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Different Sorption Behaviors for Wine Polyphenols in Contact with Oak Wood

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The evolution of polyphenols of enological interest— monomeric anthocyanins, (+)-catechin, (−)-epicatechin, gallic acid, and *trans*-resveratrol—in the presence of oak wood was investigated in aging-model conditions. Disappearance kinetics showed that, except for gallic acid, all of the wine polyphenols tend to disappear from the model wine in presence of oak wood, to reach an equilibrium after 20 days of contact. At equilibrium, the higher disappearance rates were obtained for monomeric anthocyanins and *trans*-resveratrol with values of 20 and 50%, respectively. For monomeric anthocyanins, the rate of disappearance seemed to be independent of their nature. In order to evaluate the contribution of sorption to oak wood in the disappearance phenomena, sorption kinetics were determined for *trans*-resveratrol and malvidin-3-glucoside through the extraction and the quantification of the fraction sorbed to wood. These curves showed that the wood intake of *trans*-resveratrol and malvidin-3-glucoside followed a two-step behavior, with a higher rate during the first 2 days, likely due to a surface sorption mechanism, and then a slower rate to reach the equilibrium, which could be related to a diffusion mechanism. The comparison of disappeared and sorbed amounts at equilibrium showed that a minor part of the disappeared monomeric anthocyanins were sorbed by wood. In contrast, half of the concentration decrease of *trans*-resveratrol in wine finds its origin in a sorption mechanism by oak wood. Results in real wine show similar sorption kinetics.

KEYWORDS: Oak wood; model wine; polyphenols; sorption.

INTRODUCTION

During aging in oak barrels, wine phenolic compounds composition is modified as a result of mass transfer at the interface between wood and wine (*1*−*3*). Among the different phenolic compounds present in wine, anthocyanins contribute to the stability of the color of wine. Most of these polyphenols are highly unstable and are quickly transformed into several pigments, and various types of reactions occur during the aging process of wines. Although initially related to grape composition, wine proanthocyanidins were found to evolve during wine aging through acid-catalyzed depolymerization (*4*). The disappearance of anthocyanins occurs simultaneously with the formation of more-stable oligomeric pigments (*5*). Indirect condensation involving acetaldehyde could concern both anthocyanin−tannin and tannin−tannin condensation (*6*, *7*) by ethyl linkages, resulting in more-stable compounds (*8*, *9*). Anthocynins and/or flavanols form "new pigments" with other low-molecular-weight molecules such as pyruvic acid, vinylphenol, or glyoxylic acid, which maintain wine color intensity for longer periods (*10*−*12*). If numerous other studies have analyzed the reactions between polyphenols to explain their evolution during wine aging, few experimental results about the contribution of sorption phenomena to wood have actually been reported to account for the disappearance of polyphenolic compounds.

The ability of wood to sorb monomeric hydrocarbons (*13*) and environmental contaminants (*14*) has been demonstrated. These results strongly suggest that during barrel aging, oak wood could be a likely candidate for the sorption of wine polyphenolic compounds. In a previous paper, we reported on the sorption of aroma phenolic compounds by oak wood in conditions simulating the oak aging of wine (*15*). We showed that the wood-model wine partition coefficient depends on the physicochemical characteristics of aroma compounds (solubility and hydrophobicity). The aim of the present work was to investigate the capacity of cooperage oak wood to sorb polyphenolic compounds and to compare its affinity for different classes of polyphenols mixed together in a model system. This study was carried out with a model wine solution enriched with five Pinot

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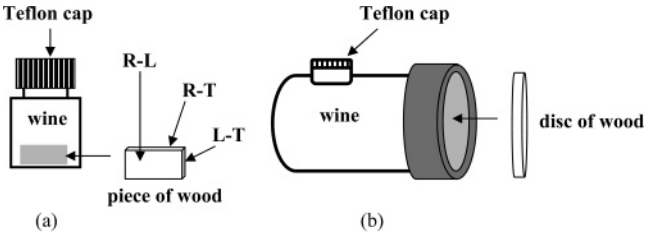

Figure 1. Representation of the *closed* (a) and the *open* system (b). Note that for the closed system, the wine is directly in contact with the three distinct surfaces of wood, the radial–longitudinal (R–L), the radial–tangential (R–T), and the longitudinal–tangential (L–T) surfaces, the latter showing to the wine the longitudinal macropores of the wood. In contrast, for the open system, which corresponds to real barrel aging, the wine is only in contact with the R–L surface.

