STUDY OF PHENOLIC POTENTIAL OF SEASONED AND TOASTED PORTUGUESE WOOD SPECIES (*QUERCUS PYRENAICA* AND *CASTANEA SATIVA*)

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Abstract

Aim: The phenolic potential and suitability of seasoned and toasted Portuguese chestnut (*Castanea sativa* Mill) and oak wood (*Quercus pyrenaica*) as alternative cooperage materials were evaluated.

Methods and results: Low-molecular-weight phenols and ellagitannins from seasoned and toasted Portuguese wood species were analysed by HPLC. *C. sativa* was found to be richer in phenolic compounds than *Q. pyrenaica*. High concentrations of vescalagin and gallic acid were specific to *C. sativa*. Toasting significantly reduced the ellagitannin content in both wood types, albeit less markedly in *C. sativa*. As regards phenolic aldehydes, *C. sativa* contained substantially greater amounts of vanillic aldehyde, an odour-active compound, than *Q. pyrenaica*.

Conclusion: Both types of Portuguese wood are suitable for use as cooperage materials, although chestnut wood is better suited to the heat treatment involved in the coopering process.

Significance and impact of the study: Portuguese wood species provide an effective alternative to the oak wood species traditionally used for aging alcoholic beverages.

Key words: cooperage wood, Portuguese species, phenolic composition, toasting effect

Résumé

Objectif: Le potentiel phénolique et l'aptitude des bois de châtaignier (*Castanea sativa* Mill) et de chêne (*Quercus pyrenaica*) portugais séchés et chauffés comme alternative au bois de tonnellerie traditionnelle ont été évalués.

Méthodes et résultats: Les phénols de faible poids moléculaire et les ellagitanins ont été analysés dans les deux espèces de bois portugais. Les échantillons de *C. sativa* étaient plus riches en composés phénoliques que les échantillons de *Q. pyrenaica*. Les concentrations élevées de vescalagin et d'acide gallique étaient caractéristiques de l'espèce *C. sativa*. Le toastage a entrainé une diminution considérable de la teneur en ellagitanins dans les deux types de bois. Cependant, cette diminution était moins prononcée dans les échantillons de *C. sativa* que dans ceux de *Q. pyrenaica*. En ce qui concerne les aldéhydes phénoliques, *C. sativa* présentait des quantités beaucoup plus importantes d'aldéhyde vanillique, un composé odorant, comparé aux échantillons de *Q. pyrenaica*.

Conclusion: Les deux types de bois portugais peuvent être utilisés en tonnellerie. Cependant le bois de châtaignier est plus adapté à la chauffe.

Signification et impact de l'étude: Les espèces portugaises de bois offrent une bonne alternative à l'utilisation de bois de chêne traditionnellement utilisés pour le vieillissement des boissons alcoolisées.

Mots clés: bois de tonnellerie, espèces portugaises, composition phénolique, toastage

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INTRODUCTION

The use of wooden barrels is a traditional, common practice for aging wines and other beverages by virtue of the favourable effects of wood on aged products. Contact with the barrel alters the composition of beverages through the release of various volatile compounds and polyphenols. Thus, tannins, phenolic acids, and free and glycosidic ellagitannins (β-1-O-ethylvescalagin, flavano-ellagitannins, and anthocyano-ellagitannins) play a central role in the astringency, bitterness, roundness and colour of wines and distilled spirits aged in wood barrels (Chassaing *et al.*, 2010; Saucier *et al.*, 2006; Jourdes *et al.*, 2011).

Oak wood is by far the most widely used for this purpose. Traditionally, three oak species have been extensively used for barrel production: namely, *Quercus alba* L., *Quercus petraea* (Matt.) Liebl. and *Quercus robur* L. American forests are the main sources of the former species and French forests those of the latter two. Indeed, winemakers typically refer to the wood types commonly used to age wine as American oak or French oak. Their widespread use has fostered studies on the influence of geographical location (American vs. French forests) on the chemical composition of oak wood (Chatonnet and Dubourdieu, 1998; Doussot *et al.*, 2002; Nishimura and Matsuyama, 1989; Pérez-Coello and Díaz-Maroto, 2009; Prida and Puech, 2006; Glabasnia and Hofmann, 2007).

