition, WT1 presented the highest concentration of total ellagitannins at two sampling dates, whereas WT6 presented the highest concentration of these compounds after 90 days.

3.2.3. Chromatic properties

Fig. 4 shows the color intensity and hue (h°) values of the wines enriched with the different CETs. WT3 wine presented reduced color intensity values at the end of the study (90 days) in respect to the other sampling dates, whereas the rest of the wines presented similar values throughout the study. In contrast, all wines showed increased hue (h°) values at the third sampling date. Although WT3, WT4 and WT6 exhibited the highest values of color intensity at the first sampling date, all the wines had similar values after 90 days. In contrast, the hue (h°) values exhibited an inverse tendency: the aforementioned three treatments resulted in the lowest values among all wines.

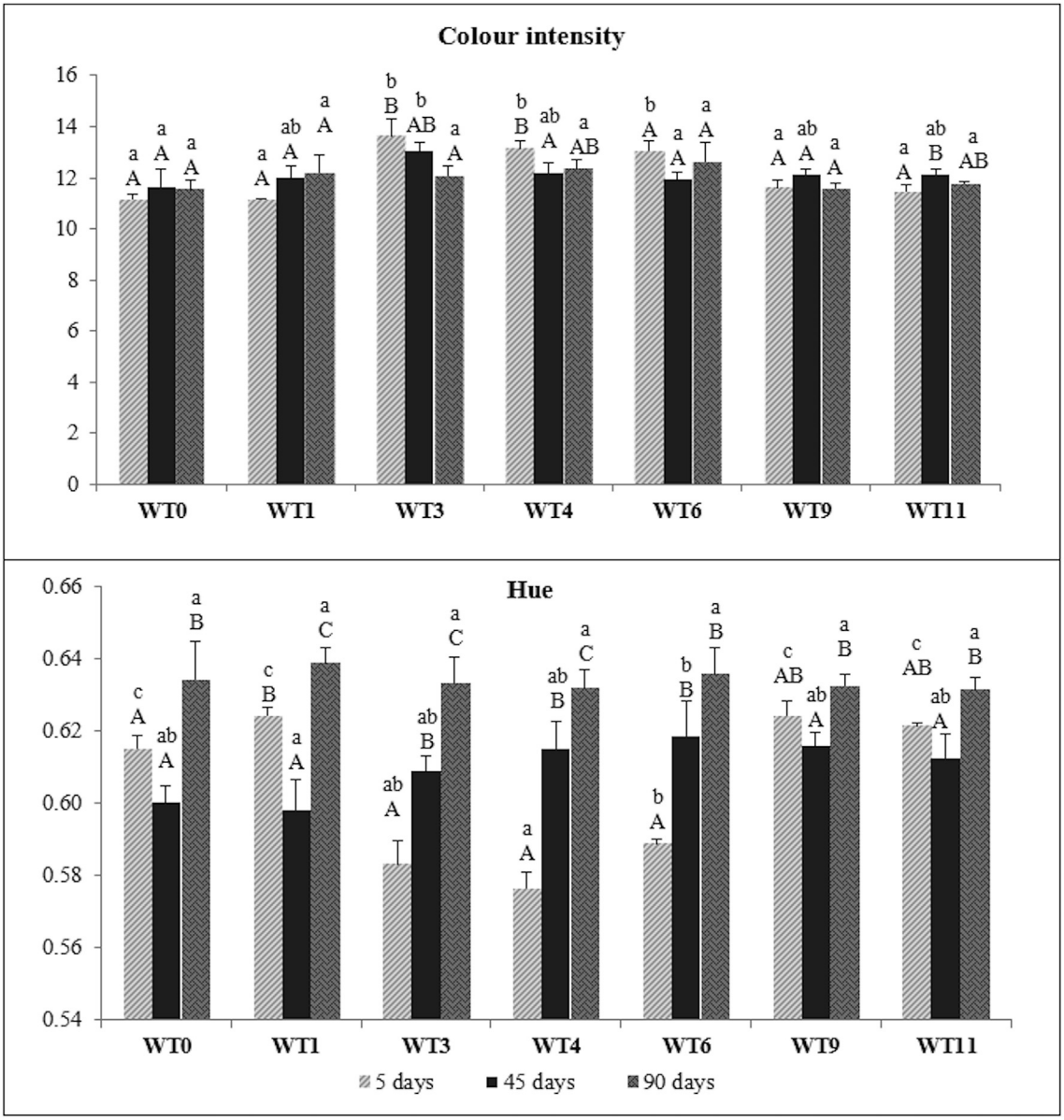

Fig. 4. Color intensity and hue values of Carménère wines. Different small letters on top of the bars stand for statistically significant differences between wines (WTn) in the same sampling date. Different capital letters on top of the bars stand for statistically significant differences between sampling dates (5, 45 and 90 days) for the same wine (Tukey test, $p \leq 0.05$).

3.2.4. Monomeric, oligomeric and polymeric proanthocyanidin fractions

Fig. 5 shows that the polymeric fraction was the most abundant, whereas the monomeric fraction was the least represented. In addition, in the majority of wines, the monomeric fraction values decreased between the first and last sampling dates; the exceptions were WT0 and WT11, which showed no significant differences during the assay. In contrast, the oligomeric fractions of WT6 and WT11 increased considerably between the first and third sampling dates. No generalized modification of the polymer fraction during this study was observed. Likewise, the highest concentrations of the monomeric proanthocyanidin fractions were observed in WT4 and WT3 at the first sampling date, whereas the concentrations of the oligomeric fractions in WT9 and WT11 were higher than in the

