

## Evolution of the phenolic content of red wines from *Vitis vinifera* L. during ageing in bottle

María Monagas, Carmen Gómez-Cordovés, Begoña Bartolomé \*

*Instituto de Fermentaciones Industriales, CSIC. Juan de la Cierva 3, 28006 Madrid, Spain*

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### Abstract

The evolution of the phenolic content, as measured by spectrophotometric methodologies [total polyphenols (TP), low-polymerized polyphenols (LPP), total anthocyanins (TA), catechins (CAT), proanthocyanidins (PRO) and *o*-diphenols (OD)], was studied in young red wines from *Vitis vinifera* L. cv Tempranillo, Graciano and Cabernet Sauvignon during 26 months of ageing in bottle. Although the wines showed differences in their initial phenolic profiles, the evolution trend of the different families of phenolic compounds was similar in the wines from the three grape varieties. TA markedly decreased during ageing in bottle (43% for Tempranillo, 65% for Graciano and 66% for Cabernet Sauvignon), following a first-order kinetic. Calculation of the kinetic parameters revealed that the disappearance rate of TA was 2-fold lower for Tempranillo wine than for Graciano and Cabernet Sauvignon wines, which exhibited similar kinetics. This decrease in TA (due to the disappearance of monomeric anthocyanins), together with a increase registered in CAT and PRO (due to the cleavage of proanthocyanidins and their structural transformations), was consistent with a decrease in LPP, suggesting the occurrence of condensation reactions during ageing in bottle. The evolution trends observed for TP and OD during ageing in bottle were the results of changes in the different groups of phenolic compounds involved in both determinations. Global phenolic determinations, usually performed in wineries, provided useful information in relation to the evolution of wine polyphenols during ageing in bottle.

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### 1. Introduction

Phenolic compounds constitute one of the most important quality parameters of wines since they contribute to their organoleptic characteristics, particularly colour, astringency, and bitterness. Wine phenolics belong to two main groups, non-flavonoid (namely, hydroxybenzoic and hydroxycinnamic acids and their derivatives, stilbenes and phenolic alcohols) and flavonoid (namely, anthocyanins, flavanols, flavonols and dihydroflavonols) compounds. Anthocyanins are the main phenolic compounds involved in the colour of

red wines. The astringency and bitterness of young wines is mainly due to phenolic acids and flavanols (Ribichaud & Noble, 1990). Hydroxycinnamic acids and flavanols, together with flavonols, also act as copigments of anthocyanins (Eiro & Heinonen, 2002; Escribano-Bailón, Dangles, & Brouillard, 1996; Mistry, Cai, Lilley, & Haslam, 1991). Phenolic compounds, especially flavonoids and stilbenes, have been recognized as responsible for several beneficial physiological effects associated with red wine consumption, mostly due to their antioxidant and anti-inflammatory properties (Frankel, Kanner, German, Parks, & Kinsella, 1993; Stoclet, Kleschyov, Andriambelosen, Dielbolt, & Andriantsitohaina, 1999).

During wine maturation and ageing, phenolic compounds participate in numerous chemical reactions.

\* Corresponding author. Tel.: +34 91 562 29 00; fax: +34 91 564 48 53.

*E-mail address:* [bartolome@ifi.csic.es](mailto:bartolome@ifi.csic.es) (B. Bartolomé).

Anthocyanins are progressively transformed into more stable oligomeric and polymeric pigments which give rise to important changes in the colour (from bright-red to brick-red hues) and in the astringency of wines. Different mechanisms have been proposed for the formation of these oligomeric and polymeric pigments. Besides the direct (Somers, 1971) and acetaldehyde-mediated (Timberlake & Bridle, 1976) anthocyanin-flavanol condensation reactions, other anthocyanin condensation reactions leading to the so-called pyranoanthocyanins (namely, anthocyanin-pyruvic acids, anthocyanin-vinylphenol and anthocyanin-vinylflavanol adducts, among others) have recently been demonstrated to occur during red wine ageing (Bakker & Timberlake, 1997; Fulcrand, Cameira Dos Santos, Sarni-Manchado, Cheynier, & FabreBonvin, 1996; Mateus, Silva, Santos-Buelga, Rivas-Gonzalo, & De Freitas, 2002; Monagas, Núñez, Bartolomé, & Gómez-Cordoves, 2003b; Schwarz, Wabnitz, & Winterhalter, 2003). In addition, flavanols are involved in oxidative browning reactions, and in interactions with proteins that result in haze formation (Cheynier & Ricardo da Silva, 1991; Ricardo da Silva et al., 1991). Flavanols also participate in direct, and in acetaldehyde- and glyoxylic acid-mediated condensation reactions with other flavanols (Es-Safi et al., 1999; Fulcrand, Cheynier, Oszmianski, & Moutounet, 1997; Haslam, 1980; Saucier, Little, & Glories, 1997). The concentrations of anthocyanins, copigments, acetaldehyde and other yeast metabolites, as well as the pH, temperature, and presence of oxygen and sulfur dioxide, among others, are factors that affect the progress of chemical reactions involving phenolics during wine ageing (Dallas, Ricardo da Silva, & Lauriano, 1995; Somers & Evans, 1986; Romero & Bakker, 1999, 2000).