However, extensive exploitation of the above-mentioned species, together with the current interest in obtaining products with novel sensory properties, has raised the need to seek effective alternatives to the traditional oak wood species. Recent studies have assessed the suitability of chestnut (*Castanea sativa*) and *Quercus pyrenaica* (an autochthonous oak species of the Iberian Peninsula) for use as cooperage materials. Information on the chemical composition of these species is scant. The volatile composition of *C. sativa* and *Q. pyrenaica* wood from Spain was recently compared with that of traditional oak wood species used in cooperage (Alañón *et al.*, 2012). The influence of geographical location, site and silvicultural variables on the volatile composition of Spanish*Q. pyrenaica* samples was also evaluated (Alañón *et al.*, 2011b). Based on the results, the volatile profile of both *C. sativa* and *Q. pyrenaica* provides an excellent flavouring alternative to traditional oak wood species. Also, the phenolic composition of French chestnut was recently examined by Sanz *et al.* (2010).

Portuguese wood has recently been considered for use in beverage aging processes. Thus, Portuguese chestnut wood has been used to age brandies (Canas *et al.*, 1999). However, the chemical composition of these Portuguese species (*C. sativa* and *Q. pyrenaica*) has scarcely been studied, particularly as regards phenolic profile.

In this work, the chemical composition of Portuguese *C. sativa* and *Q. pyrenaica* specimens was studied. This preliminary analysis focused on the polyphenol fraction, which is one of the most important factors governing the suitability of wood for cooperage by virtue of its influence on colour stability, co-pigmentation, protection from oxidation, and astringency in aged wines (Brouillard and Dangles, 1994; Cejudo-Bastante *et al.*, 2011; Darias-Martin *et al.*, 2001; Del-Alamo and Nevares, 2006; Jordão *et al.*, 2007; Monedero *et al.*, 2000; Roure and Anderson, 2006; Vivas and Glories, 1996; Quideau *et al.*, 2005).

Toasting, which is commonly used in cooperage to improve the sensory properties of aged wines, has a strong influence on the polyphenolic composition of wood; also, as revealed by recent human sensory experiments, it decreases wood astringency by converting vescalagin and castalagin into less astringent degradation products (Glabasnia and Hofmann, 2007).

The purpose of this work was to assess the quality and cooperage potential of these two Portuguese wood species in toasted and untoasted form on account of the growing interest in alternatives to traditional oak wood species for cooperage in recent years.

MATERIALS AND METHODS

1. Wood samples

Seasoned and medium-toasted chestnut wood (*C. sativa*) and oak wood (*Q. pyrenaica*) collected from Gerês forests (Portugal) were provided by J.M. Gonçalves Lda Cooperage (Palaçoulo). The wood staves were naturally seasoned in piles outside for 24 months. Part of the staves was submitted to medium toast (160–170 ºC for 30 min). Both seasoned and medium-toasted wood samples were cut into approximately 4-mm thick sections, milled at room temperature to pass a 2-mm screen, homogenised and then kept in a dry atmosphere until analysis.

2. Isolation of ellagitannins and low-molecular-weight (LMW) phenols from oak chips

Five hundred milligrams of wood chips were extracted in duplicate with 10 mL of water/acetone (3:7, v/v) at

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room temperature with constant stirring for 180 min. Then, 2-mL aliquots were filtered through a Millipore membrane (pore diameter 0.45 µm) based on the method described by Jordão *et al.* (2007). The filtrate was concentrated under nitrogen stream in order to remove the acetone.

The resulting aqueous phase was fractionated by liquid-liquid extraction with 2 mL of ethyl acetate and 2 mL of diethyl ether using the method developed by Fernandez de Simón *et al.* (1999). Both phases were separated after freezing. The organic phase was dried in a rotary evaporator, redissolved in 1 mL of methanol, and injected (20-µL aliquots) into HPLC for LMW phenol determination. The aqueous phase was adjusted to 3 mL with bi-distilled water and injected (20-µL aliquots) into HPLC for ellagitannin determination.

3. HPLC analysis of ellagitannins

HPLC analysis was carried out on a 500B HPLC system (Konik Instrument, Spain) with a 7176-LC Rheodyne injection valve connected to a Konik UV-Vis model 206 PHD diode-array detector. Detection was made at 280 nm. The column used was a reverse-phase C18 LiChrospher® 100 (Merck, Darmstadt) with dimensions of 250 x 4 mm and a particle size of 5 µm.

