

Comparison of volatile composition of cooperage oak wood of different origins (*Quercus pyrenaica* vs. *Quercus alba* and *Quercus petraea*)

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Hydroalcoholic extracts of Portuguese oak wood chips (Quercus pyrenaica) from different origins (Gerês and Guarda forest), American oak chips (Quercus alba) and French oak chips (Quercus petraea) were analyzed by means of gas chromatography. The influence of heat treatment and the coarseness of the grain on the content of some volatile compounds in relation to those of the oak wood species was studied too. Twelve volatile oak compounds (furfural, methyl-5-furfural, hydroxymethyl-5-furfural, cyclotene, furaneol, cis- and trans- β -methyl- γ -octalactones, guaiacol, methyl-guaiacol, eugenol, isoegenol, vanillin and syringaldehyde) were quantified. For these compounds, quantitative differences were found between the oak wood species, which were especially important in American and French species in relation to the Portuguese oak wood species. On the other hand, the coarseness of the grain did not affect the values of the compounds quantified in all oak wood chips species studied. As expected the concentrations of all volatile compounds quantified in three oak wood chips species increased by increasing the toasting process. This increase was especially important in furanic derivatives (furfural, hydroxymethyl-5-furfural and methyl-5-furfural) from Portuguese oak wood chips but less evident in isomers of β -methyl- γ -octalactone, except in American species.

Keywords: Oak wood, *Q. pyrenaica*, *Q. alba*, *Q. petraea*, toasting, volatile compounds, coarseness of grain

Vergleich der flüchtigen Inhaltsstoffe von Eichenholz unterschiedlicher Herkünfte (Quercus pyrenaica, Quercus alba und Quercus petraea). Die flüchtigen Inhaltsstoffe wässrig-alkoholischer-Extrakte aus portugiesischen Eichenbrettchen (Quercus pyrenaica) unterschiedlicher Herkünfte (Gerês und Guarda) sowie amerikanischer (Quercus alba) und französischer Eichenbrettchen (Quercus petraea) wurden mittels gaschromatographischer Methoden analysiert. Es wurde auch der Einfluss der Wärmebehandlung und der Porosität des Holzes (Dichte der Jahresringe) auf den Gehalt von zwölf flüchtigen Eichenholzsubstanzen (Furfural, Methyl-5-furfural, Hydroxymethyl-5-furfural, Cyclotene, Furaneol, cis- und trans- β -Methyl- γ -oktallakton, Methyl-guaiacol, Eugenol, Isoeugenol, Vanillin und Syringaldehyd) in Beziehung zu der Eichenart studiert. Quantitative Unterschiede wurden für diese Substanzen zwischen den Eichenarten gefunden, die Unterschiede waren besonders ausgeprägt zwischen den amerikanischen und französischen Arten einerseits, und den portugiesischen Eichenarten andererseits. Die Gehalte aller untersuchten Substanzen wurden von der Porosität des Holzes nicht beeinflusst. Mit der Intensität des Toastings nahm die Konzentration aller flüchtigen Substanzen zu. Diese Zunahme war besonders für Furfural und seine Derivate (Hydroxymethyl-5-furfural und Methyl-5-furfural) der portugiesischen Eichenbrettchen ausgeprägt, aber weniger offensichtlich bei den Isomeren von β -Methyl- γ -oktallakton, mit Ausnahme der amerikanischen Eichenholzarten.

Schlagwörter: Eichenholz, *Q. pyrenaica*, *Q. alba*, *Q. petraea*, Toastung, flüchtige Zusammensetzung

Comparaison des composants volatils du bois de chêne d'origines différentes (Quercus pyrenaica, Quercus alba et Quercus petraea). Des extraits hydro-alcooliques de copeaux de bois de chêne portugais (Quercus pyrenaica) issus de différentes origines (de la forêt de Gerês et Guarda), de copeaux de bois de chêne américain (Quercus alba) et de copeaux de bois de chêne français (Quercus petraea) ont été analysés par chromatographie en phase gazeuse. Lin-

fluence du traitement thermique du bois et de l'épaisseur du grain, dans la teneur en quelques composés volatils, en relation avec l'espèce de bois de chêne, a été étudiée. Douze composés volatils issus du bois de chêne (furfural, 5-méthylfurfural, 5-hydroxyméthylfurfural, cyclohexène, furaneol, *cis* et *trans*- β -méthyl- γ -octalactone, guaiacol, méthylguaiacol, eugénol, isoeugénol, vanilline et syringaldéhyde) ont été quantifiés. Pour ces composés, des différentes quantitatives ont été trouvées parmi les espèces de bois de chêne, et qui sont assez importantes dans les espèces de chêne américain et français par rapport au chêne portugais. De plus, l'épaisseur de grain n'a pas eu d'effet sur la teneur des composés volatils quantifiés. Comme attendu, les concentrations de tous les composés volatils quantifiés dans les copeaux de bois de chêne, des trois espèces étudiées, ont augmenté en fonction de l'augmentation de l'intensité de la chauffe. Cette augmentation a été particulièrement importante pour les dérivés furaniques (furfural, 5-méthylfurfural, 5-hydroxyméthylfurfural), issus des copeaux de bois de chêne portugais, toutefois moins évident dans le cas des isomères de β -méthyl- γ -octalactone, sauf pour les espèces américaines.

