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ORIGINAL ARTICLE

**António M. Jordão · Jorge M. Ricardo-da-Silva
Olga Laureano · An Adams · Jan Demyttenaere
Roland Verhé · Norbert De Kimpe**

Volatile composition analysis by solid-phase microextraction applied to oak wood used in cooperage (*Quercus pyrenaica* and *Quercus petraea*): effect of botanical species and toasting process

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Abstract The purpose of this study was to investigate the sorption of selected volatile substances from oak wood-chip samples (*Quercus pyrenaica* Willd. and *Quercus petraea* L.) subjected to different toasting levels, namely, without toasting, with medium toasting, and with strong toasting, through the use of solid-phase microextraction (SPME). The main volatile compounds identified as a function of the toasting level and botanical species were furfural, hexanal, α-pinene, D-limonene, decanal, vitispirane, ethyl hexanoate, *cis*-3-methyl-γ-octalactone ("oak lactone" or "whisky lactone"), α-terpineol, *p*-xylene, and nonanal. Considering the data obtained from the toasted woods (medium and strong intensity) in comparison with those of nontoasted woods, it can be pointed out that the average peak area and the number of compounds identified in the gas chromatogram decreased during the toasting process. In general, regarding the compounds analyzed, quantitative differences were found between the two oak wood species under study. High values of volatile compounds were found in *Quercus pyrenaica* oak wood chips. In addition, for the number of compounds identified in oak wood extracts and directly extracted from solid oak wood chips by SPME, it is concluded that the best extraction process for volatile compounds from oak wood is the use of oak wood-chip liquid extracts.

Key words *Quercus pyrenaica* · *Quercus petraea* · Toasting level · Solid-phase microextraction · Volatile compounds

A.M. Jordão · J.M. Ricardo-da-Silva (✉) · O. Laureano
Universidade Técnica de Lisboa, Instituto Superior de Agronomia, Laboratório Ferreira Lapa (Sector de Enologia), Lisboa 1349-017, Portugal
Tel. +351-21-365-3542; Fax +351-21-365-3200
e-mail: jricardosil@isa.utl.pt

A. Adams · J. Demyttenaere[1] · R. Verhé · N. De Kimpe
Department of Organic Chemistry, Faculty of Agricultural and Applied Biological Sciences, Ghent University, Coupure Links 653, Ghent B-9000, Belgium

Present address:
[1] European Flavour and Fragrance Association (EFFA), Square Marie-Louise 49, Brussels B-1000, Belgium

Introduction

Oak barrel storage and ageing has been recognized as an integral part of fine winemaking for over 200 years. Wines are aged in oak barrels with three main objectives in mind, namely: the enrichment of the wine with substances released by the oak, the reactions due to contact with air diffusing in through the pores of the wood, and the development of certain interactive chemical reactions that slowly take place in wines. Aroma substances formed during oak wood ageing are important in wine as they contribute to the quality of the final product.

The concentration of extractive compounds found in oak wood is influenced by two sets of factors: the oak species and geographic origin[1–10] on the one hand, and the processing of the wood in cooperage (the method used to obtain the staves and the seasoning process used) and the degree of oak toasting during the barrel's manufacture,[11–14] on the other hand.

Despite these factors, the process of barrel toasting probably has the most important influence on the chemical compounds of the wood, which are susceptible to migrating into wine during their ageing, affecting the organoleptic properties of the wine.[15–17] As a consequence of the toasting process, there is a thermal degradation of some oak wood components, such as oak lignin, polysaccharides, and the two isomeric lactones called "oak" or "whisky" lactones,[18–20] and the appearance of new classes of odoriferous volatile substances such as pyrazines, furans, and phenols.[21] However, some compounds can be extracted from the unheated wood in small quantities (for example vanillin, phenols, such as eugenol, and traces of phenolic aldehydes).[9,22–24]

Within the analysis of food flavor, particularly of wine, sample preparation is the most time-consuming step. It is also the primary cause of losses of analytics from the matrix. Conventional methods, such as steam distillation or direct solvent extraction, give rise to extracts with a flavor composition that is representative for the liquid matrix but not for the headspace. Another drawback of conventional methods is that the extracts have to be concentrated prior to analysis, resulting in losses of low-boiling volatiles.

