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Polyphenolic compounds as chemical markers of wine ageing in contact with cherry, chestnut, false acacia, ash and oak wood

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ABSTRACT

The nonanthocyanic phenolic composition of four red wines, one white, and one rosé aged using barrels and chips of cherry, chestnut, false acacia, ash and oak wood was studied by LC-DAD-ESI/MS, to identify the phenolic compounds that woods other than oak contribute to wines, and if some of them can be used as chemical markers of ageing with them. A total of 68 nonanthocyanic phenolic compounds were identified, 15 found only in wines aged with acacia wood, 6 with cherry wood, and 1 with chestnut wood. Thus, the nonanthocyanic phenolic profile could be a useful tool to identify wines aged in contact with these woods. In addition, some differences in the nonanthocyanic phenolic composition of wines were detected related to both the levels of compounds provided by each wood species and the different evolution of flavonols and flavanols in wines during ageing in barrels or in contact with chips.

1. Introduction

In recent years, some papers about the chemical composition of non-oak heartwoods have been shown in scientific literature, with a view to their use in cooperage, although only oak and chestnut are approved by OIV to wine ageing (De Rosso, Cancian, Panighel, Dalla Bedona & Flamini, 2009; Fernández de Simón, Esteruelas, Muñoz, Cadahía, & Sanz, 2009; Flamini, Dalla Bedona, Cancian, Panighel, & De Rosso, 2007; Rodriguez, Suarez, Diñero, Del Valle, & Piccinelli, 2010; Sanz et al., 2010a, 2010b, 2011, 2012a, 2012b). Thus, heartwood from species as false acacia (*Robinia pseudoacacia*), chestnut (*Castanea sativa*), and cherry (*Prunus avium*), and more rarely, ash (*Fraxinus excelsior* and *F. vulgaris*), mulberry (*Morus alba* and *M. nigra*), beech (*Fagus sylvatica*), alder (*Alnus glutinosa*) and some local woods are being considered as possible sources of wood for the production of wines and their derived products, like spirits, and especially vinegars, in order to give them a special personality. The most studied compounds were polyphenols, pointing out important chemical differences in relation to oak wood that should be taken into account when considering its use in cooperage. The oak heartwood shows high levels of monomer ellagitannins, such as castalagin, roburin E, vescalagin, and grandinin, and low molecular weight (LMW) phenolic compounds, ellagic and gallic acids, besides lignin derivatives, especially vanillin that can vary greatly depending on the species and geographical origin of the wood as well as the processing that undergoes in cooperage (Cadahía, Muñoz, Fernández de Simón, & García-Vallejo, 2001; Chatonnet, Boidron, & Pons, 1989). Oak heartwood does not contain other kinds of phenolic compounds, for example flavonoids.

Chestnut heartwood shows the most similar polyphenolic profile to oak, although its LMW phenolic and tannic contents are higher, highlighting the presence of gallotannins and the high levels of gallic acid (Canas, Leandro, Spranger, & Belchior, 2000; Sanz et al., 2010b). The other studied woods show many qualitative and quantitative differences in their polyphenolic profile, including condensed tannins as both type procyanidin and prorobinetin, other flavonoids (flavanonols, flavanones, chalcones, aurones, flavonols and flavones), secoiridoids, phenylethanoids, dilignols and oligolignols. In all woods, the toasting at cooperage results in a progressive increase in lignin constituents with regard to intensity, and at the same time, in a degradation of most other polyphenols, leading to a minor differentiation among species. However, both before and after toasting the polyphenolic profile can be used to identify the species of wood (Sanz et al., 2012b).

Although most of woods used in cooperage, as well as in chips and barrels, are toasted at different intensities, and so the differences in the polyphenolic profile of a wine aged with different woods could be very small, the useful phenolic markers to discriminate among wood species could also allow us to differentiate the wines aged with them. Little information about the effects of

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non-oak woods on the characteristics of wines, vinegars, and other beverages, compared to oak, has been presented in literature. Someone have pointed out a different evolution of the phenolic and volatile composition, and organoleptic properties in beverages aged in barrels or in contact with chips made of different woods (Caldeira, Anjos, Portal, Belchior, & Canas, 2010; Cerezo, Espartero, Winterhalter, García-Parrilla, & Troncoso, 2009; Cerezo et al., 2008; Chinnici, Natali, Sonni, Bellachioma, & Riponi, 2011; De Rosso, Panighel, Dalla Vedova, Stella & Flamini, 2009; Kozlovic, Jeromel, Maslov, Pollnitz, & Orlic, 2010; Sanz et al., 2012c). In some cases, phenolic markers that allow discriminate the wood used for ageing have been identified. This is the case of red wines and vinegars aged in acacia barrels, in which compounds like dihydrorobinetin, robinetin and other flavonoids were detected, but were not detected when beverages ageing in contact with oak wood (Cerezo et al., 2009; Sanz et al., 2012c).

Some authors highlight that wines or vinegars aged in non-oak barrels had better organoleptic characteristics (Chinnici et al., 2011; Hillmann, Mattes, Brockhoff, Dunkel Meyerhof, & Hofmann, 2012; Kozlovic et al., 2010). However the physical–mechanical properties of wood barrel, like porosity that influence the gas exchange during ageing, can in some cases promote a fast polyphenol oxidation (Chinnici et al., 2011; De Rosso et al., 2009; Torija et al., 2009). That effect could be minimised using non-oak wood alternative to barrel products like powder, shavings, chips, cubes, or staves, as cheaper substitute techniques.