Mots clés: bois de chêne, *Q. pyrenaica*, *Q. alba*, *Q. petraea*, chauffe, composition volatile, épaisseur de grain.

Oak barrel aging has been recognized as an integral part of fine winemaking for over 200 years. Wines are aged in oak barrels with three main objectives: the enrichment of the wine with substances released by the oak; reactions due to contact with air diffusing through pores in the wood; and the development of certain interactive chemical reactions that take place slowly in wines (CHATONNET et al., 1990).

In Europe, wines are traditionally aged in barrels made mainly from the oak species *Quercus alba* (American oak) and *Quercus robur* and *Quercus petraea*, the varieties most commonly found in the French forests. The concentration of potential extractable compounds found in oak wood is influenced by two sets of factors, on the one hand, the oak species and geographic origin (CHATONNET, 1992; GREGORCIC et al., 1994; GUICHARD et al., 1995; MASSON et al., 1996; FERNÁNDEZ DE SIMÓN et al., 1996; CHATONNET et al., 1997a, 1997b; CHATONNET and DUBOURDIEU, 1998; CADAHÍA et al., 2001), and on the other hand the processing of the wood in cooperage (the method used to obtain the staves and the seasoning process used) and the degree of toasting during the barrel's manufacture (CHATONNET et al., 1989; SARNI et al., 1990; CUTZACH et al., 1997; CHATONNET et al., 1999).

Despite these factors, the process of barrel toasting probably has the main influence on the chemical compounds of the wood, which are susceptible to migrating into wine during their aging, affecting their organoleptic properties (CHATONNET et al., 1990; FRANCIS et al., 1992; PÉREZ-COELLO et al., 2000). As a consequence of the toasting process, there is a thermal degradation of some oak wood components: oak lignin, polysaccharides and the two isomeric lactones called "oak"- or "whisky"-lactones (SEFTON et al., 1993; GIMENEZ-MARTINEZ et al., 1996; CADAHÍA et al., 2001) and the appearance of new classes of odoriferous volatile substances

such as pyrazines, furans and phenols (PUECH and MAGA, 1993; GIMENEZ-MARTINEZ et al., 1996). However some compounds can be extracted from the unheated wood in small quantities (for example vanillin, volatile phenols, mainly eugenol and traces of phenolic aldehydes) (MONTIES, 1987; BOIDRON et al., 1988; DUBOIS, 1989; CADAHÍA et al., 2001).

In general the concentration of eugenol, vanillin and oak lactones in oak wood can be increased by medium or heavy toast levels (CHATONNET et al., 1989; GIMENEZ-MARTINEZ et al., 1996; CADAHÍA et al., 2001).

Several studies have suggested that American oak contains higher levels of oak extractable aromatic compounds than French oak (GUYMON and CROWELL, 1970 and 1972; MULLER et al., 1973; MARCO et al., 1994; FERNÁNDEZ DE SIMÓN et al., 1996). On the other hand, according to previous studies (ROUS and ANDERSON, 1983; CHATONNET et al., 1997a; CHATONNET and DUBOURDIEU, 1998; CADAHÍA et al., 2001) French oak has a higher extractable phenolic potential than American oak.

The bouquet and flavour of wine matured in oak wood are largely due to the presence of the compounds quantified in this work. Thus the knowledge of the olfactory perception thresholds of these various measurable molecules makes it possible to specify the real aromatic impact of each of them, as well as to evaluate the sensory importance of the modification in wine aroma composition. Previous studies (CHATONNET et al., 1992) published the perception thresholds of some compounds quantified in our study using hydroalcoholic solutions: furfural (15 mg/l), methyl-5-furfural (16 mg/l), *trans*- β -méthyl- γ -octalactone (0.11 mg/l), *cis*- β -méthyl- γ -octalactone (0.025 mg/l), vanillin (0.065 mg/l), guaiacol (0.02 mg/l) and eugenol (0.015 mg/l).

Stave wood was commonly classified according to the notion of 'grain', described as 'fine, medium or coarse'. Some authors (GETAZ et al., 1996; MOSEDALE and FORD,

1996) suggested that structural characteristics of oak wood could influence the concentration of wood extractable components. However, FEUILLAT et al. (1997) reported that species is a better indicator than wood ring ('grain') when we study the chemical cask characteristics that probably affect wine and spirit quality.

The effect of heat and species on the concentrations of volatile oak compounds has been studied several times (MARTINEZ et al., 1996; CHATONNET and DUBOURDIEU, 1998; CHATONNET et al., 1999; PÉREZ-COELLO et al., 1999; CADAHÍA et al., 2001). However, simultaneous studies about the influence of various factors (botanical species, heat treatment and coarseness of the grain) on the concentration of some volatile compounds in oak wood from three different sources are not common, especially with *Quercus pyrenaica*, which grows in Portugal.

Thus, this paper reports a global study on the influence of toasting intensity (medium and heavy toasting), coarseness of grain (fine, medium and coarse) and botanical species (*Quercus alba* from the United States of America, *Quercus petraea* from France and *Quercus pyrenaica* from two regions of Portugal - Gerês and Guarda) on some oak-derived volatile contents on the main oak wood species used in Portugal for barrel production.