Solid-phase microextraction (SPME) provides many advantages over conventional sample preparation techniques (liquid, liquid–solid, and supercritical fluid extraction techniques). The SPME method is simple to use, fast and inexpensive, does not require solvent extraction, requires less sample preparation and manipulation time per sample, and allows characterization of the headspace in contact with the sample.[25] According to Pollnitz et al.,[26] this technique resulted in cleaner chromatograms, but with lower sensitivity than obtained from organic solvent extracts. However, in other cases, the proposed SPME strategies were not suitable for the analysis of the most polar compounds of wine.[27]

Other authors[28] reported that SPME is a highly suitable technique for analysis of the volatile composition of wines. In the same study, it was reported that the relative peak area of some compounds was greater when they were dissolved in water than when they were dissolved in a solution with 10% ethanol (usual in alcoholic beverages). Chatonnet et al.[14] stated that the SPME technique requires only a few minutes, while the maceration technique requires several days. Nevertheless, when compared with liquid–liquid extraction of wood with an internal standard, calibration of SPME for quantitative assays remains more difficult.

Although SPME has also been applied to the determination of specific trace components, such as diacetyl,[29] volatile and low volatile sulfides and disulfides,[30] wine flavor compounds,[28,31–33] oak lactones in barrel-aged wines,[26] the cork taint compound 2,4,6-trichloroanisole (TCA)[34] and even 3-alkyl-2-methoxypyrazines in spiked model wines,[35] it is not commonly applied to the analysis of volatile compounds in oak wood chips from *Quercus petraea* and especially from *Quercus pyrenaica*.

Thus, in this study, SPME was used for the analysis of the headspace of samples obtained from heated and unheated oak wood chips in order to identify the aroma substances from two different oak wood botanical species (*Quercus petraea* from France and *Quercus pyrenaica* from Portugal) used in cooperage.

Materials and methods

Oak wood samples

Attempts were made to obtain wood that was most representative of the species studied. The oak wood samples of *Quercus pyrenaica* (Gerês forest) that is grown in Portugal and the other species, *Quercus petraea* (from a French forest, Allier region), were kindly provided by J.M. Gonçalves Lda Cooperage (Palaçoulo, northern Portugal). The anatomical identification of these wood species has already been reported.[36–38]

The oak wood samples were made up of heartwood of trees ranging from 75 to 120 years of age, coming from homogeneous forest. For each species, 30 different tree samples were collected. In the cooperage, the oak wood staves in piles were seasoned in the open air for 24 months.

The staves from *Quercus pyrenaica* Willd. and *Quercus petraea* L., which were taken from the middle part of wood piles, were submitted to two different toasting intensities and temperatures: medium toasting (20 min at 160°–170°C on the wood surface) and strong toasting (27 min at 250°–260°C on the wood surface). In the toasted stave pieces, the layer of toasted wood was cut off to a depth of about 4 mm (maximum depth). For this study the coarseness of the grain used was: fine (1.0–2.8 mm) and medium (3.0–3.5 mm). Oak wood samples were taken from non-toasted and toasted staves and were reduced into chips with a particle size of less than 2 mm. They were then homogenized and kept in a dry atmosphere until analysis.

Extraction of odorous compounds from the wood

In order to reproduce extraction conditions that are similar to those in wine, the oak wood-chip samples used in this study were placed in 500 ml of a model alcohol solution at a concentration of 20 g/l [pH 3.5 and 12% (w/w) alcohol content] 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 SPME extraction process. For the solid oak wood-chip samples, the samples were directly extracted by headspace SPME.

SPME extraction and analysis

The SPME holder (for manual sampling) and fiber used in the analyses were purchased from Supelco (Bornem, Belgium). The fiber used in this work was coated with a 50/30 μm divinylbenzene-carboxen-polydimethylsiloxane (DVB-CAR-PDMS) phase. This fiber showed higher performance extraction efficiency than the 100-μm PDMS fiber previously tested (data not shown). Thus, the 100-μm PDMS fiber demonstrated a low extraction power for oak wood compounds. In addition, previous studies showed that DVB-CAR-PDMS fiber resulted in better performance for extracting different aroma compounds from wine[31] and model wine solutions.[35]

