Food Research International 87 (2016) 197–203

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Influence of the botanical origin and toasting level on the ellagitannin content of wines aged in new and used oak barrels

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A R T I C L E I N F O

Article history:
Received 23 May 2016
Received in revised form 14 July 2016
Accepted 22 July 2016
Available online 25 July 2016

Keywords:
Ellagitannins
Wine
Oak
Botanical origin
Toasting level

A B S T R A C T

The influence of the botanical origin (French oak: *Quercus petraea* and American oak: *Quercus alba*) and different toasting levels (light, medium and heavy) on the ellagitannin content of wines aged in oak barrels has been studied. This took place in two consecutive vintages in order to study what happens after the barrels have been already used for one year with another wine. This study was carried out with two red wines (Cabernet Sauvignon) and with two decolored white wines (Macabeo) from vintages 2012 and 2013 in order to work with a simpler matrix which facilitates chemical analysis. The results show that the botanical origin, toasting level and the number of times that the barrels have been used exert a major influence on the final ellagitannin concentration. In general, the behavior of all the individual ellagitannins was very similar to that described for the total ellagitannins. Briefly, the levels of total ellagitannins concentration in the decolored white wine aged for 12 months in new French barrels ranged between 31.2 mg/L in the lightly toasted and 4.7 mg/L in the heavy toasted. In contrast, these levels were quite lower in American new barrels ranging between 3.6 mg/L and 0.9 mg/L. Finally, the total ellagitannin concentration decreased an average of 63% in the wines aged in the one year used barrels.

1. Introduction

High-quality red wines are traditionally aged in oak barrels to improve their sensorial characteristics. Oak aging causes some interesting changes in red wines, leading to color stabilization, lower astringency, and the disappearance of excess vegetative notes (Garde-Cerdán & Ancín-Azpilicueta, 2006). These transformations seem to be associated with small quantities of oxygen that penetrate the porosity of the wood, the interstices between staves, and the bunghole (Del Alamo-Sanza & Nevares, 2014). The contact with oak wood also enriches the wine in many volatile substances such as vanillin, whiskey lactones, furans, volatile phenols, etc that improve the intensity and complexity of the wine's flavor (Rodríguez-Rodríguez & Gómez-Plaza, 2012; Pérez-Juan & Luque de Castro, 2015). Finally, oak wood also releases some non-volatile substances such as ellagitannins into the wine, which contribute to wine texture sensations such as astringency and mouthfeel (Stark et al., 2010; Sáenz-Navajas, Fernández-Zurbano, & Ferreira, 2012; Michel et al., 2013). It has also been reported that ellagitannins can act as natural antioxidant and protect other wine compounds against oxidation thanks to their great capability to react with oxygen (Navarro et al., 2016).

Although there are >150 species of oaks classified in the genus *Quercus*, only three of them are currently used in cooperage for wine aging. More specifically, the American white oak (*Quercus alba*) and two European oaks, the sessile oak (*Quercus petraea*) and the pedunculate oak (*Quercus robur*), commonly known as the French oaks. Although the great differences between them, *Q. petraea* and *Q. alba* are generally considered to provide greater aromatic richness than *Q. robur*, whereas the latter oak provides more ellagitannins (Masson, Puech, & Moutounet, 1994; Díaz-Maroto, Guchu, Castro-Vázquez, de Torres, & Pérez-Coello, 2008). *Q. petraea* and *Q. alba* have practically monopolized the cooperage market for wines in recent years probably for this reason (Vivas, 2002).

Ellagitannins have a specific structure, consisting of open-chain glucose esterified at position 4 and 6 by a hexahydroxydiphenoyl unit (HHDP) and a nonahydroxyterphenoyl unit (NHTP) esterified at position 2, 3, and 5 with a C-glycosidic bond between the carbon of the glucose and position 2 of trihydroxyphenoyl unit (Quideau et al., 2004; Takuo, Takashi, Tsutomu, & Hideyuki, 2009).