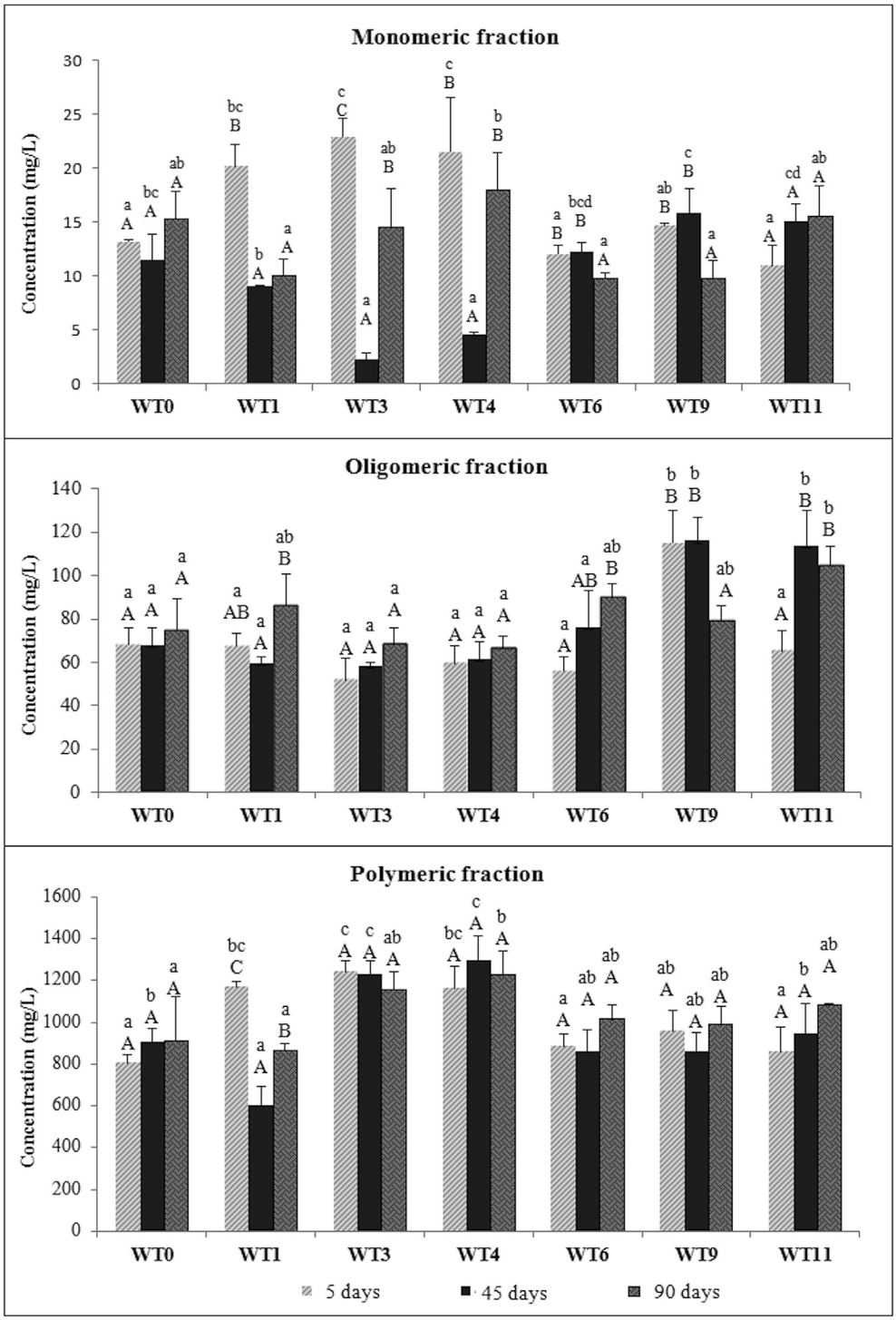

Fig. 5. Flavan-3-ols content of monomeric, oligomeric, and polymeric fractions of Carménère wines. Different small letters on top of the bars stand for statistically significant differences between wines (WTn) in the same sampling date. Different capital letters on top of the bars stand for statistically significant differences between sampling dates (5, 45 and 90 days) for the same wine (Tukey test, $p \leq 0.05$).

corresponding fractions of most of the other wines at two sampling dates. Finally, WT3 and WT4 also exhibited the highest concentrations of the polymeric fraction at two sampling dates.

3.2.5. Glycosylated, acetylated, and coumaroylated anthocyanins

Table 3 presents the distribution of anthocyanin groups as identified by HPLC-DAD. Those groups corresponded to delphinidin, cyanidin, petunidin, peonidin and malvidin esterified with either glucose (glycosylated anthocyanins), acetic acid (acetylated anthocyanins) and *p*-coumaric acid (coumaroylated anthocyanins). Concentrations of the three groups of anthocyanins gradually decreased towards the last sampling, but in proportion the coumaroylated anthocyanins presented the largest decrease between the first and third sampling dates (average decrease 28%). In addition, there were limited differences among wines with added CETs. Thus, WT3 and WT4 presented significantly higher contents of glycosylated and coumaroylated anthocyanins than the rest of the treatments after 45 days.

3.2.6. Low-molecular-weight phenol compounds

Table 4 lists the 20 compounds identified and quantified via HPLC-DAD. The non-flavonoids were gallic acid (GA), protocatechuic acid (PA), caftaric acid (CR), caffeic acid (CF), cutaric acid (CT), *p*-coumaric acid (PC), ferulic acid (FA), syringic acid (SA), vanillic acid (VA), ellagic acid (EA), gallotannins (GT), resveratrol (RE), tyrosol (TR) and tryptophol (TF). The flavonoid compounds were catechin (CA), epicatechin (EC), various proanthocyanidins (P), proanthocyanidin gallates (GP), flavonols (FL) and dihydroflavonols (DF). In all treatments, the most abundant compounds were gallic acid, flavonols, dihydroflavonols and tyrosol, whereas the less abundant ones were ferulic acid, ellagic acid and gallotannins.

Additionally, in WT1, WT3 and WT4, the concentrations of *p*-coumaric acid, ferulic acid, syringic acid, ellagic acid, gallotannins, proanthocyanidin gallates and dihydroflavonols were found to be increased significantly at the end of the study. In contrast, the content of resveratrol in the wines decreased dramatically during the assay. Comparatively, WT11 presented high concentrations of syringic acid and dihydroflavonols, whereas WT9 exhibited the highest amounts of tyrosol. Both treatments were associated with high concentrations of proanthocyanidin gallates at all sampling dates. WT3 stood up for its significant (−)-epicatechin content, whereas WT4 exhibited high concentrations of (+)-catechin. Finally, WT0 and WT1 presented the highest concentrations of flavonols over the 45 days of the study.