20-µL aliquots of water extract were injected into HPLC. The elution conditions were as follows: flow rate 1 mL min^{-1} and temperature 30 ºC. Two solvents were used for elution: A: MeOH/PO_4H_3 (999: 1) and B: H_2O/PO_4H_3 (999: 1) based on the method described by Fernández de Simón *et al.* (1999), with slight modifications in the gradient profile: 0-8 % A in 0-70 min, 8-50 % A in 70-80 min, 50-100 % A in 80-90 min. The column was washed between injections with methanol/water (500: 500, v/v) for 15 min. All solvents employed were purchased from Fluka-Biochemika (Switzerland).

Chromatographic peaks were identified based on the UV-data spectra and by comparing the retention time and elution order with data described in the literature (Jordão *et al.*, 2007; Fernández de Simón *et al.*, 1999; Viriot *et al.*, 1994). Quantification was carried out by the external standard method using water solutions spiked with known amounts of ellagic acid (Fluka-Biochemika). Results are expressed in µg g^{-1} ellagic acid equivalents (based on dry wood).

4. HPLC analysis of LMW phenols

HPLC analysis was carried out by using the Konik Instrument HPLC system described above.

20-µL aliquots of organic extract were injected into HPLC. The elution conditions were as follows: flow rate 1 mL min^{-1} and temperature 30 ºC. Two solvents were used for elution: A: H_2O/PO_4H_3 (999: 1) and B: MeOH/PO_4H_3 (999: 1). A linear gradient from 0 to 100 % B in 50 min was used, based on the method proposed by Fernández de Simón *et al.* (1999).

Peak identifications were based on comparison of their retention time and UV spectra with those of pure standards. Quantitative determinations were carried out from the results of four determinations using external standard curves of ellagic acid. Results are expressed in µg g^{-1} ellagic acid equivalents as above.

5. Statistical analysis

Analysis of variance and multivariate analyses were performed using SPSS 17.0 for Windows statistical package. Differences among chemical data were assessed for significance at $P \leq 0.05$ using the Student–Newman–Keuls test.

RESULTS AND DISCUSSION

1. Ellagitannins

The content of ellagitannins is an important factor to be considered in choosing cooperage wood for aging beverages. Ellagitannins are impressively efficient oxidation regulators capable of rapidly absorbing dissolved oxygen and facilitating hydroperoxidation of wine constituents. Also, they stabilize and strengthen crimson hues and hinder oxidation of phenolic compounds in wine, thereby preventing the development of a brick-yellow colour. In addition, ellagitannins reduce the astringency of wine via their involvement in polymerization reactions (Vivas and Glories, 1996). However, an extremely high content of ellagitannins is not recommended as it can boost bitterness in aged wines (Vivas, 2002). Therefore, since the ellagitannin content varies with wood species (Masson *et al.*, 1996), not all species are suitable as cooperage materials for beverage aging.

The ellagitannin profiles of Portuguese *C. sativa* and *Q. pyrenaica* wood were similar to those of oak species typically used in cooperage. The wood samples examined here were found to contain eight ellagitannins including roburin A–E, grandinin, vescalagin, castalagin and three unknown compounds designated E-I, E-II and E-III (Table 1).

The total ellagitannin content of *C. sativa* was higher than that of *Q. pyrenaica*. That of seasoned *C. sativa* (33.81 mg g^{-1}) was quite similar to that reported for seasoned French oak wood from *Q. petraea* (34.41 mg g^{-1}), which is among the most widely

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Table 1 - HPLC quantitative evaluation and standard deviation of ellagitannin content in seasoned and medium-toasted *Castanea sativa* and *Quercus pyrenaica* wood. Data are expressed in mg g^{-1} of ellagic acid equivalents based on dry wood.