Several authors have studied the evolution of individual phenolic compounds during wine ageing (Gómez-Plaza, Gil-Muñoz, López-Roca, & Martínez, 2000; Pérez-Magariño & González-San José, 2004; Revilla & González-San José, 2003; Zafrilla et al., 2003). However, these studies have been performed using analytical techniques, such as HPLC-DAD, which are usually not available in wineries for routine polyphenol analysis. In contrast, classic polyphenol methods, based on global spectrophotometric determinations, are more affordable for wineries for routine analysis (Del Alamo, Bernal, & Gómez-Cordoves, 2000; Fernández de Simón, Hernández, Cadahía, Dueñas, & Estrella, 2003; Gómez-Cordoves & González-San José, 1995; Mazza, Fukumoto, Delaquis, Girard, & Ewert, 1999). Considering that wineries usually rely on global chemical determinations, together with sensory analysis, to make decisions concerning product quality improvements, the aim of the present work was to study the evolution of the main families of phenolic compounds during wine ageing in bottle, using spectrometric methodologies. For that pur-

pose, wines from *Vitis vinifera* L. cv Tempranillo, Graciano and Cabernet Sauvignon grown in Spain, have been analyzed for total polyphenols (TP), low-polymerized polyphenols (LPP), total anthocyanins (TA), catechins (CAT), proanthocyanidins (PRO) and *ortho*-diphenols (OD) after 3, 7, 9, 12, 19.5 and 26 months of ageing in bottle, a period embracing their commercial life. Interpretation of the results obtained in function of the principles of each methodology is also provided.

## 2. Materials and methods

### 2.1. Materials

Vanillin and Folin–Ciocalteu reagent were purchased from Merck (Darmstadt, Germany). Cyanidin and malvidin-3-glucoside chlorides were obtained from Extrasynthèse (Genay, France). (+)-Catechin and gallic acid were purchased from Sigma (USA).

### 2.2. Winemaking

Monovarietal young red wines made from grapes of *V. vinifera* cv. Tempranillo, Graciano and Cabernet Sauvignon, grown in the same geographical area and elaborated at the Viticulture and Enology Station of Navarra (EVENA, Olite, Spain) (vintage, 2000), were used for this study. The characteristics of the different grape varieties are presented in Table 1. For the winemaking, a lot of 220 kg of grapes of each variety was de-stemmed, crushed and collected in 200 l stainless-steel wine vats. Semi-industrial scale fermentations were performed with a yeast inoculum of 25 g/Hl (80% EVENA *Saccharomyces cerevisiae* Na33 yeast strain; 20% Lallemend *Saccharomyces bayanus* EC118 yeast strain) at a temperature up to 27 °C. The cap was punched down twice a day until it remained submerged during a 14-day maceration period. At the end of the alcoholic

Table 1  
Vineyard yield and classical parameters determined in grapes and young wines

	Tempranillo	Graciano	Cabernet Sauvignon
<i>Grapes</i>			
Vineyard yield (kg/Ha)	8815	5093	6730
pH	3.9	3.6	3.7
Sugar (°Brix)	21.1	24.3	21.9
<i>Wines</i>			
pH	4.3	3.5	3.6
Alcohol (% vol)	13.2	13.7	12.8
Density (g/l)	0.993	0.990	0.992
Volatile acidity (g/l)	0.34	0.19	0.18
Total acidity (g/l)	4.0	5.7	5.9
Total dried extract (g/l)	30.4	25.9	28.1