3.2.7. Sensorial analysis of wines

Fig. 6 shows the TDS curves for the sensations of astringency and bitterness. In general, the onset time for astringency varied between 16.6 and 19.5 s, with no significant differences among treatments during the study (Table 5). Likewise, the duration of astringency dominance was found to be increased at the end of the study in most wines enriched with CETs. However, although there were no evident differences among the various treatments, a higher percentage of dominance for the WT4 wine was observed compared with the other treatments (Fig. 6). In contrast, the intensity of astringency at 20 s did not exhibit any significant difference among the various treatments at any sampling date. Finally, no significant dominance of bitter taste was found during the study period (Fig. 6).

4. Discussion

In this study, eleven CETs of plant origin from oak (nine) and grapes (two) were characterized. Hydroalcoholic solutions of those CETs were prepared and characterized via spectrophotometric and HPLC-DAD techniques. Several authors have reported that the seeds and skins of grapes possess relevant amounts of flavan-3-ols (Canals et al., 2005; Monagas et al., 2005; Obreque-Slier et al., 2013), whereas the woods used for aging do not contain significant amounts of those compounds (Cadahía, Conde, Fernández de Simón, & García-Vallejo, 1998). However, oak wood contains abundant hydrolyzable tannins whereas grape seeds and grape skins have failed to exhibit presence of these compounds (Barros, Gironés-Vilaplana, Teixeira Colado-González, Moreno, Gil-Izquierdo, Rosa, & Domínguez-Perles, 2014; Chira & Teissedre, 2013; Zhentian, Jervis, & Helm, 1999). Both observations are strongly supported by the results of this study; wood-derived CETs exhibited low concentrations of mono-, oligo- and polymeric proanthocyanidins whereas grape-derived CETs presented insignificant amounts of hydrolyzable tannins. This last observation is further supported by the higher content of proanthocyanidins (catechin and epicatechin) detected via HPLC-DAD in the grape CETs (CET3 and CET4), which corroborates the importance of these CETs as a relevant source of proanthocyanidins. In the case of hydrolyzable tannins and phenolic acids, some CETs in this study (CET5, CET7, CET8 and CET10) exhibited significantly higher concentrations than those reported for oak wood (1–25.8 mg/g)

Table 3
Extractable anthocyanins content (mg/L) of Carménère wines enriched with commercial enological tannins (WTn).

	WT0	WT1	Anthocyanin glycosides			WT9	WT11
			WT3	WT4	WT6		
5	277.1 ± 3.3 aC	283.1 ± 5.7 aC	280.4 ± 1.9 aC	280.5 ± 3.2 aC	284.2 ± 0.9aC	284.1 ± 0.2aC	281.2 ± 1.4 aC
45	257.6 ± 0.7 dB	241.7 ± 1.2 abB	248.4 ± 2.3 cB	248.6 ± 1.7 cB	237.5 ± 3.4 aB	243.9 ± 1.2 bcB	244.3 ± 2.2 bcB
90	229.7 ± 5.9 aA	224.2 ± 5.6 aA	219.1 ± 3.9 aA	224.3 ± 2.7 aA	221.2 ± 3.1 aA	219.0 ± 3.0 aA	223.1 ± 0.6 aA
Anthocyanin acetilglycosides							
5	40.2 ± 0.7 aC	41.7 ± 0.9 aC	41.6 ± 0.7 aB	41.6 ± 0.9 aC	41.3 ± 1.2 aB	41.8 ± 0.4 aC	41.7 ± 1.8 aC
45	36.5 ± 0.2 aB	36.9 ± 2.2 aB	35.7 ± 0.3 aA	35.8 ± 0.9 aB	34.3 ± 0.1 aA	36.8 ± 1.5 aB	35.7 ± 1.1 aB
90	32.7 ± 0.9 aA	31.2 ± 0.8 aA	33.43 ± 1.7 aA	31.3 ± 0.5 aA	34.1 ± 0.4 aA	32.5 ± 1.4 aA	31.8 ± 1.3 aA
Anthocyanin coumarilglycosides							
5	21.8 ± 0.2 aC	22.4 ± 0.4 aC	22.2 ± 0.2 aC	22.1 ± 0.3 aC	22.4 ± 0.2 aC	22.4 ± 0.1 aC	22.2 ± 0.1 aC
45	18.7 ± 0.4 bB	17.4 ± 0.2 aB	18.5 ± 0.2 bB	18.5 ± 0.4 bB	17.0 ± 0.3 aB	17.6 ± 0.2 aB	17.6 ± 0.3 aB
90	17.0 ± 0.1 bA	16.1 ± 0.6 aA	16.0 ± 0.3 aA	16.3 ± 0.1 abA	16.3 ± 0.1 abA	15.7 ± 0.3 aA	16.0 ± 0.1 aA

Values represent means ± standard deviations (triplicates). Different small letters in single rows stand for statistically significant differences between wines (WTn) in a same sampling date and different capital letters in single columns stand for statistically significant differences between sampling dates (5, 45 and 90 days) for a same wine (Tukey test, $p \leq 0.05$).

Table 4
Low molecular weight phenolic compounds (mg/L) of Carménère wines enriched with commercial enological tannins (WTn).