Noir native monomeric anthocyanins (delphinidin-3-*O*-glucoside (Dp3glc), cyanidin-3-*O*-glucoside (Cy3glc), petunidin-3-*O*-glucoside (Pt3glc), peonidin-3-*O*-glucoside (Pn3glc), malvidin-3-*O*-glucoside (Mv3glc)), two monomeric flavanols ((+)-catechin and (−)-epicatechin), a stilbene (*trans*-resveratrol), and a benzoic acid (gallic acid) and, for comparison, a real Pinot Noir wine.

MATERIALS AND METHODS

Analytical Reagents and Chemical Standards. Gallic acid was purchased from Fluka (Buchs, Switzerland), and *trans*-resveratrol, (+)-catechin, and (−)-epicatechin were obtained from Sigma-Aldrich (St. Louis, MO). The anthocyanins were obtained by extraction from the skins of Pinot Noir grapes. Ethanol, L-malic acid, acetic acid, potassium sulfate, and magnesium sulfate were obtained from Merck (Darmstadt, Germany). Their purities were >95% ethanol, 99.9% purity L-malic acid (>99%), acetic acid (>99.8%), potassium sulfate (99%), and magnesium sulfate (99%). Solutions were made with ultrapure water, obtained from a Milli-Q System (Millipore, Bedford, MA). The model wine is a 12.5% v/v hydro-alcoholic solution of pH 3.5 (*16*). The red wine used in this study was elaborated in 2005 by the experimental station of the University of Burgundy (Marsannay la Côte, France).

Wood Samples. Small pieces of wood (2 × 10 × 20 mm) and discs of wood (diameter = 40 mm and thickness = 2 mm) used for closed and open systems, respectively (see below), were donated by the Office National des Forêts (ONF, France) and taken from *Quercus robur* (*pedunculata*) oak trees from the Cîteaux forest (France). In this study, wood samples did not follow any heat treatment.

Purification and Extraction of Monomeric Anthocyanins. Pinot Noir (*Vitis vinifera*) grapes were used for grape skin extraction according to the following procedure: berries were peeled, the skin being separated from the rest of the grape, i.e., seeds and pulp. The skin material (300 g) was pre-extracted by using an Ultra-Turax device for 3 min with ethanol−HCl (9.9/0.1) as the solvent. The pooled homogenate was kept at 10 °C for 30 min and then centrifuged at 4500 *g* for 5 min at 10 °C. The resulting supernatants were combined and concentrated under vacuum at 35 °C until a 150 mL residual volume was achieved. The concentrated extract was passed through a polyamide (CC6, Macherey Nagel) 600 × 25 mm column, percolated with 1000 mL of water−HCl (9.9/0.1) at 1 mL·min^{-1} and eluted with 500 mL of ethanol−water−HCl (70/29.97/0.03) at the same flow rate. Then, the monomeric anthocyanins fraction was concentrated under vacuum at 35 °C until 50 mL of residual volume was achieved and kept frozen (−18 °C) prior to use. The purity of the five Pinot Noir monomeric anthocyanins was determined by high-performance liquid chromatography (HPLC).

Kinetics of Disappearance of Phenolic Compounds in Model Wine and in Real Wine. *Closed System*. Experimental samples were acquired by immersing one piece of wood (0.2−0.3 g) into a 25 mL glass flask (**Figure 1a**) completely filled with the model wine or with Pinot Noir wine (total volume of about 35 mL). Flasks were tightly closed with Teflon caps and protected from light to prevent losses or the degradation of anthocyanins by oxygen. This system will be referred to as the "closed" system throughout the text. Phenolic compounds were added at the concentration of 50 mg/kg to the model wine, except for the anthocyanins obtained by extraction from the skin of the grapes, for which the final concentrations were between 10 mg/kg for the Cy3glc and 200 mg/kg for the Mv3glc anthocyanins. These concentrations are commonly found in wine. Each analysis was done in triplicate. All the experimental samples and the control sample (model wine without wood) were stored at 10 °C in a dark room without stirring. When one plate of wood was immersed, the ratio of wood surface area to the volume of the model solution was 140 cm^2/L compared to 118 cm^2/L for a 228 L Burgundy wine barrel. Volumes of 50 μL of the solution phase were withdrawn at different intervals of time and were subsequently analyzed by the means of HPLC, with external calibration. The wood plates were taken out, and they were subsequently analyzed to determine the sorbed amount.

Open System. Experimental samples were acquired by putting in contact one face of a disc of wood with model wine (**Figure 1b**). In this way, the exchange through the wood and with air is allowed. Three experimental samples and one control sample (without wood), were completely filled with the model wine (total volume of about 90 mL). The ratio between the wood surface and the volume of the model wine was also 140 cm^2/L. The experimental and control samples were stored in a "model cellar" (dark room at 10 °C and 90% relative humidity) and without stirring.