Materials and methods

Oak wood samples

Several pieces of oak wood (from thirty different tree samples) were collected for each species, coarseness of the grain and geographical origin. The oak wood samples were from heartwood of trees ranging from 75 and 120 years of age. All the different oak wood stave samples (one stave from each tree) used were seasoned in the open air for 24 months and provided by the J.M. Gonçalves Lda. Company (Palaçoulo, North of Portugal). Oak wood chip samples (particles with a size less than 2 mm) obtained from staves (heated and unheated) were homogenized and then kept in a dry atmosphere until analyzed.

Thus, *Quercus alba* L. from USA forests (Missouri), *Quercus petraea* L. from French forests (Allier region) and *Quercus pyrenaica* L. from Portugal (Guarda and Gerês forest) were submitted to a different toasting intensity and temperature: medium toasting (20 min at 160 to 170 °C on the wood surface) and heavy toasting

(27 min at 250 to 260 °C on the wood surface). In this study the levels of coarseness of the grain were: fine (1.0 to 2.8 mm) and medium (3.0 to 3.5 mm). In the case of the Portuguese oak wood chips only medium grain was used.

Extraction of odorous compounds from the wood

In order to reproduce extraction conditions similar to those in wine, the oak wood chip samples used in this study (20 g/l) were placed in 500 ml of model alcohol solution (12 % alcohol content and adjusted at pH 3.5 with 2 g/l of tartaric acid) for 15 days at 20 °C in the dark and stirred daily. At the end of this maceration, the extract was filtered through glass wool prior to the extraction process.

Sample preparation for analysis

For furanone group compounds, 100 ml of the filtrate were extracted with 20, 10 and 5 ml of dichloromethane with magnetic stirring (5 min, 600 rpm) using 1 ml of 3-octanol at 50 mg/l as an internal standard. On the other hand, for volatile phenol group compounds, 50 ml of the filtrate were extracted with 10 and 4 ml (twice) of dichloromethane-pentane (1:1) with magnetic stirring (5 min, 600 rpm), using 10 ml of 3,4-dimethylphenol at 50 mg/l as an internal standard. The organic phases of each fraction were dried over anhydrous sodium sulfate and concentrated at 0.5 ml under a stream of nitrogen in a 10 ml graduated concentrating tube (CHATONNET and BOIDRON, 1988; YOKOTSUKA et al., 1994).

Chromatographic conditions

Each extract (2 ml) was injected into a gas chromatograph equipped with a FID detector (Carlo Erba 8000 Top), a capillary Carbowax 20M column (0.25 mm x 0.25 mm x 60 m, Bellefonte, USA) and an injector in a splitless mode (50:1) with a temperature of 250 °C (air 100 Kpa and hydrogen 50 Kpa).

The column temperature programme was from 70 °C to 230 °C at 3 °C/min, isothermic for 20 min, from 230 °C to 240 °C at 5 °C/min and a final isothermic over a period of 30 min. Helium was used as a carrier gas. All analyses were done with repetition. The volatile compounds studied were quantified by comparison with references and analysed under the same conditions. Furfural, syringaldehyde, hydroxymethyl-5-furfural and

isoeugenol were purchased from Fluka (Buchs, Switzerland), guaiacol, eugenol, vanillin and cyclotene from Merck (Darmstadt, Germany), *cis*- and *trans*-methyl-octalactone, furaneol and methyl-guaiacol from Aldrich (Steinheim, Germany).

Statistical analyses

In order to study the influence of botanical species, heat treatment and coarseness of the grain on the content of some volatile compounds in the various oak wood chips studied, an analysis of variance and comparison of treatment means (ANOVA, one-way) was performed using SPSS software program version 11.0 (SPSS Inc. Headquarters, Chicago, Illinois, USA).

Results and Discussion

Influence of botanical species and coarseness of grain

Figure 1 shows the total volatile compounds quantified in oak chips of different botanical species and coarseness of the grain without toasting. The results suggest for the volatile compounds studied that *Quercus alba* (American oak wood chips) and *Quercus petraea* (French oak wood chips) had a much higher content of extractable volatile compounds than *Quercus pyrenaica* (Portuguese oak wood chips). In fact, there is a significant difference between *Q. pyrenaica* and the other two species studied (*Q. alba* and *petraea*). Thus *Q. pyrenaica* oak is the poorest wood with a medium value of 33.2 mg/g dry wood (for oak wood from Gerês forest) for the total volatile compounds quantified while for *Q. alba* oak chips highest values were quantified (about 65.0 mg/g dry wood). On the other hand, it was not possible to distinguish significantly different values for the total volatile compounds between oak wood chips of the two species *Q. alba* and *Q. petraea*. This result is in accordance with previous studies on French and American oak woods (FEUILLAT et al., 1997; MOSEDALE et al., 2001), but in disaccordance with earlier findings (GUYMON and CROWELL, 1970 and 1972; MULLER et al., 1973; MARCO et al., 1994; FERNÁNDEZ DE SIMÓN et al., 1996).