	Castanea sativa				*Quercus pyrenaica*			
	Seasoned		Medium-toasted		Seasoned		Medium-toasted	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Roburin A	0.60 [a]	0,06	0.22 [b]	0,03	0.51 [c]	0,12	0.32 [d]	0,01
Roburin B	0.33 [a]	0,03	0.06 [b]	0,00	0.65 [c]	0,10	0.27 [d]	0,00
Roburin C	0.04 [a]	0,01	0.02 [b]	0,00	0.62 [c]	0,12	0.20 [d]	0,01
Grandinin	0.34 [a]	0,03	0.15 [b]	0,01	1.58 [c]	0,14	0.41 [a]	0,02
Roburin D	0.13 [a]	0,02	0.06 [b]	0,00	1.10 [c]	0,10	0.34 [d]	0,01
Vescalagin	20.30 [a]	1,91	4.32 [b]	0,08	5.86 [c]	0,95	0.62 [d]	0,03
Unknown E- I	0.25 [a]	0,02	0.09 [b]	0,01	3.81 [c]	0,52	0.52 [d]	0,05
Roburin E	2.91 [a]	0,12	1.09 [b]	0,09	1.59 [c]	0,42	0.46 [d]	0,01
Unknown E- II	0.76 [a]	0,05	0.28 [b]	0,01	0.51 [c]	0,09	0.09 [d]	0,00
Castalagin	6.71 [a]	0,22	4.59 [b]	0,16	5.96 [c]	0,86	1.70 [d]	0,02
Unknown E-III	1.44 [a]	0,08	1.30 [a]	0,05	1.41 [a]	0,25	0.87 [b]	0,00
Total ellagitannin	33,81		12,18		23,6		5,8	

appreciated wood species for cooperage (Prida and Puech, 2006). Also, the total ellagitannin content of seasoned *Q. pyrenaica* wood (23.60 mg g^{-1}) was comparable to those of seasoned wood from East European *Q. petraea* species: 28.35, 24.12 and 22.00 mg g^{-1} for Moldavian, Ukrainian and Romanian samples, respectively (Prida and Puech, 2006). Our seasoned wood samples had lower ellagitannin content than *Q. robur* wood (around 45 mg g^{-1} whatever its origin). On the other hand, the total amounts of ellagitannins in seasoned *C. sativa* and *Q. pyrenaica* wood were considerably higher than that found in the American oak species most commonly used in cooperage (*viz. Q. alba*, 8.36 mg g^{-1}) (Prida and Puech, 2006).

Vescalagin, castalagin and roburin E were the major ellagitannins in seasoned *C. sativa* wood; all were present in greater amounts in this type of wood than in seasoned *Q. pyrenaica* wood. *C. sativa* contained especially large amounts of vescalagin. This is consistent with previous results suggesting that *C. sativa* differs from *Quercus* in the low castalagin-to-vescalagin ratio (Alañón *et al.*, 2011a; Viriot *et al.*, 1994). Therefore, a high content of vescalagin is seemingly typical of *C. sativa*. By contrast, minor ellagitannins such as roburin B, C and D, grandinin and ellagitannin II were detected in smaller amounts in seasoned *C. sativa* wood than in seasoned *Q. pyrenaica* wood.

In both species, toasted wood samples had considerably lower total and individual ellagitannin contents than seasoned wood samples. This is a desirable feature of toasted wood as it prevents excessive bitterness in aged wines. The higher reduction in vescalagin level during the toasting process compared to castalagin is due to the fact that vescalagin is more thermo sensitive than castalagin (Glabasnia and Hofmann, 2006; 2007; Sarni *et al.*, 1990). Fig. 1 shows the chromatograms for seasoned and toasted *C. sativa* wood. As can be seen, both types of wood efficiently resist thermal degradation and are thus suitable for cooperage.

From a sensory point of view, the increased contents of vescalagin and castalagin in seasoned and medium-toasted *C. sativa* wood can be perceived as bitter sensations in aged beverages, as recently reported by Glabasnia and Hofmann (2006). On the other hand, roburin B and C, which were identified as key components contributing to the astringent mouthfeel in wine (Glabasnia and Hofmann, 2006), can influence the sensory perceptions of spirits and beverages aged in *Q. pyrenaica* wood barrels.

Variance analysis revealed significant differences in ellagitannin composition between medium-toasted and seasoned wood by effect of the thermal treatment. Thermal degradation of total ellagitannin amounted to 63.8 % in *C. sativa* and 75.5 % in *Q. pyrenaica*. This result suggests that *C. sativa* wood can withstand the heat treatment used in cooperage better than

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Table 2. Average levels and standard deviations of low-molecular-weight (LMW) phenols (µg g–1 ellagic acid) in seasoned and medium-toasted *Castanea sativa* and *Quercus pyrenaica* wood chips.