Quantification of Phenolic Compounds Sorbed to Wood. Phenolic compounds sorbed to oak wood in the closed system were recovered by three consecutive liquid extractions of wood pieces (4 mL of an ethanol/HCl 0.1% mixture), leading to a final volume of 12 mL. This extract, enriched in phenolic compounds, was evaporated to a final volume of 10 mL and then kept under a nitrogen gas atmosphere until analysis by HPLC. This procedure was performed on all of the wood samples used for the measurement of the kinetics of disappearance; i.e., when the concentration in solution was measured after a given time of contact, the corresponding wood sample was subjected to the extraction procedure. In order to measure the extraction efficiency of the ethanol/HCl mixture, a volume of 1 mL of solution containing 2000 mg/kg of *trans*-resveratrol and 2000 mg/kg of Mv3glc dissolved in analytical-grade ethyl alcohol was dropped onto a wood sample. After 24 h of contact, phenolic compounds were recovered as described above. The measurements were replicated at least three times. Extraction efficiency was estimated to be 55 and 91% for Mv3glc and *trans*-resveratrol, respectively.

Stability of Phenolic Compounds in a Model Wine Containing Ellagitanins. To take into account reactions that could occur between wood extractables (ellagitannins) and wine phenolic compounds, a wood plate was put in contact with the model wine during 7 days at 10 °C. After removal of the wood plate, all of the polyphenolic compounds studied were added to this model wine having extracted wood ellagitannins, and the evolution of their concentrations followed with time.

HPLC Analyses of Phenolic Compounds in the Model Wine. The phenolic compounds contained in wines and in the ethanol−HCl extracts of the corresponding wood plates were analyzed using a Waters HPLC chromatograph equipped with a Waters 626 pump, a Waters 600 S controller, and a Waters 717 plus autosampler; detection was carried out with a 996 photodiode-array detector. The system was connected to a data station (Millenium^{32}) for collection and mathematical treatment. Phenolic compounds were analyzed in 50 μL volumes of samples on a 250 × 4.6 mm i.d. 5 μm C_{18} column (VARIAN) eluted with a linear gradient. The following solvents were used: A, methanol, and B, water/formic acid (95:5). The gradients were as follows: from 5 to 8% A in 5 min, from 8 to 27% A in 45 min, from 27 to 50% A in 25 min, from 50 to 100% A in 10 min, 100% A for 5 min, back to 5% A in 2 min, and 5% A for 8 min. The column was equilibrated for 15 min prior to the injection of the following samples, and its temperature was maintained at 25 °C. The flow rate was 1 mL·min^{-1}. UV−vis spectrophotometry (Waters 996 photodiode array detector) was used to identify and quantify gallic acid, while fluorimetry (Satin Waters module + Waters 474 scanning) was used for *trans*-resveratrol.

Table 1. Mean and Standard Deviation (SD) for Each Phenolic Compound Concentration (mg/kg) in Model Wine Stored during 36 Days[a]

		anthocyanins					stilbene	flavan-3-ols		benzoic acid
time (days)		Dp3glc	Cy3glc	Pt3glc	Pn3glc	Mv3glc	*trans*-resveratrol	(+)-catechin	(–)-epicatechin	gallic acid
0	mean	26.22	8.79	26.20a	70.38	183.37	50.79	34.12cd	27.66f	41.39
	SD	0.08	0.15	0.19	1.48	0.25	0.43	0.44	0.16	0.41
1	mean	26.09	8.82	26.28a	69.11	184.21	51.23	34.29c	27.74f	41.19
	SD	0.18	0.13	0.41	2.02	2.44	0.27	0.30	0.15	0.75
2	mean	26.09	8.75	26.15a	70.77	184.82	51.00	33.60d	27.73f	41.67
	SD	0.08	0.14	0.19	0.98	1.85	0.59	0.34	0.09	0.26
7	mean	26.14	8.70	25.31b	70.70	187.41	50.08	32.85e	27.33f	41.79
	SD	0.00	0.25	0.24	0.70	0.19	1.98	0.16	0.25	0.08
10	mean	26.03	8.77	25.58ab	70.69	185.35	50.68	32.93e	27.82f	41.49
	SD	0.08	0.19	0.32	1.21	3.59	0.79	0.22	0.06	0.46
36	mean	25.32	8.70	25.14b	70.87	182.65	50.55	32.45e	26.86g	40.72
	SD	0.76	0.27	0.57	0.49	1.50	0.37	0.24	0.37	0.27

[a] Same letters indicate that the means are belonging to the same homogeneous group by the multiple comparison procedure (Newman–Keuls test, $\alpha = 0.05$)

The detection of gallic acid and flavan-3-ols ((+)-catechin and (−)-epicatechin) was set at 280 nm and that of anthocyanins at 520 nm while *trans*-resveratrol was identified with fluorimetry detectors at wavelengths λ (excitation) of 330 nm and (emission) 374 nm (*17*). The identification of each compound was established by comparing the retention time and UV−vis spectra of the peaks in model wine with those previously obtained by injection of standards. Quantification was based on the standard curve established with Mv3glc chloride from Extrasynthèse (Geney, France). Results for each anthocyanin were expressed in mg/L of equivalent Mv3glc.