Ellagitannins may reach 10% of the dry weight of oak heartwood, and they contribute to the wood's high durability (Scalbert, Monties, &

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http://dx.doi.org/10.1016/j.foodres.2016.07.016
0963-9969/

Favre, 1988; Nonier et al., 2005). Castalagin and vescalagin are the most abundant ellagitannins in oak wood, accounting for between 40% and 60% by weight of the total (Fernández de Simón, Cadahía, Conde, & García-Vallejo, 1999). These two isomers were the first ellagitannins to be isolated and described by Mayer (Mayer, Gabler, Riester, & Korger, 1967). The lyxose/xylose derivatives (grandinin and roburin E) and the dimeric forms (roburins A, B, C and D) were also subsequently described (Herve Du Penhoat, Michon, Ohassan, et al., 1991; Herve Du Penhoat, Michon, Peng, et al., 1991).

The hydroalcoholic nature of wine favors the extraction of these compounds from wood to wine (Moutounet, Rabier, Puech, Verette, & Barillere, 1989; Jordão, Ricardo-da-Silva, & Laureano, 2005) during barrel aging or when wood alternatives are used. However, the high reactivity of ellagitannins means that their levels in wine are much lower than could be expected (Michel et al., 2011). Nevertheless, according to the described sensory threshold of different ellagitannins (Glabasnia & Hofmann, 2006) their concentration in wine may in some cases be enough to contribute to wine astringency. The level of the ellagitannins in oak wood used to make barrels is also influenced by several factors (Masson, Moutounet, & Puech, 1995; Zhang, Cai, Duan, Reeves, & He, 2015) such as its geographical origin (e.g. American or French oaks) (Canas, Leandro, Spranger, & Belchior, 2000; Prida & Puech, 2006), the oak species (*Q. robur* releases higher concentrations of ellagitannins than *Q. petraea*, and this in turn releases higher concentrations of ellagitannins than *Q. alba*) (Prida & Puech, 2002), the number of times that the barrels have been used (the levels of ellagitannins extracted are much lower in used barrels) (Vivas & Saint-Cricq de Gaulejac, 1998) and the forest management practices of the tree (Vivas, 2002). Moreover, the manufacture of barrels in cooperage also has a major influence on its composition, with consequent effects on the wine's flavor. First, the logs must be processed to obtain the staves. Due to the different structures of their heartwood, American oak can be sawed, but French oak needs to be split in order to respect the natural grain. Sawing French oak would make it porous and affect its tightness.

Later, the staves must be subjected to a drying process, to ensure the mechanical resistance of the barrels and to eliminate some substances that contribute to bitterness and astringency (Josephe & Marché, 1972; Masson, Baumes, Moutounet, & Puech, 2000). This process usually takes 2 or 3 years. Once the drying time is finished, the staves are heated to form the barrels. The heating time needed to form the barrel is around 15 min. However, cooperages usually extend this time in order to improve the sensory attributes that the barrel gives the wine. Three toasting levels are usually offered: light, medium and heavy, with different sensory styles (Chatonnet, 1992; Rodríguez-Rodríguez & Gómez-Plaza, 2011). Vanillin and smoke flavors (furans, volatile phenols) generally increase with toasting, whereas whiskey lactone decreases (Singleton, 1995; Koussissi et al., 2009; Farrell et al., 2015). The toasting level also exerts a major influence on the ellagitannins content of oak (Doussot, De Jéso, Quideau, & Pardon, 2002; Chira & Teissedre, 2013a). High temperatures favor the oxidation of ellagitannins and the formation of polymers and copolymers with cell-wall components which reduces their solubility (Peng, Scalbert, & Monties, 1991). The ellagitannin potential release therefore decreases when the toasting level is increased.

Finally, the successive use of the barrels leads to a depletion of the substances that the wood can release into the wine. The capacity of the barrels to enrich the wine in aromas and ellagitannins consequently decreases with their use (Garde-Cerdán, Rodríguez-Mozaz, & Ancín-Azpilicueta, 2002).