fermentation, the wines were racked and stabilized for a period of one month at  $-2\text{ }^{\circ}\text{C}$ . The wines were then filtered through SEITZ K250 filters (2.5–3.0  $\mu\text{m}$ ) (Sert Schenk Filter System GmbH, Bad Krevznach, Germany) and finally bottled (January 2001) after correcting the free  $\text{SO}_2$  level to 30 mg/l. The classical wine parameters of the young wines are shown in Table 1. Two wine samples from each variety were analyzed after 1.5, 3, 7, 9, 12, 19.5 and 26 months (mid February 2001–March 2003) of bottling and storage at  $13\text{ }^{\circ}\text{C}$  and 80–85% relative humidity. Optimum storage temperature for wines ranges between 13 and  $15\text{ }^{\circ}\text{C}$ .

### 2.3. Global phenolic determinations

Wines were assayed for total polyphenols (TP) (gallic acid, mg/l), low-polymerized polyphenols (LPP) (gallic acid, mg/l), total anthocyanins (TA) (malvidin-3-glucoside, mg/l), catechins (CAT) ((+)-catechin, mg/l), proanthocyanidins (PRO) (cyanidin, mg/l) and *ortho*-diphenols (OD) ((+)-catechin, mg/l). TP were determined using the Folin–Ciocalteu reagent (Singleton & Rossi, 1965); LPP were determined by the method of Masquellier, Michaud, and Triaud (1965), OD by the procedure of Flanzky and Aubert (1969), CAT, by the method of Swain and Hillis (1959), PRO, as described by Ribèreau-Gayon and Stonestreet (1966), and TA, as described by Paronetto (1977). Coefficients of variation (%CV) between replicates were less than 5% for the different phenolic determinations.

### 2.4. Statistical analysis

ANOVA and linear regression analysis of the data was performed using the PC software package Statgraphics Plus 2.1 (Graphics Software Systems, Rockville, MD, USA).

## 3. Results and discussion

### 3.1. Total (TP) and low-polymerized (LPP) polyphenols

Graciano wine presented the highest concentration of TP after 1.5 months of ageing in bottle (1494 mg of gallic acid/l), followed by Cabernet Sauvignon (1386 mg of gallic acid/l) and Tempranillo (1271 mg of gallic acid/l) wines (Fig. 1(a)). A two-way ANOVA analysis indicated significant differences ( $p < 0.05$ ) in the TP content in function of both, time and variety factors. During ageing in bottle, the three varieties showed very similar TP evolution trends: a progressive decrease from 9 to 12 months, followed by an increase up to 19.5 months, and then a final decrease at 26 months. The method (Singleton & Rossi, 1965) used for the determination of TP is based on the oxidation of the hydroxyl groups

of phenols in basic media by the Folin–Ciocalteu reagent (mixture of phosphotungstic and phosphomolybdic acids of yellow colour). The reduction of this reagent produces a mixture of tungstic and molybdic oxides that presents a characteristic blue colouration with a maximum absorption wavelength ( $\lambda_{\text{max}}$ ) between 725 and 760 nm. In view of this, changes observed in TP during wine ageing in bottle are possibly due to the transformation of phenolic compounds into condensed forms that possess slightly different chemical properties and reactivities towards the Folin–Ciocalteu reagent. Changes registered in TP could also be due to the enzymatic activity from residual microorganisms present in the wine.

The content of low-polymerized polyphenols (LPP = non-precipitable phenols in saturated NaCl solution, as measured by the Folin–Ciocalteu reagent) decreased during ageing in bottle accompanied by the expected increase of high-polymerized polyphenols (HPP = TP-LPP), in this case expressed as percentage (Table 2). Graciano wine presented the highest %HPP after 1.5 months of ageing in bottle (16.1%), followed by Tempranillo (12.3%) and then by Cabernet Sauvignon (11.5%). During ageing, the highest increase in %HPP was presented between 12 and 26 months (last 14 months) for Tempranillo (3.8% increase) and Cabernet Sauvignon wines (5.8% increase) but for Graciano, it was registered during the first 12 months and was also much lower (1.7% increase) than for the former varieties. Therefore, contrary to the situation presented after 1.5 months of ageing, at the end of the ageing period, Cabernet Sauvignon wine presented the highest %HPP, followed by Graciano and finally by Tempranillo.