5 days							
	WT0	WT1	WT3	WT4	WT6	WT9	WT11
GA	16.9 ± 3.5 aA	17.1 ± 2.4 aA	17.8 ± 1.2 aA	19.1 ± 0.2 aA	19.3 ± 0.6 aA	0.8 ± 2.1 aA	20.2 ± 1.9 aA
PA	9.1 ± 2.0 aA	8.2 ± 1.0 aAB	8.2 ± 0.3 aA	8.4 ± 0.3 aA	9.8 ± 0.4 aB	9.8 ± 0.8 aA	9.6 ± 0.9 aAB
CR	3.4 ± 0.0 aA	3.9 ± 0.7 abA	3.9 ± 0.3 abA	4.7 ± 0.1 bcB	5.1 ± 0.2 bcB	5.4 ± 0.6 cB	5.3 ± 0.7 cA
CF	10.8 ± 1.9 aA	10.2 ± 0.6 aA	10.2 ± 0.4 aA	10.3 ± 0.2 aA	10.9 ± 0.3 aA	11.5 ± 1.2 aA	11.5 ± 1.3 aA
CT	1.4 ± 0.0 abA	1.4 ± 0.3 aA	1.6 ± 0.1 abA	1.8 ± 0.2 abAB	1.8 ± 0.2 abB	1.9 ± 0.3 bA	1.8 ± 0.2 abA
PC	10.1 ± 1.7 aA	9.7 ± 0.4 aA	9.8 ± 0.4 aA	9.6 ± 0.2 aA	10.2 ± 0.3 aA	10.7 ± 1.1 aA	10.8 ± 1.3 aA
FA	0.3 ± 0.0 aA	0.3 ± 0.0 aA	0.3 ± 0.0 aA	0.3 ± 0.0 aA	0.3 ± 0.0 aA	0.4 ± 0.0 bA	0.4 ± 0.0 bA
SA	3.4 ± 0.3 aA	4.2 ± 0.4 abA	4.2 ± 0.2 abA	4.4 ± 0.1 abA	4.6 ± 0.2 bA	4.9 ± 0.6 bA	5.1 ± 0.6 bA
VA	3.0 ± 0.5 aA	2.7 ± 0.3 aA	2.6 ± 0.2 aA	3.0 ± 0.1 aA	3.0 ± 0.1 aB	2.9 ± 0.2 aA	2.9 ± 0.2 aA
EA	0.0 ± 0.0 aA	0.0 ± 0.0 aA	0.0 ± 0.0 aA	0.2 ± 0.0 bB	0.5 ± 0.1 cB	1.3 ± 0.3 eB	1.1 ± 0.1 Db
CA	2.3 ± 0.5 abA	2.1 ± 0.5 aA	2.6 ± 0.1 abA	3.1 ± 0.0 bB	2.6 ± 0.1 abA	2.2 ± 0.4 aA	2.2 ± 0.4 aA
EC	1.7 ± 0.2 abA	1.5 ± 0.3 aA	2.2 ± 0.1 bA	2.8 ± 0.0 cB	1.9 ± 0.1 abB	1.7 ± 0.2 abA	1.7 ± 0.3 abA
P	4.2 ± 0.1 dA	2.1 ± 0.3 bA	3.6 ± 0.2 cB	4.4 ± 0.2 dB	1.6 ± 0.1 aAB	1.4 ± 0.2 aA	1.5 ± 0.1 aB
GP	0.9 ± 0.1 bcA	1.1 ± 0.1 cA	0.7 ± 0.0 bA	0.0 ± 0.0 aA	2.2 ± 0.1 dB	2.1 ± 0.2 dA	2.0 ± 0.1 dA
GT	0.0 ± 0.0 aA	0.0 ± 0.0 aA	0.0 ± 0.0 aA	0.0 ± 0.0 aA	0.0 ± 0.0 aA	0.0 ± 0.0 aA	0.0 ± 0.0 aA
FL	15.5 ± 1.3 bA	13.5 ± 1.2 bB	16.1 ± 1.8 bB	14.8 ± 0.9 bB	14.2 ± 0.3 bA	9.6 ± 1.0 aA	15.7 ± 1.7 bB
DF	9.0 ± 0.1 aA	10.1 ± 1.0 abA	11.0 ± 0.3 bA	10.5 ± 0.1 abA	13.8 ± 0.3 cA	14.8 ± 1.5 cB	14.5 ± 0.4 cA
RE	2.3 ± 0.2 aB	2.2 ± 0.1 aB	1.9 ± 0.1 aB	2.0 ± 0.2 aB	2.2 ± 0.1 aB	2.4 ± 0.3 aB	2.4 ± 0.3 aB
TR	25.2 ± 0.2 aAB	27.5 ± 2.8 abA	29.4 ± 1.5 abA	28.9 ± 2.0 abA	30.8 ± 2.7 abA	33.5 ± 3.6 bA	30.8 ± 1.4 abA
TF	2.5 ± 0.4 aA	2.1 ± 0.1 aAB	2.2 ± 0.1 aB	2.2 ± 0.1 aB	2.3 ± 0.1 aA	2.1 ± 0.1 aA	2.1 ± 0.3 aA
45 days							
GA	19.0 ± 1.0 aA	21.1 ± 0.8 bA	20.5 ± 0.5 abB	22.1 ± 0.1 abC	19.1 ± 1.5 abA	20.1 ± 0.4 abA	20.5 ± 0.0 abA
PA	9.0 ± 1.3 aA	9.5 ± 0.2 aB	9.1 ± 0.2 aB	9.2 ± 1.1 aA	10.4 ± 0.8 aB	9.6 ± 0.4 aA	10.1 ± 0.5 aB
CR	4.4 ± 0.3 aB	4.2 ± 0.2 aA	4.4 ± 0.1 aA	4.6 ± 0.0 aB	4.1 ± 0.4 aAB	4.3 ± 0.4 aAB	4.8 ± 0.3 aA
CF	11.1 ± 0.6 aA	11.4 ± 0.3 aAB	10.9 ± 0.2 aA	11.1 ± 0.2 aB	10.9 ± 0.4 aA	10.8 ± 0.1 aA	11.1 ± 0.1 aA
CT	1.8 ± 0.1 aA	1.7 ± 0.1 aA	1.8 ± 0.0 aA	1.8 ± 0.0 aB	1.5 ± 0.2 aAB	1.6 ± 0.3 aA	1.7 ± 0.3 aA
PC	11.3 ± 0.6 aA	11.7 ± 0.2 aB	11.3 ± 0.3 aB	11.4 ± 0.2 aB	11.4 ± 0.4 aAB	11.1 ± 0.2 aA	11.4 ± 0.1 aA
FA	0.4 ± 0.1 aA	0.4 ± 0.0 aB	0.3 ± 0.0 aA	0.3 ± 0.0 aA	0.3 ± 0.0 aA	0.3 ± 0.0 aA	0.4 ± 0.0 aA
SA	4.9 ± 0.4 aB	5.2 ± 0.3 aB	4.9 ± 0.1 aAB	5.0 ± 0.0 aB	5.0 ± 0.4 aA	4.8 ± 0.1 aA	5.3 ± 0.2 aA
VA	3.2 ± 0.3 aA	3.4 ± 0.1 aB	3.0 ± 0.0 aB	2.7 ± 0.6 aA	3.2 ± 0.1 aB	2.9 ± 0.4 aA	3.4 ± 0.1 aB
EA	0.0 ± 0.0 aA	3.9 ± 0.5 bB	0.0 ± 0.0 aA	0.0 ± 0.0 aA	0.0 ± 0.0 aA	0.0 ± 0.0 aA	0.0 ± 0.0 aA