Statistical Analysis and Physicochemical Values Estimations. Data were presented as the mean ± standard deviation. Statistical comparisons were made by the one-way analysis of variance followed by the Newman-Keuls multiple comparison test (*StatBox* software). All variance analyses were carried out at the 95% confidence level. *Interactive Laboratory* (*I-Lab*) from ACD Labs (http://www.acdlabs.com/ilab) was used for the prediction of the log *P* values of the phenolic compounds.

RESULTS AND DISCUSSION

Reactivity of Phenolic Compounds in a Model Wine. It is well-known that during aging, the color of red wine changes due to interactions between monomeric anthocyanins and colorless phenolics present in grapes including (+)-catechin, (−)-epicatechin, quercetin, kaempferol, and phenolic acids (*18*−*20*). The disappearance of monomeric anthocyanins can be also attributed in part to their chemical degradation (*9*, *21*). To assess the chemical stability of Dp3glc, Cy3glc, Pt3glc, Pn3glc, Mv3glc, *trans*-resveratrol, (+)-catechin, (−)-epicatechin, and gallic acid due to possible reactions under our experimental conditions, the evolution of their concentrations with time in a model wine were monitored (**Table 1**). Except for Pt3glc, (+)-catechin, and (−)-epicatechin, no significant variations (by the Newman-Keuls test) were observed for the concentrations of the phenolic compounds. These results show a stability of phenolic compounds in a model wine with our experimental conditions. Indeed, for Pt3glc, (+)-catechin, and (−)-epicatechin, concentration variations represent less than 5% of the initial concentration. We considered that this loss was negligible compared with the losses arising from the presence of oak wood. Moreover, according to Dallas et al. (*9*), the concentrations of anthocyanins in model wine slightly decrease when they are in mixture, and their concentrations decrease in the presence of proanthocyanin B_2 and even more when acetaldehyde is present. Clearly, in our case, this nonreactivity of phenolic compounds is also related to the absence in model wine of these promoters, which allow the chemical modifications of anthocyanins.

Kinetics of Disappearance of the Phenolic Compounds in the Model Wine in a Closed System. Figure 2 displays the evolution of the normalized concentrations of monomeric anthocyanins and *trans*-resveratrol, in the presence of *pedunculata* oak wood at 10 °C. For all phenolic compounds, except for gallic acid (figure not shown), concentrations, which are initially closed to that given in **Table 1**, decrease with time in the presence of wood. For all monomeric anthocyanins (**Figure 2**) and for (+)-epicatechin (figure not shown), the same kinetic is observed: the concentration decreases monotonically with time to reach an equilibrium state in between 10 and 20 days. At equilibrium, between 20 and 30% of the initial concentration has disappeared for all of these phenolic compounds. The kinetics of *trans*-resveratrol disappearance (**Figure 2**) seems to follow a two-step process, with a fast initial sorption process during the first 5 days and a slower diffusion process between the 5th and 20th day. The equilibrium state is reached between 20 and 36 days, and the average rate of disappearance at equilibrium is closed to 50%. The same kinetic is observed for volatile phenols (*15*, *22*), which suggests that similar interactions take place between volatile phenols or *trans*-resveratrol and wood plates.

From the initial linear part of these curves, the decreasing rate constant (k) is calculated from the slope of the regression lines obtained after plotting the C/C_0 ratio as a function of time for the first 9 days of contact. The different values of k are presented in **Table 2**. Except for Dp3glc, the rates of disappearance of anthocyanins presented in **Table 2** are not significantly distinct, with a representative value of about 28 day^{-1} ($k = 26.70-30.54 \times 10^{-3}$ day^{-1}). These results suggest that all of the anthocyanins follow the same disappearance behavior. Interestingly, these kinetics of disappearance are in accordance with those commonly observed for the aging reactions that bring about losses of monomeric anthocyanins (*23*), which supports the hypothesis of the contribution of wood sorption to the mechanism of disappearance. It must be noted, however, that the disappearance of monomeric anthocyanins can also be attributed to their chemical degradation, which could occur in the presence of oak wood.