Before the first daily analysis, the fiber was conditioned for 5 min at 250°C in the gas chromatograph (GC) injector. An aliquot of 10 ml of model wine solution or 1 g of oak wood-chip sample was transferred into a 22-ml vial and the aroma compounds were extracted by headspace SPME for 30 min at 25°C. Prior to extraction, 3 g of NaCl (at saturation level) was added to each sample of the model wine solution. This was because maximum extraction is obtained from salt-saturated samples using NaCl.[39]

A magnetic stirer bar was also placed into the vial in order to maintain a constant and homogenous temperature (adjusted to 25°C using a thermostatic bath) and to improve the equilibrium of the compounds between the liquid sample and the headspace. With regard to the analysis of solid oak wood chips, the adsorption process was directly done from oak wood-chip samples used in our study. After extraction, the SPME fiber was desorbed in the GC injection part for 2 min at 250°C.

Gas chromatography-mass spectrometry

Gas chromatography-mass spectrometry (GC-MS) was performed on a HP 6890 gas chromatograph coupled with a HP 5973 mass selective detector. The gas chromatograph was equipped with a HP-5MS capillary column: 30 m × 0.25 mm i.d. coated with a 0.25-μm film of stationary phase. The column temperature was programmed from 40°C (held for 1 min) to 180°C at 5°C/min, then at 10°C/min to 220°C (held for 2 min). The carrier gas was helium (1.2 ml/min, constant flow). All analyses were done in triplicate.

The mass spectrometer was operated in electron impact mode (EI) and the masses were scanned over an *m/z* range of 40–300 amu (2–20 min) and 40–400 amu (20–35 min). The identification of sample compounds was based on comparison of the mass spectrum obtained with the mass spectral library (NIST/Mass Spectral Database version 1.d) and on the calculation of linear retention indices (LRI) followed by comparison with the literature.[40]

Statistical analyses

In order to study the influence of botanical species and heat treatment on the peak area of some volatile compounds in the oak wood chips under study, an analysis of variance and comparison of treatment means (ANOVA, one-way) was performed using SPSS software version 11.0 (SPSS, Chicago, Illinois, USA).

Results and discussion

Volatile compounds identified in oak wood by SPME

Wood is a highly complex substrate to analyse, due to its structure and the number and variety of its components ranging from almost insoluble macromolecules, for example, lignin and cellulose, to low molecular weight aliphatic acids and alcohols. Table 1 shows the different volatile compounds identified and the linear retention index (LRI) for the oak wood species studied (*Quercus pyrenaica* Willd. and *Quercus petraea* L.). Twenty different volatile compounds were identified by GC-MS. The majority of these compounds were detected in hydroalcoholic oak wood extracts (model wine solutions with 12% volume).

The results show that only five of the compounds identified (hexanal, furfural, α-pinene, D-limone, and α-terpineol) in *Quercus pyrenaica* by SPME were detected by direct analysis from solid oak wood samples (Table 1). Therefore, the best qualitative process for the extraction of aroma

Table 1. Volatile compounds identified from oak wood-chip samples (*Quercus petraea* and *Quercus pyrenaica*) determined by solid-phase microextraction (SPME)

Compounds	Linear retention índex (LRI)	Solid oak wood sample *Quercus pyrenaica*[a]	Hydroalcoholic oak wood extracts	
			Quercus pyrenaica	*Quercus petraea*
Esters				
Ethyl hexanoate	999	nd	D	D
Ethyl octanoate	1201	nd	D	D
Ethyl nonanoate	1302	nd	D	nd
Ethyl decanoate	1404	nd	D	D
Dibutyl maleate	1549	nd	D	nd
Aldehydes (acyclic or aliphatic)				
Hexanal	800	D	D	D
Nonanal	1105	nd	nd	D
Decanal	1208	nd	D	D
Aldehydes (cyclic or aromatic)				
Furfural	833	D	D	D
5-Methylfurfural	962	nd	nd	D
Monoterpenes				
α-Pinene	931	D	nd	nd
D-Limonene	1027	D	nd	nd
α-Terpineol	1194	D	nd	nd
Ketones				
2-(3*H*)-Furanone	1336	nd	D	D
Aromatic compounds				
p-Xylene	865	nd	D	D
Toluene	761			
1,3,5-Trimethylbenzene	991	nd	D	nd
Sesquiterpene				
Vitispirane	1286	nd	D	nd
Lactones				
cis-3-Methyl-γ-octalactone	1331	nd	D	D
Other compound				
1,1-Diethoxyethane	726	nd	D	D