### 3.2. Total anthocyanins (TA)

After 1.5 months of ageing in bottle, Tempranillo wine presented a higher total anthocyanins (TA) concentration (626 mg of malvidin-3-glucoside/l) than Cabernet Sauvignon (617 mg of malvidin-3-glucoside/l) and Graciano (583 mg of malvidin-3-glucoside/l) wines (Fig. 1(b)). A progressive decrease in the TA content of wines was observed during ageing in bottle, and was more pronounced during the first 12 months of ageing, especially for Graciano and Cabernet Sauvignon wines, and less so in the period embracing the following 14 months of ageing. Losses in total anthocyanins, registered after the 26 months of ageing in bottle, were very similar for Graciano (65%) and Cabernet Sauvignon (66%) wines and much higher than for Tempranillo (43%). A two-way ANOVA analysis showed significant differences ( $p < 0.05$ ) in function of time and variety factors. The method used for TA determination is based on the pH structural-dependent property of anthocyanins. Four different anthocyanin structures exist in equilibrium in

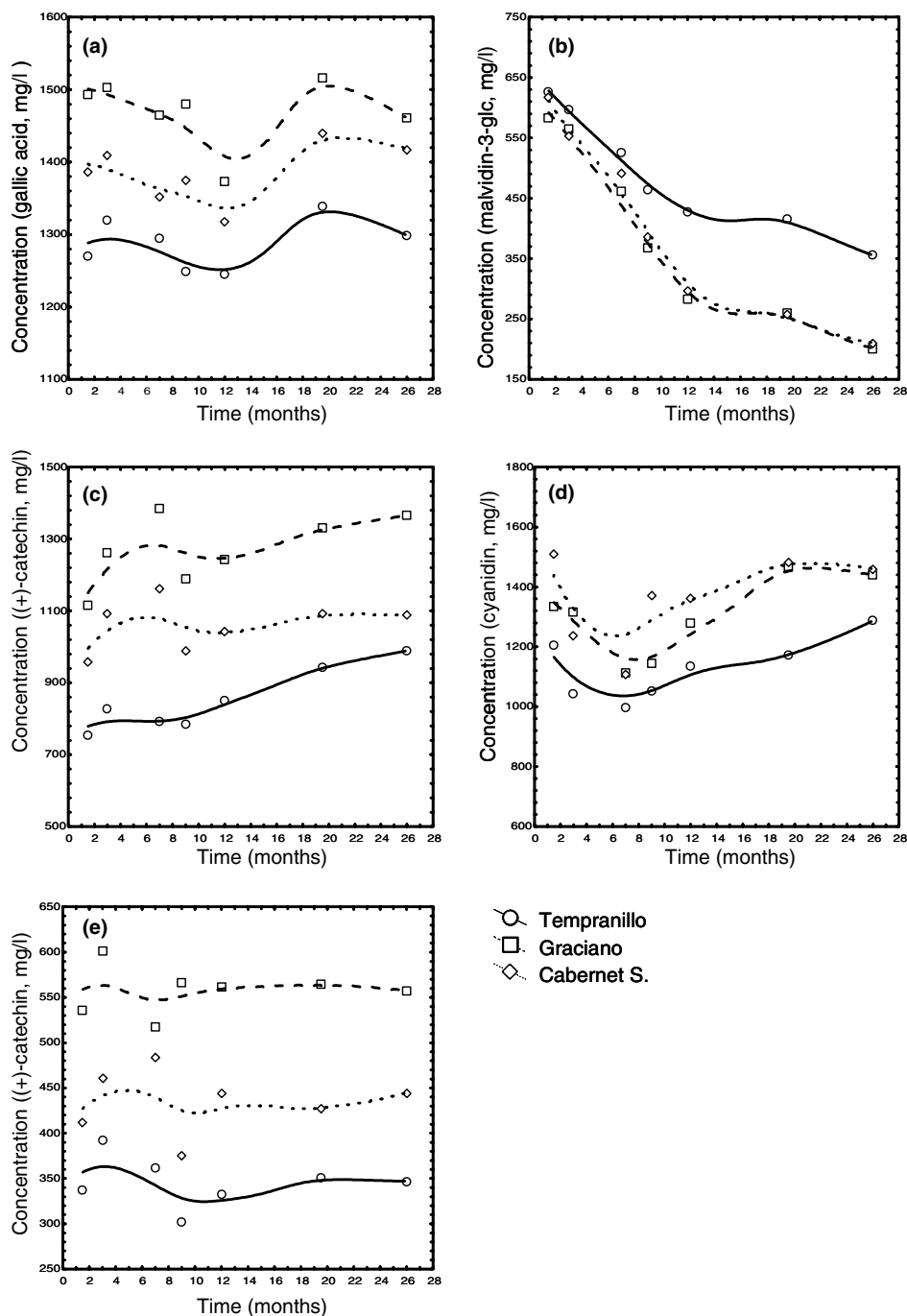


Fig. 1. Evolution of total phenol and of the different groups of phenolic compounds during ageing in bottle: (a) total polyphenols (TP); (b) total anthocyanins (TA); (c) catechins (CAT); (d) proanthocyanidins (PRO); (e) *o*-diphenols (OD).

acidic or neutral medium: the flavylium cation (red), the quinoidal base (blue), the carbinol pseudo-base (colourless) and the chalcone (colourless) (Brouillard, 1982). In solutions of similar pH to red wines ( $\text{pH} \approx 3.5$ ), approximately 12.2% of free anthocyanins exist in the red flavylium form, the equilibrium being largely displaced toward to the colourless carbinol pseudo-base (45.2%) and chalcone forms (27.6%), and a little displaced toward the blue quinoidal base (15.0%) (Glories, 1984).

The difference in absorbance measured at 525 nm when the pH is changed from 3.5 to 0, is taken as a measure of total anthocyanins. Considering that oligomeric and polymeric pigments are more resistant to pH changes than monomeric anthocyanins (Bakker & Timberlake, 1997; Escribano-Bailón et al., 1996), the TA determination mostly includes *free monomeric or simple* anthocyanins. Therefore, the decrease observed in TA during ageing in bottle is consistent with the participation of

Table 2  
Low-polymerized polyphenols (LPP) and high-polymerized polyphenols (HPP) in Tempranillo, Graciano and Cabernet Sauvignon wines