The values also show that the geographical origin for *Q. pyrenaica* (Portuguese oak wood chips) did not affect the content of the total compounds quantified. Thus, these results indicate as previously reported by

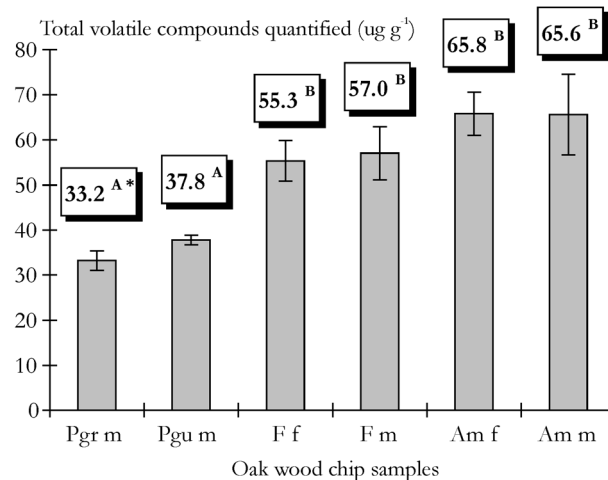


Fig. 1: Influence of botanical species and coarseness of grain on total volatile compound contents (medium values in $\mu\text{g/g}$ dry wood) in Portuguese (*Q. pyrenaica* L.), French (*Q. petraea* L.) and American (*Q. alba* L.) oak wood chips. (abbreviations - see Table 1)

* Analysis of variance and comparison of treatment means (ANOVA). Means followed by the same letter are not significantly different ($p < 0.05$).

other authors (MILLER et al., 1992; CANAS et al., 2000) that botanical species seems to be more important than the geographic origin in explaining the difference in the composition of the woods.

Stave wood is commonly classified according to the notion of 'grain', described as 'fine, medium or coarse'. This classification indicates certain porosity associated with the frequency of vessels (number, size, proportion of spring wood to summer wood, etc). In our study, the results (Fig. 1) for the total volatile compounds quantified suggest that the effect of wood anatomy ('grain') was low or insignificant in all botanical species studied. On the other hand, CHATONNET et al. (1997b) reported for Russian oak wood high values of volatile compounds with odourant properties in wood with fine grain.

Table 1 shows the detailed contents of furan and pyran derivatives (furfural, hydroxymethyl-5-furfural, cyclotene, furaneol and γ -lactones) and volatile phenols (guaiacol, methyl-guaiacol, eugenol, isoeugenol, vanillin and syringaldehyde) in extracts of wood chips from different botanical species, grain and origin (only for Portuguese oak wood chips).

The main feature of the chemical composition of *Q. pyrenaica* was a lower concentration of volatile phenols

Table 1:

Influence of botanical species and coarseness of grain on individual volatile compound contents (medium values in $\mu\text{g/g}$ dry wood) in Portuguese (*Q. pyrenaica* L.), French (*Q. petraea* L.) and American (*Q. alba* L.) oak wood chips

Pgr m = Portug. oak wood chips (Gerês forest) with medium grain
 Pgu m = Portug. oak wood chips (Guarda forest) with medium grain
 F f = French oak wood chips with fine grain

F m = French oak wood chips with medium grain
 Am f = American oak wood chips with fine grain
 Am m = American oak wood chips with medium grain

Compounds	Pgr m	Pgu m	F f	F m	Am f	Am m
Furfural	3.9 ± 0.7	4.5 ± 0.7	3.4 ± 2.1	7.0 ± 1.9	1.2 ± 0.9	1.8 ± 0.7
Hydroxymethyl-5-furfural	0.9 ± 0.4	1.3 ± 0.6	0.3 ± 0.2	0.5 ± 0.1	0.7 ± 0.2	0.4 ± 0.1
Cyclotene	n.d.	n.d.	n.d.	1.7 ± 0.9	n.d.	1.3 ± 0.9
Furaneol	1.0 ± 0.3	0.3 ± 0.1	n.d.	n.d.	n.d.	n.d.
Cis- β -methyl- γ -octalactone	10.0 ± 0.4	5.3 ± 0.2	21.3 ± 3.6	14.0 ± 2.7	22.3 ± 5.0	23.1 ± 0.4
Trans- β -methyl- γ -octalactone	n.d.	8.3 ± 0.5	5.0 ± 2.2	6.7 ± 1.3	5.0 ± 2.2	4.0 ± 1.4
Guaiacol	n.d.	n.d.	n.d.	1.3 ± 0.2	1.4 ± 0.4	3.3 ± 0.9
Methyl-guaiacol	n.d.	n.d.	n.d.	n.d.	1.54 ± 0.3	1.4 ± 0.2
Eugenol	n.d.	n.d.	6.5 ± 1.0	6.2 ± 0.3	4.9 ± 1.5	5.9 ± 0.1
Isoeugenol	n.d.	n.d.	4.3 ± 0.5	1.4 ± 0.1	1.1 ± 0.3	1.3 ± 0.2
Vanillin	2.5 ± 0.6	1.6 ± 0.2	2.0 ± 0.1	3.4 ± 0.5	7.5 ± 1.2	6.8 ± 3.0
Syringaldehyde	14.9 ± 0.7	16.5 ± 2.1	12.5 ± 3.3	14.8 ± 3.9	20.2 ± 3.3	16.3 ± 2.9