D, detected; nd, not detected
[a] Unheated oak wood-chip samples

compounds from oak wood was the hydroalcoholic extraction. The maceration process of oak wood chips in hydroalcoholic solutions permits the dissolution of a great number of volatile compounds in the liquid phase, allowing the SPME extraction of more compounds. Only the extremely volatile compounds or the major quantitative compounds present in the headspace of solid oak wood samples can be detected by SPME.

The amount of an analytic adsorbed on the SPME fiber and the resulting sensitivity is determined both by sorption kinetics and by the distribution coefficient of the compound. Direct analyses from solid oak wood chips require a much longer equilibration time due to slow diffusion in comparison with liquid samples with agitation. Using solid samples, the mass transport of the analytics is limited by migration through the matrix. Naturally, the compounds closer (more volatile or in high quantitative content) to the fiber penetrate into it faster than the more distant analytics. Thus, slow diffusion from the solid sample reduces the concentration gradient at the fiber coating surface, thereby limiting the analytic transport into the fiber.

To accelerate the volatilization of the wood's volatile compounds in the gas phase and to increase the number of compounds analyzed, other authors[14] heated 1 g of dry oak wood for 30 min at 80°C in a ventilated oven. The headspace was then sampled by inserting a fiber used for SPME. Using this procedure, similar results were obtained in comparison with the use of hydroalcoholic model solutions in liquid–liquid extraction.

Additionally, a long extraction time may help the less volatile components or the compounds with relatively large molecular size to escape to the headspace. The sample temperature and the exposure time are parameters that can be optimized experimentally in the future. Previously, other authors[33] studied the optimization of SPME for the analysis of wine aroma compounds and found that sampling times of up to 60 min and a sample temperature of 35°C can result in an increased sensitivity for less volatile analytics, especially polar compounds. Nevertheless, for more volatile or nonpolar analytics, lower temperatures and shorter sampling times may be optimal. Zhang and Pawliszyn[41] reported that the sensitivity of the SPME coating to less volatile compounds was high, but low partition coefficients for these compounds between the sample and the headspace resulted in long equilibration times, which explains the ester behavior.

In this study (Tables 1 and 2), only D-limonene, α-terpineol, and α-pinene were detected in solid oak wood samples from unheated *Quercus pyrenaica*. These terpenes were not detected in the aqueous ethanol extracts, which is probably due to their insolubility in water in combination with the competitive effect of ethanol.

Table 2 shows the average peak area of the compounds detected in unheated solid oak wood chips in comparison with the area values from hydroalcoholic extracts. Only hexanal and furfural were detected in both samples. For hexanal, similar results were obtained in both oak wood samples (solid samples and hydroalcoholic wood extracts). However, for furfural, higher peak areas were measured in the analysis of solid oak wood chips than in hydroalcoholic oak wood extracts (Table 2).

These results indicate that the best SPME extraction process of aroma compounds from oak wood is by using oak wood-chip extracts (model wine solutions) except for the analysis of monoterpenes. Furthermore, it can be suggested from these results that SPME is an appropriate sampling technique to analyze an important number of oak wood volatile compounds.

Influence of the botanical species

The concentration of extractive compounds found in oak wood is influenced by several factors, especially the oak species.[2–5,8,20,42] According to Miller et al.,[43] the botanical species is an important factor to explain the difference in the composition of wood.

Table 3 shows the volatile compounds identified and semiquantified (using the chromatographic peak area in arbitrary units) in *Quercus pyrenaica* and *Quercus petraea*. From the total average peak area of the volatile compounds identified, it is concluded that *Quercus pyrenaica* (Portuguese oak) released significantly more volatile compounds than *Quercus petraea* (a total average peak area of 2.53×10^7 and 8.65×10^6, respectively, for *Quercus pyrenaica* and *Quercus petraea* oak wood chips).