Variety	Time in bottle (months)	LPP	HPP(%)
Tempranillo	1.5	1114 (1.9) <sup>a</sup>	12.3
	12	1071 (1.3)	13.9
	26	1069 (1.3)	17.7
Graciano	1.5	1254 (1.3)	16.1
	12	1216 (0.8)	17.8
	26	1192 (0.8)	18.4
Cabernet Sauvignon	1.5	1227 (2.9)	11.5
	12	1093 (0.1)	17.0
	26	1095 (0.1)	22.8

LPP, low-polymerized polyphenols (gallic acid, mg/l); HPP (%), % of high-polymerized polyphenols (TP-LPP/TP × 100).

<sup>a</sup> Data represents the mean of duplicate determinations (coefficient of variation, %).

monomeric anthocyanins in numerous condensation reactions during ageing in bottle, as well as in hydrolytic and other degradation reactions (Santos-Buelga, Francia-Aricha, De Pascual-Teresa, & Rivas-Gonzalo, 1999), to a minor extent.

As observed by other authors (Bakker, 1986; Dallas et al., 1995; Mateus & De Freitas, 2001), the anthocyanin decline followed a first-order kinetic, which is defined by the equation  $\ln[A] = -kt + \ln[A]_0$ , where  $[A]$  is the pigment concentration (mg/l) and  $t$  is the period (months) of ageing in bottle. The reaction rate constant ( $k$ ) for TA was determined by calculating the slope of the curve  $\ln[A]$  vs  $t$  by linear regression analysis. The reaction quarter-life ( $t_{1/4}$ ) and half-life ( $t_{1/2}$ ), corresponding to the time required for a 25 and a 50% reduction of the initial anthocyanin concentration, respectively, were also calculated by the equation  $t_{1/x} = (\ln x - \ln(x - 1))/k$ , where  $[A]_0/x$  is the reduced concentration. The results of the kinetic study are presented in Table 3. Anthocyanins in Tempranillo exhibited a 2-fold lower disappearance rate (lower  $k$ , higher  $t_{1/4}$  and  $t_{1/2}$ ) than in Graciano and Cabernet Sauvignon wines, which exhibited similar kinetics. In other words, the time required for a 25% ( $t_{1/4}$ ) reduction of the initial anthocyanin concentration in

Table 3  
Disappearance rate of total anthocyanins in Tempranillo, Graciano and Cabernet Sauvignon wines

	$t_{1/4}$ (months)	$t_{1/2}$ (months)	$k \times 10^{-3}$ (months <sup>-1</sup> )	$R^2$
Tempranillo	13.1	31.2	22.0	0.9106
Graciano	6.5	15.6	44.4	0.9315
Cabernet Sauvignon	6.5	15.5	44.6	0.9362

$t_{1/4}$ : time required for a 25% reduction of the initial anthocyanin concentration;  $t_{1/2}$ : time required for a 50% reduction of the initial anthocyanin concentration;  $k$ : constant rate.