The results obtained show that the process of the disappearance of the major anthocyanidin monoglucosides follows first-order kinetics, in agreement with previous works (*24*). However, the k values are 10 times higher in our study, and this difference can be explained by the geometry of the system: whereas in real barrel aging conditions, only one face of wood is exposed to wine, in our closed system (**Figure 1**), six faces of wood are exposed to wine, favoring an enhanced sorption.

For *trans*-resveratrol, as described above, two slopes are observed, with an initial fast decrease in concentrations ($k =$

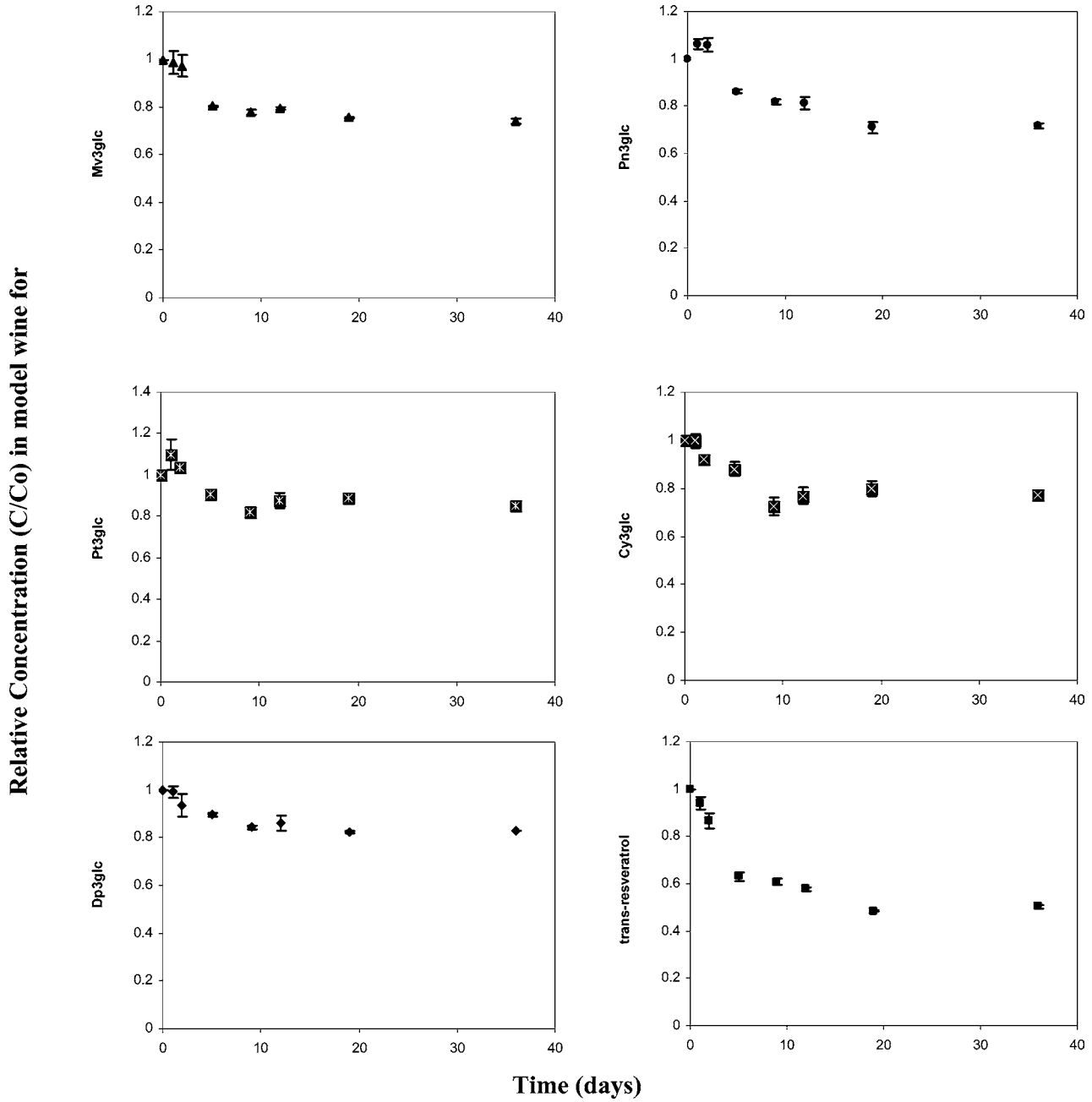

Figure 2. Relative concentration of anthocyanins and of stilbene in model wine in presence of *pedunculata* oak wood as a function of time (days) at 10 °C.