n.d. = not detected

than the other two species (*Q. alba* and *Q. petraea*) studied. The volatile phenols, especially the guaiacol, methyl-guaiacol, eugenol and isoeugenol, were not detected in untoasted Portuguese oak wood chips. On the other hand, the quantity of vanillin (1.6 to 2.5 mg/g) and syringaldehyde (14.9 to 16.5 $\mu\text{g/g}$) in *Q. pyrenaica* was similar in terms of the values quantified for the other oak wood species. The β -methyl- γ -octalactones isomers (oak lactones), compounds with high sensory impact (CHATONNET, 1991; PÉREZ-COELLO et al., 1997), have frequently been used to distinguish oak wood species. The *cis*- and *trans*- β -methyl- γ -octalactones were present in all samples in relatively high concentrations especially for *Q. alba* (22.3 to 23.1 $\mu\text{g/g}$ for *cis*- β -methyl- γ -octalactone and 4.0 to 5.0 $\mu\text{g/g}$ for *trans*- β -methyl- γ -octalactone) and *Q. petraea* (14.0 to 21.3 $\mu\text{g/g}$ for *cis*- β -methyl- γ -octalactone and 5.0 to 6.7 $\mu\text{g/g}$ for *trans*- β -methyl- γ -octalactone). In previous studies similar results have also been found for the same species (SEFTON et al., 1993; CHATONNET and DUBOURDIEU, 1998; PÉREZ-COELLO et al., 1999). For all oak wood species, *cis*-isomer of oak lactone was the most abundant isomer form (Table 1), except for *Q. pyrenaica* oak wood chips from the Guarda forest where *trans*-isomer (8.3 $\mu\text{g/g}$) of oak lactone was slightly more abundant than *cis*-isomer (5.3 $\mu\text{g/g}$). On the other hand, for *Q. pyrenaica* from Gerês forest *trans*-isomer was not detected.

For some authors the *cis*- to *trans*-oak lactone ratio is characteristic of the wood's source (WATERHOUSE and

TOWEY, 1994; CHATONNET and DUBOURDIEU, 1998). Although this ratio can be characteristic of the wood's source, other authors (FRANCIS et al., 1992; CHATONNET et al., 1994) indicated that it is not as useful to consider the *cis/trans* ratio of the various β -methyl- γ -octalactone isomers in view of its dependence on time and wood drying conditions. In our study only *Quercus pyrenaica* from the Guarda region had a *cis/trans* ratio lower than 1 as a consequence of the value of *trans*-form being more abundant than *cis*-form. Thus the ratio was lower in the Portuguese oak wood from the Guarda forest (0.63 of ratio), while the relative concentration of the *cis/trans* was highest in the French (4.2 ratio for fine grain), followed by the American oak wood extract (5.7 ratio for medium grain).

Influence of heat treatment on the wood

Heating operations modify the macromolecular structure of wood, leading to a degradation of polysaccharides, polyphenols and the appearance of new compounds and an increase of odiferous volatile substances such as furan and some phenols.

The effect of heat treatment on total volatile compounds quantified is shown in Figure 2. A great increase of the values after heat treatment can be observed in all situations (toasting conditions see experimental) in comparison to the values obtained in unheated wood chips (Figure 1). These results are in accordance with previous studies (PUECH and MAGA, 1993; GUI-