Tempranillo wine was approximately of the order required for a 50% ( $t_{1/2}$ ) reduction of the initial anthocyanin content in Graciano and Cabernet Sauvignon wines (Table 3). Other authors (Mateus & De Freitas, 2001; McCloskey & Yengoyan, 1981) have also found differences in the anthocyanin kinetic of wines manufactured from different grape varieties, attributing the results found to the particular chemical composition of each wine. In this study, the pH of the wine, which was higher (lower total acidity) in Tempranillo than in Graciano and Cabernet Sauvignon wines (Table 1), due to the ability of the former variety to form more potassium salts, may also explain the anthocyanin kinetic differences found among varieties, since a low pH assures a higher proportion of anthocyanins in flavylium form and, therefore, a higher amount of anthocyanin reactive species acting as electrophiles. Besides, a low pH also promotes the C—C bond cleavage of procyanidins from which intermediate-sized carbocations are liberated to participate in anthocyanin–flavanol and flavanol–flavanol direct condensation reactions (Haslam, 1980; Salas, Fulcrand, Meude, & Cheynier, 2003) (see also Section 3.4).

### 3.3. Catechins (CAT)

As seen for TP, the catechins (CAT) concentration after 1.5 months of ageing in bottle was higher for Graciano (1114 mg of (+)-catechin/l) followed by Cabernet Sauvignon (960 mg of (+)-catechin/l) and Tempranillo (756 mg of (+)-catechin/l) (Fig. 1(c)). During ageing in bottle, no defined trend for CAT was observed, although a slight increase in concentration was presented after 12 months, representing, at the end of the ageing period, a 44.1%, 22.6% and 13.5% increase of the initial CAT concentration in Tempranillo, Graciano and Cabernet Sauvignon, respectively. Consequently, statistically significant differences ( $p < 0.05$ ) were found for CAT in function of time and grape variety. In this assay, monomeric flavanols and oligomeric and polymeric proanthocyanidins (tannins) react with vanillin in acidic media to yield chromophores absorbing at 500 nm (Swain & Hillis, 1959). This reaction is specific for *meta*-dihydroxyphenyl moieties and thus for the free A-rings of monomeric flavanols and for the upper flavanol unit of proanthocyanidin oligomers and polymers. Since polymeric forms represent the largest percentage of wine flavanols (Monagas, Gómez-Cordovés, Bartolomé, Laureano, & Ricardo da Silva, 2003a; Sun, Ricardo da Silva, & Spranger, 1998), the CAT values obtained are more indicative of the concentration of the end units of polymers than of free monomeric flavanols. Besides, monomeric and oligomeric flavanols usually decline during ageing (Gómez-Plaza et al., 2000; Pérez-Magariño & González-San José, 2004; Revilla & González-San José, 2003), a situation that was not observed in this case (Fig. 1(c)). These changes found in



CAT could be the result of the interflavanic bond cleavage of proanthocyanidins during ageing (Haslam, 1980), generating smaller size polymers and thus increasing the concentration of available end units. In fact, the higher CAT increase of Tempranillo wine (44.1%) during ageing in bottle is also consistent with the higher mean degree of polymerization (mDP) of its polymeric proanthocyanidins (13.0 for Tempranillo, 6.9 for Graciano and 9.0 for Cabernet Sauvignon) (Monagas et al., 2003a), which could form more molecules with lower mDP (i.e., higher number of end units) from the cleavage of the polymeric forms.