	Castanea sativa				***Quercus pyrenaica***			
	Seasoned		Medium-toasted		Seasoned		Medium-toasted	
	Acids							
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Gallic acid	590.54 [a]	7,47	488.54 [b]	9,25	117.78 [c]	3,50	88.91 [d]	2,86
Vanillic acid	74.67 [a]	5,42	34.03 [b]	1,99	8.57 [c]	0,84	1.82 [c]	0,18
Caffeic acid	37.08 [a]	1,68	22.82 [b]	1,05	6.22 [c]	0,40	2.91 [d]	0,14
Syringic acid	15.99 [a]	0,77	5.74 [b]	0,30	3.06 [c]	0,13	2.00 [c]	0,10
Ferulic acid	6.76 [a]	0,08	4.19 [b]	0,24	5.36 [c]	0,57	2.99 [d]	0,09
Ellagic acid	325.71 [a]	24,45	441.71 [b]	23,03	296.90 [a]	7,14	420.27 [b]	14,79
	Aldehydes							
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Vanillic aldehyde	72.06 [a]	7,06	153.70 [b]	14,08	7.91 [c]	0,81	14.89 [c]	0,46
Syringaldehyde	78.73 [a]	4,41	134.47 [b]	10,41	14.20 [c]	1,66	33.55 [d]	0,62
Coniferaldehyde	2.57 [a]	0,21	11.86 [b]	0,21	12.96 [b]	0,58	15.72 [c]	1,13
Sinapaldehyde	5.38 [a]	0,33	78.50 [b]	8,07	8.41 [a]	0,07	26.79 [c]	0,68
Total LMW phenols	1209,5		1375,57		481,37		609,85	

Q. pyrenaica. As can be seen from Figure 2, all individual ellagitannins except roburin A and B exhibited less marked thermal degradation in *C. sativa* wood than in *Q. pyrenaica* wood.

Consistent with previous findings in other oak wood species (Cadahía *et al.*, 2001 ; Matricardi and Waterhouse, 1999), medium toasting caused very strong degradation of vescalagin and castalagin in the two types of wood. Vescalagin was seemingly the individual ellagitannin most prone to thermal degradation, with 78.8 % degradation in *C. sativa* samples and 89.5 % in *Q. pyrenaica*.

The unknown ellagitannin-III exhibited no significant differences between the two types of seasoned wood. However, toasting at 160–170 ºC for 30 min decreased the E-III content to a greater extent in *Q. pyrenaica* that in *C. sativa*. E-III was the individual ellagitannin least prone to thermal degradation, with only 9.8 % degradation in *C. sativa* and 8.3 % in *Q. pyrenaica*.

2. LMW phenol content

Table 2 shows the contents of LMW phenols in seasoned and medium-toasted wood samples as determined from the organic extracts. Toasting hardly altered the total content of LMW phenols. This was a result of the decrease in the amount of phenolic acids and the increase in that of phenolic aldehydes.

As regards phenolic acids, both types of seasoned wood, particularly that from *C. sativa*, contained large amounts of gallic acid. This is consistent with previous studies where gallic acid was found in increased amounts in *C. sativa* relative to other cooperage oak wood species (Canas *et al.*, 2000) except *Q. robur*, whose gallic acid content was similar to that of chestnut wood (Alañón *et al.*, 2011a). Toasting considerably decreased the content of gallic acid in *C. sativa* wood (from 590.54 to 488.54 µg g^{-1}). A similar effect was previously observed by Sanz *et al.* (2010). The especially high contents of seasoned and toasted *C. sativa* wood in such a powerful antioxidant as gallic acid (Li *et al.*, 2005) can greatly contribute to the overall antioxidant power of aged wines.

Other phenolic acids such as vanillic, caffeic, syringic, and ferulic were found in greater amounts in seasoned *C. sativa* wood than in *Q. pyrenaica* wood. Toasting considerably reduced their contents in both types of wood as a consequence of thermal degradation (Table 2). By contrast, toasting increased ellagic acid contents as a consequence of its release through thermal degradation of ellagitannins (Viriot *et al.*, 1993). As can be seen from Figure 2, thermal degradation of all phenolic acids, except syringic, was more marked in *Q. pyrenaica*. This result confirms the increased suitability of *C. sativa* for toasting relative to *Q. pyrenaica*. It should be noted that gallic acid