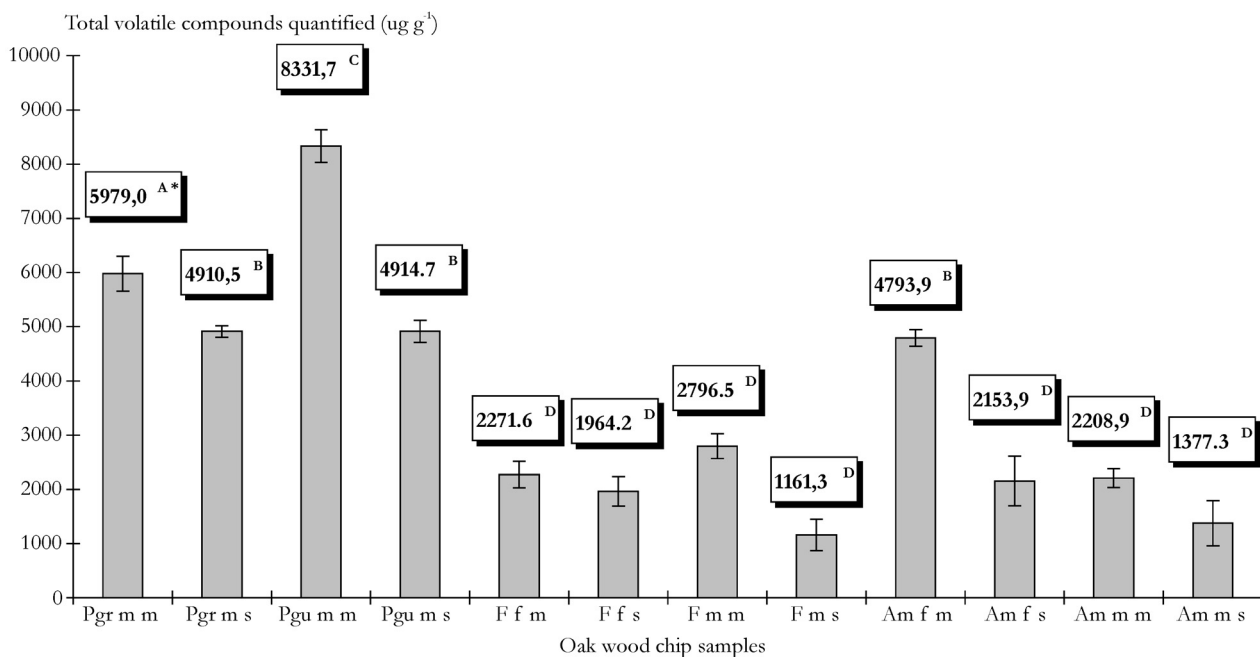


Fig. 2: Influence of heat treatment (medium toasting) on total volatile compound contents (medium values in $\mu\text{g/g}$ dry wood) in Portuguese (*Q. pyrenaica* L.), French (*Q. petraea* L.) and American (*Q. alba* L.) oak wood chips

Pgr m m - Portuguese oak wood chips (Gerês forest) with medium toasting and grain; Pgr m s - Portuguese oak wood chips (Gerês forest) with medium grain and strong toasting; Pgu m m - Portuguese oak wood chips (Guarda forest) with medium toasting and grain; Pgu m s - Portuguese oak wood chips (Guarda forest) with medium grain and strong toasting; F f m - French oak wood chips with fine grain and medium toasting; F f s - French oak wood chips with fine grain and strong toasting; F m m - French oak wood chips with medium grain and toasting; F m s - French oak wood chips with medium grain and strong toasting; Am f m - American oak wood chips with fine grain and medium toasting; Am f s - American oak wood chips with fine grain and strong toasting; Am m m - American oak wood chips with medium grain and toasting; Am m s - American oak wood chips with medium grain and strong toasting.

* Analysis of variance and comparison of treatment means (ANOVA). Means followed by the same letter are not significantly different ($p < 0.05$).

CHARD et al., 1995; GIMENEZ-MARTINEZ et al., 1996; CADAHÍA et al., 2001). These increases were independent of the toasting intensity, coarseness of grain, botanical species and origin (forest). However, the increase of the values was more evident for medium toasting. For heavy toasting (27 min) this increase was lower than in medium toasting. This is because toasting for long periods leads to uncontrolled decomposition namely of lignin, which in turn causes the formation of much less reactive compounds or even the destruction of part of the compounds formed during the first stages of toasting process. The increase of the total values was most evident in Portuguese oak wood chips with medium toasting and medium grain from Gerês forest and Guarda forest (from 33.2 to 5979.0 and from 37.8 to 8331.7 $\mu\text{g/g}$, respectively) followed by American oak

wood chips with medium toasting and fine grain (from 65.8 to 4793.9 $\mu\text{g/g}$) and French oak wood chips with medium toasting and medium grain (from 57.0 to 2796.5 $\mu\text{g/g}$). The result shows that, for American (*Quercus alba*) and French (*Quercus petraea*) oak wood chips, the increase of the values with toasting process was less evident in relation to Portuguese oak wood chips. It appears that for American and French oak species the heat treatment causes lower lignin decomposition and therefore, less volatile compounds are formed than in Portuguese oak wood. On the other hand, it is possible that staves from American oak, especially with medium grain, were obtained by sawing, whereas those from Portuguese oaks were obtained by cracking. For CADAHÍA et al. (2001) this difference in the process of wood cutting could modify the

Table 2a:

Influence of heat treatment (medium toasting) on individual volatile compound contents (medium values in $\mu\text{g/g}$ dry wood) in Portuguese (*Q. pyrenaica* L.), French (*Q. petraea* L.) and American (*Q. alba* L.) oak wood chips (abbreviations - see Table 1)

Compounds	Pgr m	Pgu m	F f	F m	Am f	Am m
Furfural	2176.6 \pm 273.5	2670.0 \pm 194.1	723.0 \pm 76.9	772.5 \pm 116.2	960.0 \pm 358.1	357.5 \pm 213.4
Methyl-5-furfural	327.5 \pm 38.8	465.0 \pm 19.7	258.0 \pm 4.2	199.0 \pm 12.7	487.0 \pm 15.5	91.0 \pm 14.1
Hydroxymethyl-5-furfural	3344.2 \pm 241.5	5078.3 \pm 94.2	1203.9 \pm 231.2	1722.3 \pm 122.6	3221.1 \pm 123.0	1678.3 \pm 345.0
Cyclotene	0.7 \pm 0.2	0.8 \pm 0.1	n.d.	1.4 \pm 0	3.0 \pm 0.1	2.0 \pm 0.1
Furaneol	0.9 \pm 0.1	1.1 \pm 0	n.d.	0.1 \pm 0	n.d.	n.d.
Cis- β -methyl- γ -octalact.	13.7 \pm 1.4	3.6 \pm 0.6	18.5 \pm 0.4	14.1 \pm 1.0	45.5 \pm 1.6	26.5 \pm 0.8
Trans- β -methyl- γ -octalact.	4.8 \pm 0.9	7.0 \pm 0.5	5.4 \pm 0	11.3 \pm 1.6	6.4 \pm 0.2	7.4 \pm 1.2
Guaiacol	1.6 \pm 0.2	2.5 \pm 0.4	2.9 \pm 0.8	3.4 \pm 0.6	7.3 \pm 0.8	3.7 \pm 1.1
Methyl-guaiacol	2.5 \pm 0.6	2.5 \pm 0.2	N.D.	1.6 \pm 0	5.1 \pm 0.4	2.6 \pm 0.5
Eugenol	0.6 \pm 0	1.4 \pm 0.5	4.0 \pm 0.3	1.7 \pm 0.3	11.6 \pm 1.2	6.2 \pm 0.3
Isoeugenol	0.54 \pm 0.3	0.65 \pm 0.2	0.5 \pm 0	0.8 \pm 0.1	1.3 \pm 0.6	1.9 \pm 0.3
Vanillin	23.4 \pm 5.0	10.5 \pm 1.7	6.9 \pm 1.2	8.3 \pm 2.1	11.1 \pm 1.2	7.7 \pm 1.6
Syringaldehyde	82.0 \pm 2.6	88.4 \pm 5.0	48.5 \pm 10.5	60.0 \pm 7.4	34.5 \pm 0.7	24.1 \pm 1.6