Hexanal, furfural, vitispirane, and ethyl nonanoate were not detected in the unheated French oak wood chips (*Q. petraea*). This is especially important for furfural, because this compound has an important role in the organoleptic properties of wines matured in oak barrels. Nevertheless, other authors[44–46] detected furfural in oak wood from

Table 2. Average peak area of furfural, hexanal, D-limonene, α-terpineol, and α-pinene from unheated solid oak wood-chip samples and from hydroalcoholic oak wood extracts (*Quercus pyrenaica*) determined by SPME

Compounds	Solid oak wood samples		Hydroalcoholic oak wood-extract samples	
	Average peak area	Standard deviation	Average peak area	Standard deviation
Hexanal	5.77×10^5	4.19×10^4	5.65×10^5	1.38×10^4
Furfural	4.47×10^6	4.55×10^5	1.68×10^6	8.77×10^4
D-Limonene	1.51×10^6	6.75×10^4	nd	–
α-Terpineol	1.09×10^6	1.15×10^5	nd	–
α-Pinene	5.36×10^5	1.62×10^4	nd	–

Data given as area units of chromatograph peaks, mean of three analyses
nd, Not detected

Table 3. Average peak area of volatile compounds from unheated *Quercus pyrenaica* and *Quercus petraea* hydroalcoholic oak wood solutions by SPME

Compounds	*Quercus pyrenaica*		*Quercus petraea*	
	Average peak area	Standard deviation	Average peak area	Standard deviation
1,1-Diethoxyethane	7.0×10^6	1.12×10^5	5.0×10^3	1.0×10^2
Hexanal	5.65×10^5	1.38×10^4	nd	–
Furfural	1.68×10^6	8.77×10^4	nd	–
p-Xylene	1.4×10^6	4.42×10^4	1.11×10^6	3.11×10^3
Ethyl hexanoate	2.27×10^6	1.05×10^5	9.73×10^5	2.24×10^2
Nonanal	2.71×10^6	1.82×10^5	2.44×10^6	1.34×10^2
Ethyl octanoate	1.33×10^6	2.42×10^4	1.22×10^6	1.90×10^3
n-Decanal	1.36×10^6	1.54×10^5	8.66×10^5	2.59×10^2
Vitispirane	1.19×10^6	7.75×10^4	nd	–
Ethyl nonanoate	9.40×10^5	1.21×10^5	nd	nd
cis-3-Methyl-γ-octalactone	1.20×10^6	3.75×10^4	1.26×10^6	1.1×10^3
Ethyl decanoate	6.70×10^5	7.47×10^4	5.94×10^5	1.70×10^3
Total average peak area	2.53×10^7*		8.65×10^6*	

Data given as area units of chromatograph peaks, mean of three analyses
nd, Not detected
* $P < 0.05$ by analysis of variance

Quercus petraea by using liquid–liquid extraction. It is possible that furfural was present in a concentration that was too low to be detected by SPME under the given experimental conditions. Thus, these data suggest that the use of other SPME conditions, such as the sample volume, exposure time, or temperature, could improve the adsorption of the compounds (for example, furfural in low concentrations). In addition, according to Pozo-Bayón et al.[28] it is also necessary to verify the influence of the presence of ethanol on the extraction of the compounds by the fiber. Thus, these authors reported for other compounds (butyl acetate and 1-hexanol) that the peak area of these two compounds is greater when they are dissolved in water than when they are dissolved in a solution with 10% ethanol.

1,1-Diethoxyethane, ethyl hexanoate, hexanal, furfural, ethyl nonanoate, and decanal were present in higher amounts in *Quercus pyrenaica* extracts as compared with *Quercus petraea*. Furthermore, the average peak areas of the other compounds were similar in both oak wood species under study. Pérez-Coello et al.[47] have already identified hexanal, furfural, nonanal, decanal, and ethyl decanoate in *Quercus petraea* using two different fractionation methods, i.e., Soxhlet extraction and simultaneous distillation-extraction followed by GC-MS analysis.

The β-methyl-γ-octalactones (oak lactones) are the most interesting organoleptic components of the wood because of their very low odor thresholds.[48] According to Chatonnet et al.,[48] the *cis* form is sensorially the most important and shows a perception threshold in wines aged in oak wood barrels of 92 μg/l. These compounds are regarded as the main source of the characteristic oak aroma of wood-aged wines[47,49,50] and have frequently been used to distinguish oak wood species. Nevertheless, in our study, (*cis*)-3-methyl-γ-octalactone was present in both oak wood species with similar peak area.