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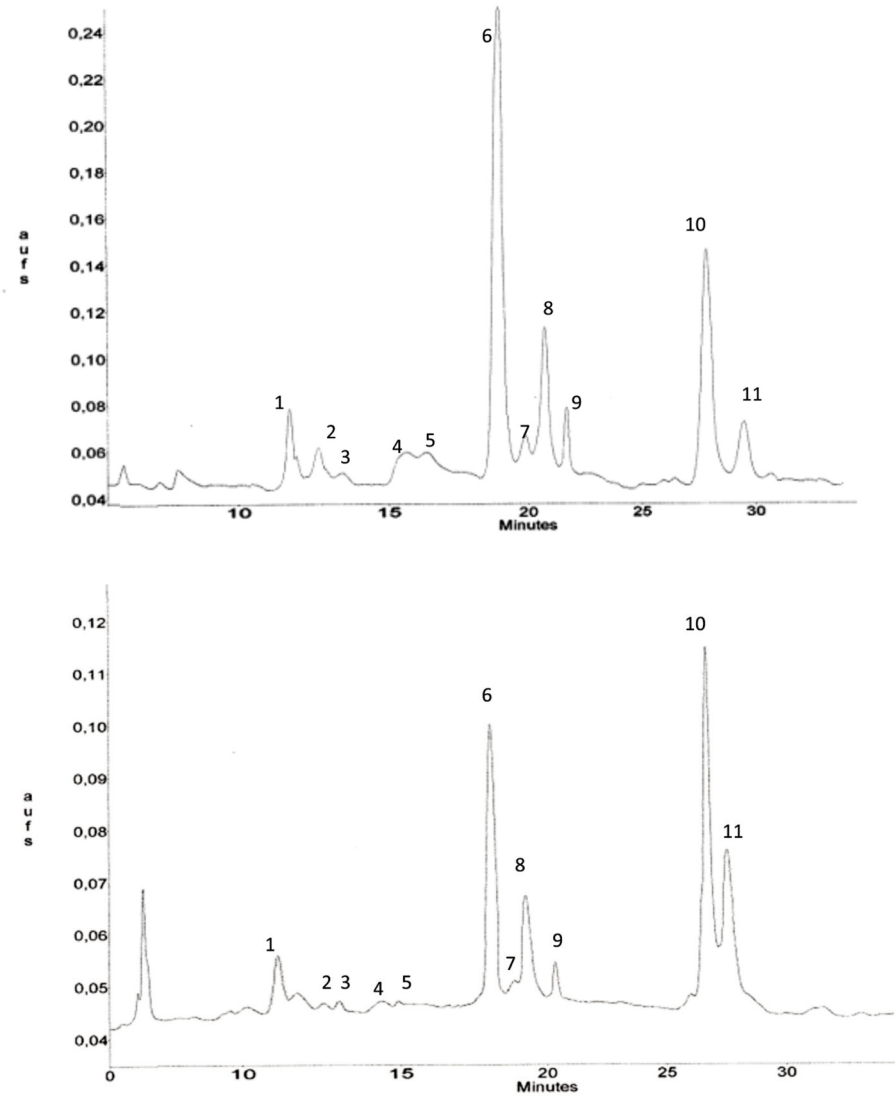


Figure 1 - HPLC ellagitannin chromatogram of seasoned (1a) and medium-toasted (1b) Portuguese *Castanea sativa* wood. Peak assignments: 1, Roburin A; 2, Roburin B; 3, Roburin C; 4, Grandinin; 5, Roburin D; 6, Vescalagin; 7, Unknown-I; 8, Roburin E; 9, Unknown-II; 10, Castalagin; 11, Unknown-III.

was the least prone to thermal degradation, with only 17.3 % degradation in *C. sativa* and 24.6 % in *Q. pyrenaica*. However, this was a result of its release through thermal degradation of gallotannins during the toasting treatment, which seemingly occurs to a greater extent in *C. sativa* owing to its increased content in gallotannins (Sanz *et al.*, 2010).