The polyphenolic profile variability of beverages, and their evolution during ageing, can make the analysis of markers found in the wood more complex. In wines, this variability can be attributed to several factors, including some aspects of the raw material (grape variety, climatologic conditions, agronomic characteristics, degree of grape ripening) and winemaking process (time of maceration and fermentation in contact with the grape skins and seeds, pressing, fining, etc.) (Castillo-Muñoz, Gómez, García, & Hermosín, 2007; Monagas, Suárez, Gómez-Cordovés, & Bartolomé, 2005). These differences remain throughout ageing, even though a clear evolution in the concentrations of most phenolic compounds happens. In this context, it is important to have tools that reveal the botanical origin of wood used to wine ageing, as well as if woods other than oak have been used.

The main goal of this work is to know the phenolic compounds that wood other than oak contributes to the wines, and if some of them can be used as chemical markers of ageing with non-oak woods. For this aim, medium toasting chips and 225 L barrels were made with cherry, chestnut, acacia, ash and oak wood, and the polyphenolic composition of four red wines (two 100% cv. Syrah, one 100% cv. Grenache, and one 100% cv. Tempranillo), one white wine (100% cv. white Grenache), and one rosé wine (100% cv. Grenache) aged with them was studied by LC-DAD-ESI/MS.

2. Materials and methods

2.1. Woods and wines

Cherry (*P. avium*), chestnut (*C. sativa*), acacia (*R. pseudoacacia*), ash (*F. excelsior*), and oak (French and Spanish -Navarra- *Q. petraea* and American *Q. alba*) heartwood were provided as staves for making barrels by Tonelería Intona, SL (Navarra, Spain). The wood was naturally seasoned for 24 months until 15% humidity. Barrels were made following a traditional process, at medium intensity level of toasting, over a wood fire (185 °C for 45 min). The barrel heads were not toasted. All barrels were with a capacity of 225 L and staves of 28 mm thickness. Moreover, some staves of each were cut after seasoning at chip size (1 × 0.5 cm, approximately), and toasted at a medium intensity level (200 °C for 35 min), in an industrial-scale convection oven, with special oven trays for chips. All the wood was manufactured (seasoned and toasted) by the same cooperage.

Two red wines from D.O. Cataluña and Somontano (Spain) were produced on an industrial scale in 2009, from cv. Syrah (100%) grapes, according to traditional methods. They were put into the cherry, chestnut, acacia, European ash, and French oak barrels (4 of each wood) in November 2009, and were kept during 6 (short ageing) and 12 months (long ageing) respectively, and finally bottled. During this storage time in barrels, wine samples from each barrel were taken, after ageing 2, 4, 6, 9 and 12 months. All wines were analysed in duplicate, so 320 samples were analysed.

Other red wine from D.O. Navarra was produced on an industrial scale in 2010, from cv. Grenache (100%) grapes, according to traditional methods. It was put into the cherry, chestnut, acacia, European ash, French, American and Spanish oak barrels (4 of each wood) in January 2010, and was kept during 12 months, taken wine samples from each barrel after ageing 6 and 12 months. The same wine was in contact with chips of the same woods during 2 months in stainless steel 50 L tanks, with two quantities of chips: 150 and 75 g for each tank. Four thanks of each wood and each dosage were used. Other three wines were aged in contact with chips of the same woods during two months in stainless steel 50 L tanks. Two were from D.O. Navarra and produced on an industrial scale in 2010, according to traditional methods: one white wine from cv. White Grenache (100%) grapes and one rosé wine from cv. Grenache (100%) grapes. The dosage of chips was 75 g for each tank. Lastly, a dosage of 300 g of chips for each tank was used with a red wine from D.O. Rioja (100% Tempranillo grapes), produced on an industrial scale in 2010 according to traditional methods. All of the tanks with wood were micro-oxygenated using an Eco2 device (Oenodev, France) and ceramic diffusers with a dosage rate from 1.5 to 2 mL/L/month. All wines were analysed in duplicate at the end of ageing (448 samples).

2.2. Chemicals

Reference compounds were obtained from commercial sources with purity higher 98%: caffeic acid, 2,4-dihydroxybenzoic (β-resorcylic) aldehyde, methyl gallate, ethyl gallate, gallic acid and protocatechualdehyde (Fluka Chimie AG, Buchs, Switzerland), 2,4-dihydroxybenzoic acid (β-resorcylic), methyl vanillate, and methyl syringate (Aldrich Chimie, Neu-Ulm, Germany), ellagic acid and aromadendrin (Apin, Oxon, UK), (+)-catechin, (-)-epicatechin, quercetin, protocatechuic acid, syringic acid, benzoic acid, and taxifolin (Sigma Chemical, St. Louis, MO), eriodictyol (Roth, Kalsruhe, Germany), dihydrorobinetin, fustin, robinetin, isorhamnetin, vanillic acid, ferulic acid, procyanidin B1 and B2, naringenin, isosakuranetin, butein, prunin, kaempferol, p-coumaric acid, p-hydroxybenzoic acid, tyrosol, tryptofol, myricetin, quercetin-3-glucoside, quercetin-3-galactoside, and resveratrol (Extrasynthèse, Genay, France), and robtein (Transmit, Marburg, Germany). Methanol, diethyl ether, ethyl acetate, anhydrous sodium sulphate, and acetic acid were purchased from Panreac (Barcelona, Spain). Acetonitrile HPLC grade was from Scharlab (Barcelona, Spain) and formic acid and ammonium acetate MS spectroscopy from Fluka Chimie AG (Buchs, Switzerland)

2.3. Extraction of phenolic compounds

The wine samples from each barrel or tank were analysed separately, following the previously described method by Cadahía (Cadahía, Fernández de Simón, Sanz, Poveda, & Colio, 2009). Samples, concentrated to 25% of their initial volume, were extracted with diethyl ether and ethyl acetate. The organic fractions were combined and evaporated to dryness, and the residue re-dissolved