CA	2.3 ± 0.2 abcA	2.2 ± 0.1 abcA	2.7 ± 0.0 cdA	3.1 ± 0.2 dB	1.8 ± 0.4 aA	2.0 ± 0.1 abA	2.4 ± 0.3 bcA
EC	1.9 ± 0.1cA	1.7 ± 0.1 abcA	2.2 ± 0.0 dA	2.8 ± 0.0 eB	1.5 ± 0.1 aA	1.6 ± 0.1 abA	1.8 ± 0.1 bcA
P	3.8 ± 0.1 aA	3.3 ± 0.3 aB	3.7 ± 0.1 aB	4.0 ± 0.3 aB	1.3 ± 0.2 aA	1.2 ± 0.1 aA	1.0 ± 0.2 aA
GP	1.4 ± 0.1 bB	1.5 ± 0.1 bB	0.8 ± 0.0 aA	0.8 ± 0.0 aB	0.9 ± 0.3 aA	2.0 ± 0.3 cA	2.2 ± 0.2 cA
GT	0.0 ± 0.0 aA	0.5 ± 0.1 bB	0.0 ± 0.0 aA	0.0 ± 0.0 aA	0.0 ± 0.0 aA	0.0 ± 0.0 aA	0.0 ± 0.0 aA
FL	20.7 ± 1.5 bB	20.9 ± 2.2 bC	16.5 ± 0.6 abB	17.4 ± 0.9 abC	14.3 ± 4.1 aA	15.8 ± 0.8 abB	16.2 ± 0.3 abB
DF	10.7 ± 0.8 aA	12.5 ± 0.3 bcB	11.8 ± 0.7 abcA	11.3 ± 0.2 abB	14.4 ± 0.5 dA	13.0 ± 0.3cdAB	14.5 ± 0.9 dA
RE	3.2 ± 0.0 abC	3.7 ± 0.1 cC	3.2 ± 0.1 abC	3.4 ± 0.1 bcC	2.9 ± 0.1 aC	2.9 ± 0.2 aC	3.2 ± 0.0 abC
TR	32.6 ± 1.6 aB	33.0 ± 0.9 aB	32.1 ± 0.7 aB	33.2 ± 0.4 aB	30.6 ± 2.3 aA	30.9 ± 1.7 aA	34.5 ± 2.6 aA
TF	2.4 ± 0.3 aA	2.2 ± 0.0 aB	2.2 ± 0.1 aB	2.3 ± 0.0 aB	2.1 ± 0.1 aA	2.1 ± 0.0 aA	2.2 ± 0.1 aA
90 days							
GA	18.1 ± 0.3 aA	19.6 ± 1.4 aA	20.3 ± 1.1 aB	20.3 ± 0.6 aB	17.4 ± 1.7 aA	18.7 ± 1.4 aA	20.2 ± 1.6 aA
PA	6.7 ± 1.0 aA	7.6 ± 0.8 abB	8.4 ± 0.4 abA	8.8 ± 0.5 bA	7.7 ± 0.5 abA	7.9 ± 1.2 abA	8.1 ± 0.4 abA
CR	4.5 ± 0.1 aB	4.5 ± 0.1 aA	4.5 ± 0.4 aA	4.0 ± 0.4 aA	3.6 ± 0.6 aA	4.1 ± 0.3 aA	4.6 ± 0.5 aA
CF	10.9 ± 0.2 aA	10.9 ± 0.3 aB	11.0 ± 0.2 aA	10.8 ± 0.1 aB	10.7 ± 0.6 aA	10.4 ± 0.9 aA	11.4 ± 0.6 aA
CT	1.4 ± 0.3 aA	1.7 ± 0.2 aA	1.8 ± 0.1 aA	1.5 ± 0.1 aA	1.3 ± 0.2 aA	1.5 ± 0.1 aA	1.7 ± 0.2 aA
PC	11.9 ± 0.3 aA	11.9 ± 0.2 aB	11.9 ± 0.3 aB	11.6 ± 0.1 aB	11.8 ± 0.7 aB	11.2 ± 1.0 aA	12.4 ± 0.7 aA
FA	0.4 ± 0.0 aA	0.4 ± 0.0 aB	0.4 ± 0.0 aB	0.4 ± 0.0 aB	0.4 ± 0.0 aA	0.4 ± 0.0 aA	0.5 ± 0.0 aA
SA	4.9 ± 0.1 abB	4.9 ± 0.0 abAB	4.9 ± 0.4 abB	5.0 ± 0.2 abB	4.7 ± 0.3 aA	4.8 ± 0.4 abA	5.5 ± 0.3 bA
VA	2.5 ± 0.2 aA	2.5 ± 0.2 aA	2.5 ± 0.1 aA	2.4 ± 0.5 aA	2.5 ± 0.1 aA	2.4 ± 0.2 aA	2.8 ± 0.1aA
EA	0.0 ± 0.0 aA	6.4 ± 0.9 fC	0.3 ± 0.0 cB	0.2 ± 0.0 bB	3.2 ± 0.2 eC	1.6 ± 0.0 dB	1.6 ± 0.0 dC
CA	2.4 ± 0.0 bcA	2.3 ± 0.1 bcA	2.6 ± 0.1 bcA	2.7 ± 0.5 cA	1.6 ± 0.6 aA	2.0 ± 0.1 abA	2.1 ± 0.1 abcA
EC	1.7 ± 0.1 bA	1.6 ± 0.0 bA	2.1 ± 0.2 cA	2.4 ± 0.1 cA	1.2 ± 0.2 aA	1.4 ± 0.1 abA	1.6 ± 0.2 bA
P	2.9 ± 0.4 bA	1.4 ± 0.3 aA	2.2 ± 0.5 abA	1.6 ± 0.5 aA	1.8 ± 0.2 aB	1.2 ± 0.0 aA	1.2 ± 0.2 aAB
GP	1.3 ± 0.1 bB	5.7 ± 0.0 eC	2.3 ± 0.2 cB	1.3 ± 0.3 bC	0.7 ± 0.0 aA	2.7 ± 0.2 dB	3.0 ± 0.2 dB
GT	0.0 ± 0.0 aA	0.0 ± 0.0 aA	0.0 ± 0.0 aA	0.7 ± 0.1 cB	0.2 ± 0.0 bB	0.0 ± 0.0 aA	0.2 ± 0.0 bB
FL	16.5 ± 2.0 aA	5.8 ± 0.8 aA	12.1 ± 0.9 aA	11.2 ± 0.3 aA	11.4 ± 2.1 aA	10.3 ± 0.9 aA	12.1 ± 1.0 aA
DF	11.8 ± 2.6 abA	11.8 ± 0.2 abB	15.3 ± 1.9 bcB	16.4 ± 0.2 bcC	13.5 ± 1.4 abcA	9.9 ± 2.7 aA	17.0 ± 0.3 cB
RE	0.9 ± 0.0 aA	0.9 ± 0.0 aA	1.0 ± 0.1 aA	1.0 ± 0.0 aA	1.5 ± 0.1 bA	0.9 ± 0.0 aA	1.0 ± 0.0 aA
TR	19.2 ± 8.1 aA	30.7 ± 2.1 bAB	31.2 ± 0.2 bAB	29.6 ± 0.4 bA	28.6 ± 1.6 bA	28.4 ± 2.2 bA	31.4 ± 2.0 bA
TF	2.0 ± 0.0 abA	2.0 ± 0.0 abA	2.0 ± 0.0 abA	2.0 ± 0.0 abA	2.1 ± 0.2 abA	1.9 ± 0.2 aA	2.3 ± 0.1 bA