Table 2. Phenolic Compound Decreasing Rate Constants (*k*)

phenolic compounds	k (day^{-1}) × (10^{-3})	r^2
Mv3glc[a]	27.94 ± 5.62	0.8919
Mv3glc[b]	8.89 + 0.53	0.9782
Pn3glc[a]	27.51 ± 8.21	0.7890
Pt3glc[a]	26.70 ± 7.40	0.8126
Cy3glc[a]	30.54 ± 3.47	0.9627
Dp3glc[a]	17.57 ± 2.53	0.9411
trans-resveratrol[a]	46.35 ± 9.91	0.8794
	12.30 ± 0.82	0.9956
(–)-epicatechin[a]	14.06 ± 8.32	0.4874
gallic acid[a]	6.83 ± 4.25	0.4619
(+)-catechin[a]	7.92 ± 6.10	0.3597

[a] In closed system. [b] In open system.

46.35×10^{-3} day^{-1}) during the first 5 days of contact, followed by a slower decrease ($k = 12.30 \times 10^{-3}$ day^{-1}). These results strongly suggest that different mechanisms of disappearance are involved for monomeric anthocyanins and for *trans*- resveratrol. For the latter, the higher rate of disappearance during the first 5 days is likely due to a surface sorption mechanism on the immediately accessible surface sites of the wood, whereas the slower rate to reach equilibrium could probably be related to a diffusion mechanism within the porous wood structure. In other words, rapidly accessible wood surface sites that preferentially interact with reveratrol but not with anthocyanins seem to exist. Only the less acessible sites would interact with anthocyanins (and also reveratrol) after the time required for the hydro-alcoholic solvent to reach them. As shown below, these hypotheses are supported by the quantification of the fraction sorbed to wood as a function of the time of contact.

Sorption Kinetics onto Oak Wood in a Closed System. To assess the contribution of wood sorption to the disappearance of phenolic compounds in the model wine, we have plotted (**Figure 3**) the concentration of phenolic compounds extracted