Table 2b:

Influence of heat treatment (strong toasting) on individual volatile compound contents (medium values in $\mu\text{g/g}$ dry wood) in Portuguese (*Q. pyrenaica* L.), French (*Q. petraea* L.) and American (*Q. alba* L.) oak wood chips (abbreviations - see Table 1)

Compounds	Pgr m	Pgu m	F f	F m	Am f	Am m
Furfural	1635.0 \pm 108.8	2155.0 \pm 127.0	613.0 \pm 58.3	118.0 \pm 55.6	787.5 \pm 154.8	353.5 \pm 33.2
Methyl-5-furfural	173.0 \pm 8.4	328.5 \pm 2.1	249.5 \pm 13.4	243.5 \pm 3.5	363.0 \pm 18.3	169.5 \pm 3.5
Hydroxymethyl-5-furfural	2976.8 \pm 453.6	2306.7 \pm 73.3	980.6 \pm 120.3	654.2 \pm 87.1	922.3 \pm 150.4	781.9 \pm 53.5
Cyclotene	0.8 \pm 0.1	1.2 \pm 0.3	0.9 \pm 0.1	1.22 \pm 0	2.0 \pm 0.2	1.4 \pm 0.3
Furaneol	1.0 \pm 0.1	1.0 \pm 0	n.d.	0.1 \pm 0	n.d.	n.d.
Cis- β -methyl- γ -octalact.	9.6 \pm 0.7	2.9 \pm 1.2	18.2 \pm 2.1	7.4 \pm 0.7	16.1 \pm 0.4	23.6 \pm 0.7
Trans- β -methyl- γ -octalact.	7.2 \pm 0.2	5.0 \pm 0.4	5.3 \pm 0.3	11.5 \pm 0.7	4.2 \pm 0.4	7.4 \pm 1.6
Guaiacol	1.9 \pm 0.7	1.6 \pm 0.9	2.6 \pm 0.3	1.7 \pm 0.1	5.3 \pm 0.5	3.3 \pm 0.4
Methyl-guaiacol	1.7 \pm 0.3	0.8 \pm 0.2	n.d.	0.6 \pm 0.1	4.5 \pm 0.4	2.8 \pm 0.2
Eugenol	n.d.	0.5 \pm 0.2	2.2 \pm 0.1	1.6 \pm 0.2	7.9 \pm 1.4	5.1 \pm 0.4
Isoeugenol	0.86 \pm 0.1	0.76 \pm 0.3	0.6 \pm 0.1	0.5 \pm 0	0.8 \pm 0.1	0.8 \pm 0.1
Vanillin	33.65 \pm 6.8	22.0 \pm 2.1	6.3 \pm 0.6	3.0 \pm 0.1	8.8 \pm 1.4	7.5 \pm 0.5
Syringaldehyde	69.0 \pm 5.6	88.8 \pm 2.6	85.0 \pm 11.2	118.0 \pm 7.0	31.5 \pm 1.7	20.5 \pm 0.8

physical properties of the staves or chips and could influence perhaps the response of wood to the toasting process. However, it was also observed that quality and quantity of volatile compounds are narrowly related to toasting intensity (VIVAS et al., 1991), but according to our findings it seems that the particular characteristics of each species could determine the rate of modification in toasted wood.

Considering the data obtained from all toasted oak wood species (Tables 2a and 2b) in relation to those of non-toasted wood (Table 1), it can be pointed out that in general the concentrations of individual volatile compounds increased extremely (50- to 100-fold) with the

toasting process.