The interest of wineries and cooperages in how the botanical origin and the toasting level affect wine's composition and quality has led to numerous studies. However, most of them are related with the aromatic aspects (Cadahía, Fernández de Simón, & Jalocha, 2003; García, Soares, Dias, Freitas, & Cabrita, 2012; Fernández De Simón et al., 2014; Collins, Miles, Boulton, & Ebeler, 2015) and only a few have targeted the study of the ellagitannin release (Cadahía, Varea, Muñoz, Fernández de Simón, & García-Vallejo, 2001; Fernández De Simón, Sanz, Cadahía, Poveda, & Broto, 2006), probably because its analysis is quite complicated (Stephen & Kimberly, 2012). Moreover, to our knowledge the recent studies of ellagitannins in wine have mainly been performed with wood chip maceration (Chira & Teissedre, 2013b; Chira et al., 2015; García-Estévez, Alcalde-Eon, Le Grottaglie, Rivas-Gonzalo, & Escribano-Bailón, 2015) and only a few with oak barrels (Jourdes, Michel, Saucier, Quideau, & Teissedre, 2011; Chira & Teissedre, 2015). Moreover, these latter studies were performed with new barrels of *Q. petraea*, with no study of *Q. alba* and what happens in used barrels (Saucier, Jourdes, Glories, & Quideau, 2006; Chira & Teissedre, 2015). The aim of this study was to determine the influence of the botanical origin and toasting level on the ellagitannin content of wines aged in new and used oak barrels.

2. Materials and methods

2.1. Chemicals and equipment

Methanol, formic acid and acetic acid of high performance liquid chromatography (HPLC) grade (>99%) and absolute ethanol (96%), ethyl acetate (99%) were purchased from Panreac (Barcelona, Spain). Oenological charcoal and bentonite were purchased from Agrovin (Alcázar de San Juan, Ciudad Real, Spain). Ellagitannins: castalagin (99%), vescalagin (98%), roburin A (98%), roburin B (93%), roburin C (93%), roburin D (98.5%), grandinin (98.5%) and roburin E (97%) were purchased from Adera (Pessac, France).

HPLC separation, identification and quantitation of ellagitannins were performed using an Agilent 1100 Series system (Agilent, Germany), equipped with DAD (G1315B) and an LC/MSD Trap VL (G2445C VL) electrospray ionization mass spectrometry (ESI-MSn) system, and coupled to an Agilent ChemStation (version B.01.03) data processing station. The mass spectra data were processed using Agilent LC/MS Trap software (version 5.3).

2.2. Barrels

A total of 24 new barrels (225 L) were purchased from the Boteria Torner Cooperage (Sant Cugat Sesgarrigues, Barcelona, Spain). The cooperage selected wood staves with the criteria that were as homogeneous as possible within each species. Twelve barrels were made with American white oak (*Q. alba*), and the other 12 with French oak (*Q. petraea*). Three toasting levels (light, medium and heavy) were used for each type of oak, and a similar toasting level was applied to the barrel heads. Each experimental condition was performed in duplicate, using 2 barrels.

2.3. Wines and barrel aging

This study was carried out with two Cabernet Sauvignon red wines and two decolored Macabeo white wines, obtained from the experimental cellar of the Faculty of Enology of the Rovira i Virgili University in Constantí (AOC Tarragona, Spain) from the 2012 and 2013 vintages. The red wines were used without any stabilization treatment, whereas the white wines were drastically decolored with oenological charcoal (2 g/L) and bentonite (1 g/L) in order to minimize the presence of aromas and phenolic compounds. The aim was to obtain a very neutral medium to facilitate chemical analysis.

The analytical characteristics of the wines at the start of the experiment are showed in Table 1.

In brief, wines of the 2012 vintage were placed in the new barrels in April 2013, and were aged for 12 months. Once the barrels were emptied and cleaned, they were immediately filled with the same wines from the 2013 vintage, which were also aged for 12 months. Samples of all the barrels were taken at 3, 6, 9 and 12 months for ellagitannin analysis.