Values represent means ± standard deviations (triplicates). Different small letters in single rows stand for statistically significant differences between wines (WTn) in a same sampling date and different capital letters in single columns stand for statistically significant differences between sampling dates (5, 45 and 90 days) for a same wine (Tukey test, $p \leq 0.05$). Names of the low molecular weight polyphenol compounds (abbreviated in the first column) are shown in section 3.2.6.

(Cadahía et al., 1998; Klumpers, Scalbert, & Janin, 1994). It is interesting to note that CETs from oak presented a large compositional variability, which could be due to both the extraction methods and the characteristics of the raw material used to make those products (Hartzfeld et al., 2002; Peng, Scarlbet, & Moties, 1991; Zhentian et al., 1999). These observations show that

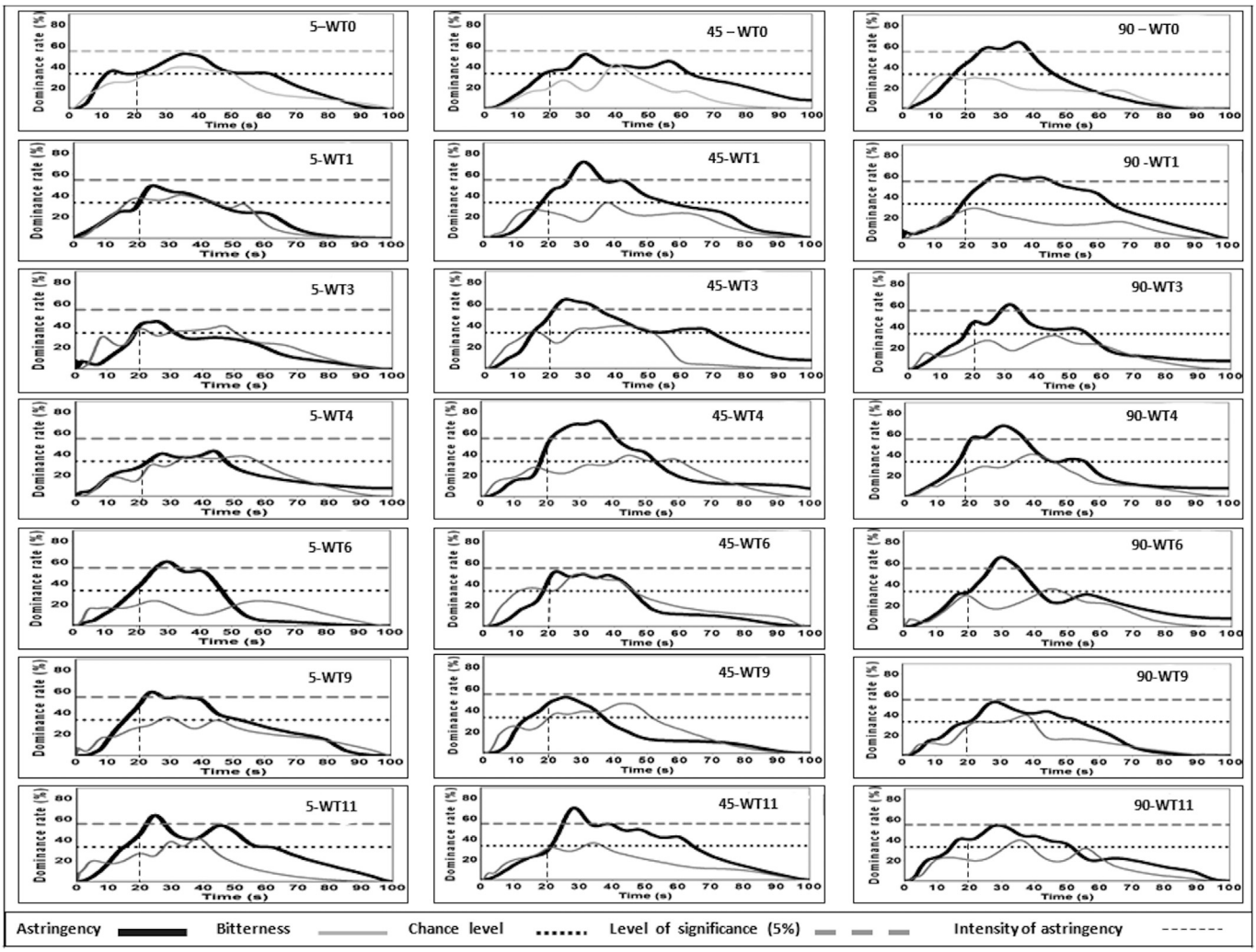

Fig. 6. Temporal dominance of sensation profile of Carménère wines enriched with CETs (WTn) during 5, 45 and 90 days of storage.

characterization of these products is highly relevant because the limited and ambiguous information provided by suppliers can turn the choice of purchase into a random process. Besides, the chemical compositional differences of these oenological products would affect differentially the wine matrix.

After demonstrating the "grape" (CET3 and CET4) and "oak" (CET1, CET2, CET5-CET11) origins of the different CETs used in this study, we proceeded to evaluate the effects of these commercial oenological products on the characteristics of a Carménère wine. For this purpose, six CETs that had been shown to possess distinct chemical characteristics (CET3 and CET4 from grape; CET1, CET6, CET9 and CET11 from wood) were selected. Five wood CETs were excluded (CET2, CET5, CET7, CET8 and CET10) because of similarities of their chemical compositions with those of the selected wood CETs. After the selective addition of CETs to wine, analytical tracing was performed for 90 days. In general, a significant decrease in total phenols, total tannins, total anthocyanins and total ellagitannins; antioxidant capacity; color intensity; and mono-, oligo- and polymer-fractions of proanthocyanidins was observed between the first and last sampling date. Only the hue value increased progressively until the last sampling date, probably due to an increase in the yellow component of wine. Such progressive increase, however, was also observed in the control wine, thus suggesting a relationship of that color parameter with wine evolution instead of CET-addition. Notably, the presence of CETs into different wines caused a greater decrease in total phenols and total anthocyanins between the first and third sampling dates. Thus, in wine with no added CETs, the total phenol and total anthocyanin contents decreased during the