### 3.4. Proanthocyanidins (PRO)

Graciano and Cabernet Sauvignon wines presented higher proanthocyanidins (PRO) levels (1334 and 1509 mg of cyanidin/l, respectively) than Tempranillo wine (1205 mg of cyanidin/l) after 1.5 months of ageing in bottle (Fig. 1(d)). A slight decrease in the concentration of PRO was observed during the first months of ageing in bottle, followed by a slight increment after 9 months of ageing. Statistically significant differences ( $p < 0.05$ ) were found in function of time and grape variety. The acid-catalyzed oxidative cleavage of the C—C interflavanic bond of proanthocyanidins in alcohol–water mixtures, such as butanol–HCl (Porter's reagent), produces anthocyanidin chromophores from the chain extension units (C-4 substituted units) (Porter, Hirstich, & Chang, 1986). This method is also known as the Bate-Smith method (Bate-Smith, 1954). In *V. vinifera* grapes and wines, two groups of proanthocyanidins are distinguished, depending on the nature of the liberated anthocyanidin: procyanidins (polymers of (+)-catechin and (–)-epicatechin) and prodelfinidins (polymers of (+)-gallocatechin and (–)-epigallocatechin), which liberate cyanidin and delphinidin, respectively. Considering the principles of the method, the trend observed for PRO could be the result of the transformation of proanthocyanidins during ageing. Carbocations generated from the acid-catalyzed interflavanic bond cleavage act as electrophilic agents (Haslam, 1980) and may react with the nucleophilic C-6 or C-8 position of the anthocyanin in its hydrated hemiacetal form, generating tannin–anthocyanin (T–A) adducts (Ribéreau-Gayon, 1982), and with other flavanols, giving rise to tannin–tannin (T–T) condensation products. Moreover, when considering the PRO evolution trend, it should also be noted that the reaction yield of the Bate-Smith reaction is highly dependent on the polymer structure, which, as above described, could largely vary during wine ageing. As stated previously, due its higher pH (lower total acidity) (Table 1), reactions involving C—C acid-catalyzed bond cleavage of proanthocyanin should be less extended in Tempranillo wine than in Graciano and Cabernet Sauvignon wines.

### 3.5. Ortho-diphenols (OD)

After 1.5 months of ageing, Graciano wine presented the highest concentration of *ortho*-diphenols (OD) (536 mg of (+)-catechin/l), followed by Cabernet Sauvignon (412 mg of (+)-catechin/l) and Tempranillo (337 mg of (+)-catechin/l) wines (Fig. 1(e)), in accordance with the results of TP (Fig. 1(a)) and, in particular, of CAT (Fig. 1(c)). However, no statistically significant differences ( $p > 0.05$ ) were found for the OD concentrations in function of time during ageing in bottle. The method of Flanzky and Aubert (1969) is based on the ability of *ortho*-dihydroxyphenols (*o*-diphenols) to form chelating complexes with transition metals or other elements, such as boron and molybdenum. Main *o*-diphenols present in wines from *V. vinifera* include: hydroxybenzoic acids (protocatechuic and gallic acids), hydroxycinnamic acids and derivatives (caffeic acid derivatives), flavonols (quercetin and myricetin derivatives), dihydroflavonols (dihydroquercetin and dihydromyricetin derivatives), monomeric, oligomeric and polymeric flavanols (procyanidins and prodelfinidins), and anthocyanins (cyanidin, delphinidin and petunidin derivatives). The evolution trend observed for OD could be the result of measuring several groups of *o*-diphenolic compounds (mainly flavanols, which represent the largest group of *o*-diphenols, and anthocyanins) that showed different behaviour during ageing in bottle (Fig. 1).

Finally, the overall global phenolic determinations performed in this work indicate that the TP evolution trend is essentially the result of changes presented in TA (decrease during the first 12 months of ageing in bottle) and, in CAT and PRO (increase starting from 12 months of ageing in bottle). The changes in AT, CAT and PRO are consistent with the decrease of LPP and with the increase of %HPP registered during ageing in bottle.

## 4. Conclusions

Global phenolic determinations, usually performed in wineries, have provided useful information in relation to the evolution of wine polyphenols during ageing in bottle. Whereas the TA determination allowed the calculation of the rate constant of anthocyanins, normally done by HPLC measurements, the CAT and PRO determinations do not allow quantifications of monomeric flavanols and oligomeric procyanidins. The evolution trends of the different families of phenolic compounds were very similar in the wines from the three varieties studied, although they showed differences in their phenolic profiles. In general, the overall results indicated that the lower CAT and PRO contents of Tempranillo (also reflected in the TP and OD values), together with

its higher pH, could be partially responsible for its lower anthocyanin disappearance rate when compared to Graciano and Cabernet Sauvignon, considering that these compounds are involved in anthocyanin condensation reactions. Finally, according to the grape variety, the changes registered in the phenolic content during ageing in bottle are expected to affect the red wine colour in different ways.

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