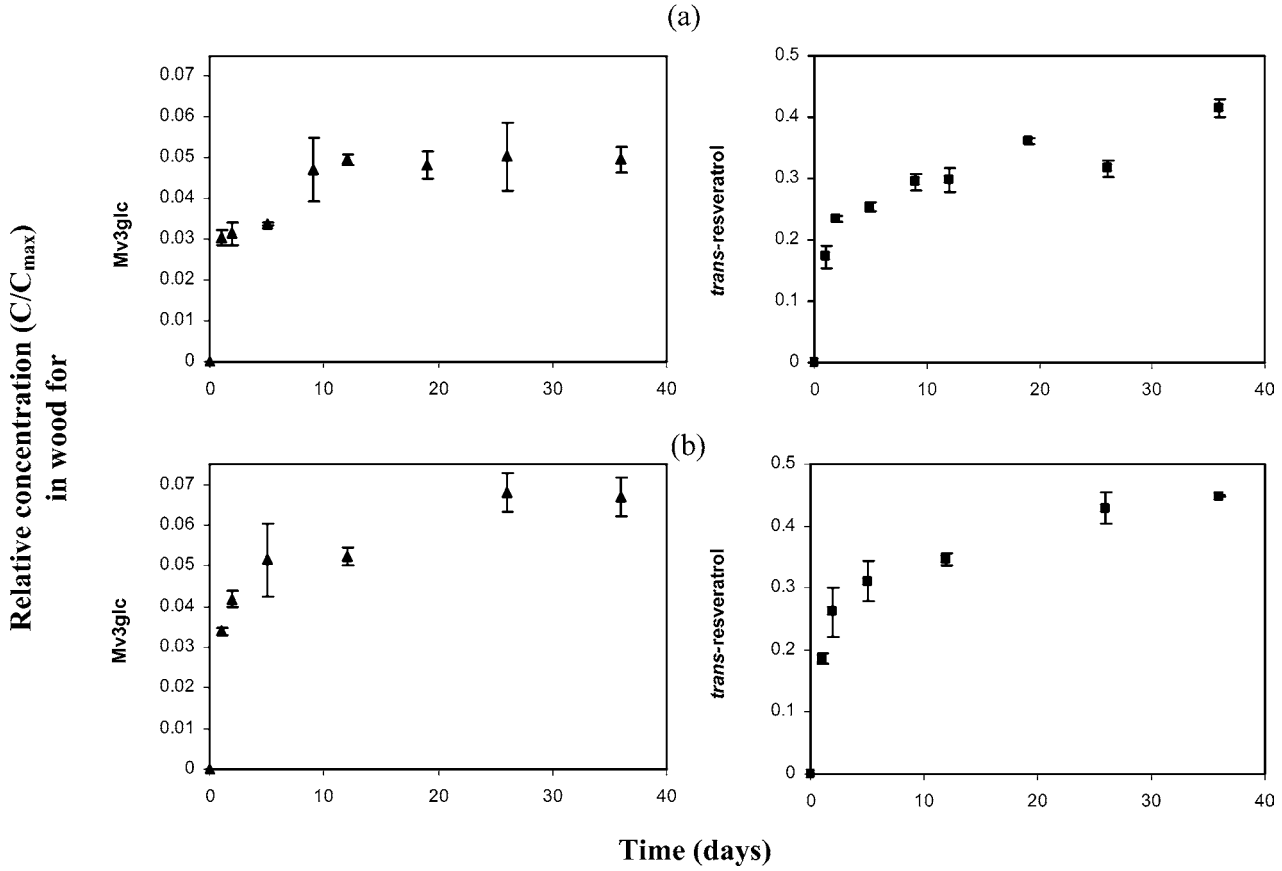

Figure 3. Relative concentration of sorbed Mv3glc (▲) and *trans*-resveratrol (■) measured after extraction of wood plates stored for different durations (days) in a model wine (a) and in a real wine (b) (for all four graphs shown, C = concentration measured after extraction and C_{max} = concentration at equilibrium).

from the wood plates, for increasing times of contact, normalized to the concentration losses at equilibrium obtained from **Figure 2**. Considering that Mv3glc is the more abundant monomeric anthocyanin in red wine and that all of the anthocyanins displayed similar disappearance behaviors, we considered it as representative of this family of phenolic compounds. Extraction efficiencies of 55 and 91% for Mv3glc and *trans*-resveratrol, respectively, were taken into account. **Figure 3a** shows the results obtained for Mv3glc and *trans*-resveratrol, which have been in contact with the wood. For these compounds, the equilibrium is reached after a period of between 10 and 20 days for Mv3glc and between 20 and 36 days for *trans*-resveratrol (**Figure 3a**). To evaluate the possible role of the wine matrix on the sorption of phenolic compounds by wood, we realized the same experiment with a Pinot Noir wine. When the same conditions were used, data obtained from both the model wine and the real wine showed that the increases of concentration in wood are similar (**Figure 3**). A sharp increase of concentration in the wood takes place during the first 2 days where half of the total concentration is sorbed, followed by a slower rate over the next 20 days. For the system with real wine, the equilibrium is reached more slowly, after a period of between 30 and 40 days (**Figure 3b**). Although there is a clear sorption effect of wood, these curves show that only 5% of the Mv3glc molecules that have disappeared from the wine solution are recovered. These results suggest that sorption mechanisms are not significantly modified in the presence of other cosolutes of wine.

On one hand, the disappearance of monomeric anthocyanins seems to be barely due to their sorption by wood, and on the other hand, half of the disappearance of *trans*-resveratrol from wine finds its origin in a sorption mechanism by oak wood. Oak wood sorption capacity for hydrophobic wine compounds such as volatiles was recently reported by Ramirez et al. (*16*) and Barrera-García et al. (*15*). If we assume an interaction with wood, these results suggest that the chemical nature of the solute also influences this interaction. *Trans*-resveratrol is more sorbed than the other phenolic compounds (close to 50%), whereas the concentration of gallic acid remains constant over the entire period of contact with wood (not shown). A possible correlation could be made between these opposite behaviors and the log P values of these compounds (0.91 and 3.74 for gallic acid and *trans*-resveratrol, respectively). This interpretation is in good agreement with the sorption of organics to wood, where it was shown that there is a correlation between the hydrophobicity and the sorption level of organic compounds (*14*, *15*, *25*).

Since both Mv3glc and the *trans*-resveratrol compounds are stable under our experimental conditions, the remaining 95% of the former and 50% of the latter that have disappeared from the model wine at equilibrium must have evolved through different pathways. A likely one could be the reaction with wood extracts (*21*) such as ellagitannins, which are easily extracted from wood by water−alcohol or water−acetone mixtures (*26*). Ellagitanins can indeed react with flavanols or anthocyanins to provide flavano−ellagitannins condensation products (*27*) or pigments (*28*). The evolution of the Mv3glc concentration in the presence of wood extracts (ellagitannins) strongly corroborates this assumption. When Mv3glc is mixed with wood extracts in a model wine solution, a decrease of approximately 30% of its initial concentration is observed after 20 days of contact (results not presented). This 30% decrease is in good agreeement with the percentage of disappearance observed in the presence of the wood plate (**Figure 2**), and moreover, the