study an average of 7% and 15%, respectively, whereas in wines with added CETs, they decreased an average of 14% and 17.5%, respectively. In contrast, in the case of total tannins and antioxidant capacity, addition of some of the CETs to wine caused a decrease in both parameters. Moreover, wines enriched with CETs had higher concentrations of total tannins towards the end of the study, whereas the wine with no added CETs and at least one of the CET-containing wines (WT4) presented decreases in the total tannin content as high as 64%. These diverse quantitative effects on the phenolic composition of wine may be at least partly due to the occurrence of polymerization and/or copigmentation reactions between different polyphenols (González-Manzano, Dueñas, Rivas-Gonzalo, Escribano-Bailón, & Santos-Buelga, 2009; Kunsági-Máté, Szabó, Nikfardjam, & Kollár, 2006). These reactions could support the formation of stable and/or insoluble polymers that would precipitate or display an increased tendency to be oxidized, thus provoking a decrease in the aforementioned parameters (Hidalgo, 2003, p. 1423; Zamora, 2003, p. 225). Interactions between the chemical complexity of some CETs and that of the wine matrix may well exacerbate differentially those

Table 5
Sensory analysis of Carménère wines enriched with commercial enological tannins (WTn).

Occurrence astringency time (seconds)			
	5 days	45 days	90 days
WT0	17.8 ± 8.0 aA	21.8 ± 9.7 aA	16.5 ± 6.8 aA
WT1	21.1 ± 6.4 aA	20.5 ± 6.3 aA	14.4 ± 5.5 aA
WT3	15.0 ± 6.1 aA	16.7 ± 6.3 aA	16.1 ± 6.6 aA
WT4	15.6 ± 6.4 aA	19.0 ± 8.0 aA	17.0 ± 5.5 aA
WT6	16.8 ± 7.1 aA	17.0 ± 6.8 aA	18.3 ± 6.09 aA
WT9	15.5 ± 5.8 aA	19.9 ± 7.9 aA	18.1 ± 7.6 aA
WT11	14.5 ± 6.3 aA	22.2 ± 8.2 aA	15.9 ± 6.3 aA
Duration of astringency dominance (seconds)			
WT0	23.9 ± 9.2 aA	26.5 ± 8.5 aA	20.8 ± 7.0 aA
WT1	17.9 ± 6.0 aA	27.5 ± 8.6 abAB	29.3 ± 10.7 aB
WT3	18.0 ± 5.3 aA	29.7 ± 9.0 bB	24.2 ± 8.3 aAB
WT4	18.0 ± 8.9 aA	29.0 ± 6.2 abAB	24.5 ± 7.4 aAB
WT6	17.9 ± 7.0 aA	18.9 ± 8.2 aA	22.8 ± 7.3 aAB
WT9	25.3 ± 10.4 abAB	18.4 ± 8.5 aA	20.8 ± 8.6 aA
WT11	26.3 ± 9.8 abA	28.0 ± 8.9 abA	25.6 ± 8.7 aA
Astringency intensity (seconds)			
WT0	9.8 ± 2.9 aA	10.3 ± 3.4 aA	8.9 ± 3.0 aA
WT1	8.2 ± 3.0 aA	10.9 ± 4.1 aA	10.2 ± 2.8 aA
WT3	7.8 ± 3.2 aA	9.5 ± 3.4 aA	9.6 ± 4.1 aA
WT4	9.2 ± 2.6 aA	10.1 ± 3.3 aA	8.9 ± 3.4 aA
WT6	9.3 ± 2.8 aA	9.5 ± 3.9 aA	8.7 ± 4.5 aA
WT9	9.4 ± 2.6 aA	9.9 ± 3.9 aA	8.9 ± 4.4 aA
WT11	9.6 ± 2.5 aA	9.3 ± 2.3 aA	8.8 ± 3.7 aA

Values represent means ± standard deviations (triplicates). Different small letters in single columns stand for statistically significant differences between wines (WTn) in a same sampling date and different capital letters in single rows stand for statistically significant differences between sampling dates (5, 45 and 90 days) for a same wine (Tukey test, $p \leq 0.05$).

complex reactions.