Furan derivatives (furfural, hydroxymethyl-5-furfural and methyl-5-furfural) were the most abundant of all the compounds under study in all oak wood species, coarseness of grain and toasting level. These compounds showed the highest increment, especially in Portuguese oak wood chips from the Guarda forest for hydroxymethyl-5-furfural (for example from 1.3 to 5078.3 $\mu\text{g/g}$) and for furfural (for example from 4.5 to 2670.0 $\mu\text{g/g}$), followed by benzoic aldehydes (for example from 16.5 to 88.8 $\mu\text{g/g}$ for syringaldehyde and from 1.6 to 22.0 $\mu\text{g/g}$ for vanillin). This increase is in accordance with other previous studies (GREGORCIC et al.,

1994; MASSON et al., 1996; GIMENEZ-MARTINEZ et al., 1996). The important increase in furanic derivatives, furfural, hydroxymethyl-5-furfural and methyl-5-furfural (not detected in the samples with untoasted oak wood), in toasted oak wood, as opposed to the untoasted oak, reflects the sugar degradation during toasting process. These compounds and other derivatives of sugar degradation products can contribute to the aroma of barrel-aged wines. On the other hand, the increase of benzoic aldehydes is a consequence of the decomposition of lignin by heat and break up, leading to the occurrences of syringaldehyde and vanillin molecules.

There are conflicting accounts in literature of the effect of heating wood on the concentration of oak lactones in wood extracts. Thus MARSAL and SARRE (1987) recorded decreased levels of oak lactones extracted from toasted wood compared to extracts of untoasted wood whereas another author (MAGA, 1989) reported an increase in oak lactone concentrations as a result of charring. On the other hand, SEFTON et al. (1993) reported that the oak lactone levels were not significantly affected by heating the wood samples to 175 °C.

In general, in our study the variation of volatile compounds from oak chips was high as a consequence of the toasting process. In contrast the isomers of β -methyl- γ -octalactone (Tables 2a and b) did not show a great increment with heat treatment, except in American oak wood with fine coarseness of grain (*Am f*). Thus, after heat treatment the quantity of extractable methyl-octalactones in American oak wood was higher, especially for *cis*-isomer (between 16.1 to 45.5 $\mu\text{g/g}$) than in the other two oak species studied (between 7.4 and 18.5 $\mu\text{g/g}$ for French and between 2.9 and 13.7 $\mu\text{g/g}$ for Portuguese oak wood chips). Portuguese oak wood chips (especially from the Guarda forest) seem to be less rich in *cis*-methyl- γ -octalactone than the other oak wood species, after the toasting process.

During wood toasting, we observed that the *cis/trans*-form of β -methyl- γ -octalactone ratio did not change in all species studied except for Portuguese oak wood chips from Guarda forest where this ratio was less than 1 as a consequence of the decrease of *cis*-form during the toasting process. GUICHARD et al. (1995) using American white oak (*Quercus alba*) related that toasting of the barrels did not modify the *cis/trans* ratio. We observed an increase in the values for volatile phenols (guaiacol, eugenol, isoeugenol and methyl-guaiacol) in all oak species studied after medium toasting. This increase was more evident in the Portuguese species (*Quercus pyrenaica*) because in unheated wood

chips we could not find the majority of these compounds. Considering the results obtained on the composition of different oak wood species, it is very clear that the toasting process in barrel cooperage has an important influence on the chemical composition of wood. These results are in accordance with previous studies (SARNI et al., 1990; FRANCIS et al., 1992). After the toasting process high values were found in American oak wood chips: 3.7 to 3.3 $\mu\text{g/g}$ guaiacol; 2.6 to 5.1 $\mu\text{g/g}$ methyl-guaiacol; 5.1 to 11.6 $\mu\text{g/g}$ eugenol and 0.8 to 1.9 $\mu\text{g/g}$ isoeugenol. After the toasting process, Portuguese oak wood chips seem to be less rich in guaiacol (1.6 to 2.5 $\mu\text{g/g}$) and eugenol (0.5 to 1.4 $\mu\text{g/g}$). On the other hand, in French oak wood chips with fine grain (*F f*) even after the heating process methyl-guaiacol was not found.

Despite these increases in values with medium toasting, after strong toasting the concentrations of compounds in general decrease in all oak wood chips species studied. For GIMENEZ-MARTINEZ et al. (1996) this is because high toasting time leads to uncontrolled decomposition of lignin, which in turn causes the formation of much less reactive compounds or even the destruction/decomposition of part of the compounds responsible for the aroma of alcoholic beverages.

Conclusions

The main feature of the composition of unheated Portuguese (*Q. pyrenaica*) oak wood chips was a lower concentration of volatile compounds than in unheated French (*Q. petraea*) and American (*Q. alba*) oak wood chips. On the other hand, the geographic origin (of Portuguese oak wood species) and coarseness of grain did not significantly affect the volatile compounds studied in this work.

It was evident that the toasting process had a major impact on the volatile compounds quantified in all oak wood chips samples irrespective of the other variables. Heating was seen to affect all of the samples and produced a strong increase in volatile compounds (especially furan derivatives). It also produced a large number of significant differences between the oak wood species studied. Our study indicates that heating is the most important variable influencing the volatile compound content of oak wood chip samples.

After the toasting process, the important content of volatile compounds quantified in oak wood chips from Portuguese species (*Q. pyrenaica*) grown in Portugal, suggest that this oak species may be regarded as an im-

portant source of aromatic compounds. So, we conclude that they can be considered suitable for barrel production even, when presented lower concentrations of aromatic compounds in the unheated oak wood. Further experiments will be necessary. However, as regarding, thermal insulation, liquid tightness and porosity are other factors that it will be necessary to study in order to establish the real qualitative and quantitative potential of *Quercus pyrenaica* in enology in relation to the other traditional oak wood species used.

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