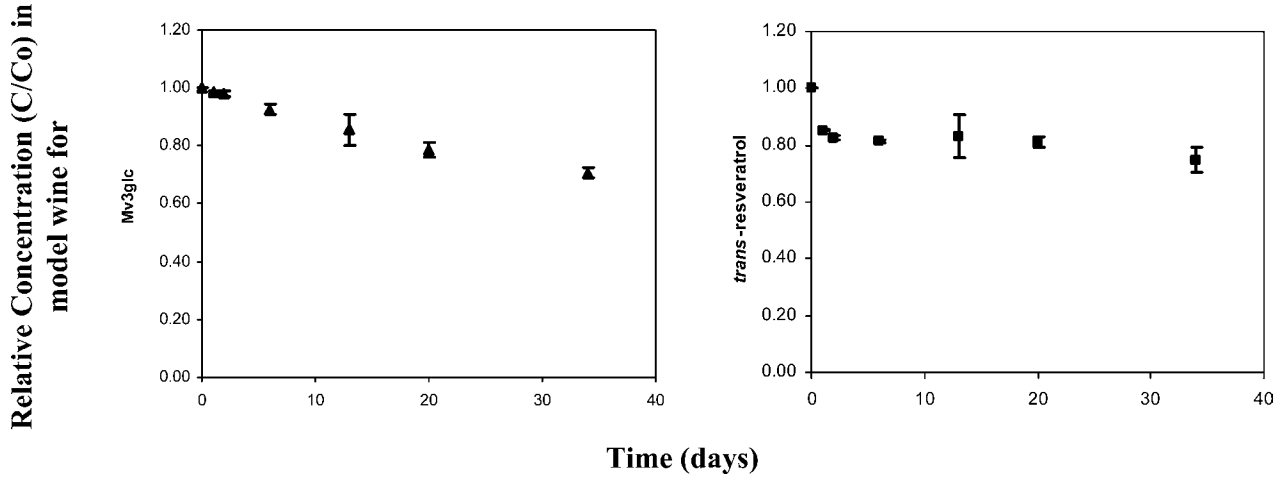

Figure 4. Relative concentration of Mv3glc (▲) and *trans*-resveratrol (■) in model wine in the aging-model open system as a function of time (days) at 10 °C.

decreasing rate constant *k* calculated when Mv3glc is in contact with wood extracts (21.03×10^{-3} day^{-1}) is also close to that of Mv3glc in the closed system (**Table 2**). Our results clearly show that oak wood definitely participates in the mechanisms of the disappearance of anthocyanins but mostly through reactions with extractibles and only marginally through sorption processes. In contrast, we have observed that for *trans*-resvetatrol, the concentration remains constant in the presence of extracted ellagitannins (not shown). Therefore, additional mechanisms are involved in the case of resveratrol, and experiments are currently underway to describe them.

Kinetics of Disappearance of Mv3glc and *trans*-Resveratrol in an Open System. During the study of the open system, exchanges between air and model wine through the wood were permitted. The changes in normalized concentrations of Mv3glc and *trans*-resveratrol are presented in **Figure 4**. The concentration of these phenolic compounds also decreases with time in the presence of wood in the open system. However, the kinetics of disappearance in the open system are slower than those of the closed system, and no equilibrium is reached after 30 days of contact for Mv3glc. This can be explained by the geometry of the system: for the open system, only one face of wood is exposed to the wine; in contrast, for the closed system, six faces are in contact with the wine with four of them having a much higher porosity than the two others. The easier diffusion of molecules, in particular through the longitudinal pores of the wood in the closed system, should clearly favor a faster reach of equilibrium, both for the sorption mechanisms as shown before for resveratrol and for promoting the ellagitanin−anthocyanin reactions as shown for Mv3glc. Interestingly, the decreasing rate constant (*k*) was calculated under these conditions, and for Mv3glc, a *k* value of 8.89×10^{-3} day^{-1} was found, close to that found with real wine experiments (*24*). These results emphasize the importance of the wood faces exposed to wine in aging systems.

In summary, we have shown that, except for gallic acid, the concentrations of anthocyanins, (+)-catechin, (−)-epicatechin, and *trans*-resveratrol in model wine are modified by the presence of oak wood. However, these modifications arise from two distinct mechanisms, which depend on the nature of the polyphenolic compounds. Anthocyanins mainly evolve through reactions with ellagitanins extracted from the wood, whereas at least 50% of the resveratrol content can be sorbed by the wood. In agreement with the results already observed for volatile compounds, the higher hydrophobicity of reseveratrol seems to drive a more-selective sorption process. Altogether, our results show that these processes are clearly dependent on the surface of wood that is in contact with the wine. In traditional barrel aging, the radial−longitudinal surface of the staves in contact with the wine exhibits the lowest macroporosity and consequently slowly regulates the evolution of polyphenolic compounds.

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