As can be seen from Table 2, toasting increased the contents of all phenolic aldehydes through thermal degradation of lignin (Hale *et al.*, 1999). Worth special note in this respect is vanillic aldehyde, not only because it was present in large amounts in the seasoned and toasted *C. sativa* wood extracts (72.06 and 153.70 μg g^{-1}, respectively), but also because it imparted sensory properties described as a "vanilla flavour". Vanillic aldehyde is an important flavour-active compound with a flavour of vanilla (Spillman *et al.*, 1997) that is much appreciated and an added value for aged wines. The contents of vanillic aldehyde in seasoned and toasted chestnut wood were much higher (around 10 times) than those in *Q. pyrenaica* wood. The high content of vanillic aldehyde in *C. sativa* was also observed in our previous research where the aroma potential of chestnut was compared with that of some oak wood species most commonly used in cooperage (Alañón *et al.*, 2012). This result explains why a beverage

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exhibits higher vanillin contents when aged in chestnut wood than when aged in oak wood (De Rosso *et al.*, 2009). Therefore, the increased vanillin content of *C. sativa* appears to be a distinctive sensory trait for this species.

Syringaldehyde, sinapaldehyde and coniferaldehyde contents were substantially increased by toasting (Figure 2), the increase in the latter two being considerably more marked in *C. sativa* than in *Q. pyrenaica*.

CONCLUSION

As shown here, Portuguese chestnut (*C. sativa*) wood and oak (*Q. pyrenaica*) wood are two effective alternatives to traditional oak wood species used in cooperage for aging beverages. The ellagitannin composition of these two types of Portuguese wood falls in the middle of the range spanned by traditional oak wood species of diverse origin. Based on their chemical composition after toasting, both types of wood can withstand the heat treatment involved in cooperage.

There are, however, some chemical differences between the two types of wood. Thus, *C. sativa* contains greater amounts of ellagitannins, which are less prone to thermal degradation during toasting. In addition, the increased amounts of phenolic acids (particularly gallic acid) present in seasoned and toasted *C. sativa* relative to *Q. pyrenaica* constitute an important factor for discriminating between the two. Also it is worth noting the richness of *C. sativa* in phenolic acids, especially in the odour-active compound vanillic aldehyde, which was substantially increased by toasting. Therefore, Portuguese chestnut (*C. sativa*) wood is an effective choice for the cooperage industry on the grounds of its phenolic composition, which can impart outstanding sensory properties to wines aged in this type of wood.

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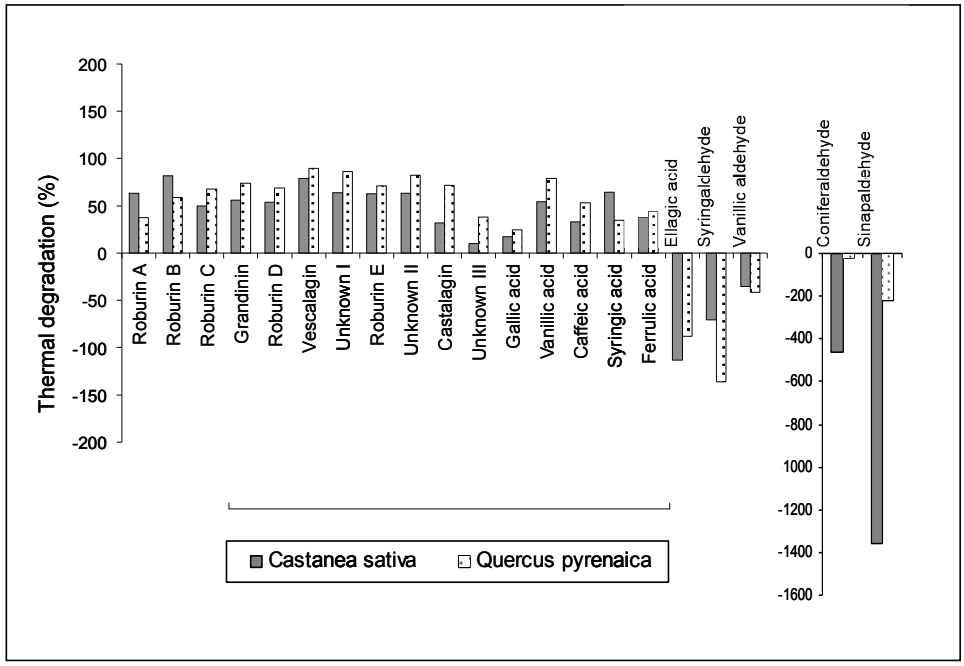


Figure 2 - Thermal degradation (%) of ellagitannins and low-molecular-weight phenols in *C. sativa* and *Q. pyrenaica* wood chips.

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