A comparative analysis of the wines demonstrated that the use of any of the CETs modified the chemical composition of the wines. Specifically, wines enriched with grape-based CETs did not exhibit ellagitannins because these compounds are available mainly in the CETs from wood (Barros et al., 2014; Chira & Teissedre, 2013; Michel et al., 2016). Likewise, wines with CETs from grape seed (WT4) showed the lowest values of total anthocyanins and antioxidant capacity in two samples. In contrast, WT1 presented the highest total phenol content and hue, whereas WT6 exhibited the highest total tannin content throughout the study. Such non-uniform variations would suggest that application of a particular CET may affect diferentially just some of the wine properties. Accordingly, the use of CETs from a common origin does not guarantee a predictable effect on the polyphenolic properties of a wine. This observation is additionally supported by our results about the monomeric, oligomeric and polymeric proanthocyanidin fractions because no consistent difference was observed among treatments. Notwithstanding, the results referred to the polymeric proanthocyanidin fraction showed that the wines enriched with grape CETs (WT3 and WT4) stood out for their high concentrations of flavan-3-ol polymers, which was certainly expected from the grape origin of those CETs. By the same token, regardless its origin, the addition of a CET to a wine would likely affect the composition of some flavan-3-ol fractions. This assertion was supported in our study by the high concentrations of the flavan-3-ol oligomeric fraction in two samples of wines that had been enriched with wood CETs (WT9 and WT11).

In the case of the low molecular weight phenolic compounds identified via HPLC-DAD, we observed some modifications between the first and third samples. Thus, following the addition of some CETs (for example, in WT1, WT3 and WT4), concentrations of some phenolic acids (e.g., *p*-coumaric, ferulic and syringic acids), procyanidingallates and dihydroflavonols were increased during the study. This behavior is likely related with the low molecular weight phenols originally present in the CETs. In contrast, the addition of some CETs caused a decrease in the content of some polyphenols, specifically (+)-catechin, (−)-epicatechin, tryptophol and resveratrol. Some authors have associated those changes to precipitation and oxidation processes (Revilla & González-San José, 2003; Figueiredo-Gonzáles et al., 2014; Michel et al., 2016). It is interesting to note that those decreases in the contents of small polyphenols is not a common phenomenon because in our study the T4 containing-wine (WT4) exhibited significantly higher concentrations of (+)-catechin and (−)-epicatechin throughout the study, whereas WT11 presented the highest contents of dihydroflavonols, procyanidin gallates and syringic acid in at least two sampling dates. Despite the above, for the rest of the compounds identified via HPLC-DAD the observed differences between the treatments were specific to sampling dates, which is in agreement with the above-mentioned non-uniform effect of CETs on wine features.

Results from other laboratories suggest that addition of CETs affects anthocyanin stability and, consequently, wine color (Bimpilas, Panagopoulou, Tsimogiannis, & Oreopoulou, 2016). This observation is highly relevant because anthocyanins by themselves are phenolic compounds that are very unstable over time, and such instability causes a decrease in wine color. Our present results support the occurrence of such phenomenon because the glycosylated, acetylated and coumaroylated anthocyanin, as quantified by HPLC chromatography, experienced a significant and drastic decrease between the first and third sampling dates. Nevertheless, it is important to emphasize that the wine with no added CET had a similar anthocyanin content as those enriched with some of the CETs in the study. Moreover, the control wine had higher anthocyanin contents than the other wines at some sampling dates, which would support the idea of a lack of interaction between phenols from CETs with the anthocyanins.

Since type and concentration of polyphenols do affect the perception of wine astringency and bitterness (Chira et al., 2015; Ma et al., 2014; Rinaldi, Jourdes, Teissedre, & Moio, 2014) the present study also included sensory assessment of wines. According to these results, the onset of astringency occurred between 16.6 s (samples of 5 and 90 days) and 19.5 s (samples of 45 days) for all treatments, largely matching the results of Valentova, Skrovanková, Panovská, and Pokorny (2002). Addition of some CETs (CET1, CET3, CET4 and CET6) also caused an increase in the duration of the astringency dominance towards the end of the study. Despite those results, addition of different CETs did not provoke a differential perception of astringency or bitterness of wines, except at some sampling dates, thus indicating that addition of these CETs does not substantially affect certain sensorial properties of wines.

Altogether, the CETs currently available on the market may exhibit highly diverse phenolic compositions that are largely related to their origin (grape or wood). However, it is important to remark that the phenolic composition of all nine wood CETs in the study was highly diverse, thus supporting the view that the use of CETs of a common origin does not ensure a similar phenolic composition and that their final contribution to the chemical composition of a wine will likely be different. Similarly, the addition of these generic oenological products does not ensure either a consistent effect on the phenolic composition and sensorial characteristics of a wine. Further studies in these regards, including CET dosage and consumer preferences are highly necessary.

Values represent means ± standard deviations (triplicates). Different small letters in single rows stand for statistically significant differences between wines (WTn) in a same sampling date and different capital letters in single columns stand for statistically

significant differences between sampling dates (5, 45 and 90 days) for a same wine (Tukey test, $p \leq 0.05$). Names of the low molecular weight polyphenol compounds (abbreviated in the first column) are shown in section 3.2.6.

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