Thus, the results of the content of the different volatile compounds analyzed by SPME for the two species studied (i.e., *Quercus pyrenaica* and *Quercus petraea*) suggest that the effect of botanical species is significant.

Influence of toasting process

Heating operations during oak barrel manufacture modify the macromolecular structure of wood, leading to degradation of polysaccharides and polyphenols, the appearance of new compounds, and an increase of odoriferous volatile substances such as furans and some phenols.

The effect of heat treatment on oak wood volatile composition quantified using SPME is shown in Table 4. An increase of the total values after heat treatment was observed for all compounds and was independent of the botanical species, when compared with the values obtained in unheated wood chips (Table 2). These results are in accordance with previous studies.[3,9,19,21]

The increases of the values were more evident between unheated wood and in oak wood with medium toasting than between oak wood with strong toasting and medium toasting. Toasting for long periods leads to uncontrolled decomposition of lignin and other compounds (especially the compounds with high volatility) or even to the destruction of part of the compounds formed during the first stages of the toasting process. For *Quercus pyrenaica*, the increase of the total average peak area was from 2.53×10^7 in unheated wood chips to 1.39×10^8 in medium toasting followed by a decrease of the area values in strong toasting (total average peak area of 6.77×10^7). For individual compounds, *p*-xylene (only in *Quercus pyrenaica* oak wood), 5-methylfurfural-2-furancarboxaldehyde, and 1,3,5-trimethylbenzene were not detected in oak wood after strong toasting. According to Gimenez-Martinez et al.,[19] this decrease is a consequence of uncontrolled decomposition of several compounds (lignin for example), which, in turn, causes the formation of much less reactive compounds or even the destruction/decomposition of part of the

Table 4. Influence of heat treatment on average peak area of volatile compound contents from *Quercus pyrenaica* and *Quercus petraea* oak wood chips determined by SPME

Compounds	*Quercus pyrenaica*				*Quercus petraea*			
	Medium toasting		Strong toasting		Medium toasting		Strong toasting	
	Average peak área	Standard deviation	Average peak area	Standard deviation	Average peak area	Standard deviation	Average peak area	Standard deviation
1,1-Diethoxyethane	7.06×10^6	9.12×10^5	8.98×10^6	9.39×10^4	6.0×10^3	1.7×10^2	4.17×10^6	2.52×10^4
Toluene	1.70×10^6	5.76×10^5	2.32×10^6	2.49×10^5	1.89×10^6	8.47×10^5	1.41×10^6	1.99×10^5
Hexanal	1.32×10^6	2.95×10^5	8.11×10^5	2.78×10^4	nd	–	9.02×10^5	4.98×10^4
Furfural	1.08×10^8	1.80×10^6	6.63×10^7	8.35×10^6	nd	–	4.67×10^7	2.14×10^6
p-Xylene	1.99×10^6	1.80×10^4	nd	–	1.11×10^6	3.11×10^5	1.17×10^6	1.96×10^5
5-Methylfurfural	9.11×10^6	1.04×10^6	nd	–	4.28×10^6	4.48×10^5	nd	–
Ethyl hexanoate	nd	–	nd	–	9.03×10^5	2.23×10^4	nd	–
1,3,5-Trimethylbenzene	5.51×10^5	4.29×10^4	nd	–	nd	–	nd	–
Nonanal	nd	–	nd	–	nd	–	nd	–
Ethyl octanoate	5.13×10^6	9.63×10^5	2.08×10^6	1.80×10^5	1.22×10^6	1.90×10^4	1.21×10^6	1.67×10^5
n-Decanal	9.38×10^5	5.11×10^4	nd	–	8.66×10^5	2.59×10^4	5.70×10^5	5.14×10^4
cis-3-Methyl-γ-octalactone	2.04×10^6	3.88×10^5	1.98×10^4	0.98×10^3	2.24×10^6	1.22×10^5	2.16×10^6	6.51×10^4
2-(3*H*)-Furanone	nd	–	6.52×10^5	9.27×10^4	1.79×10^6	1.97×10^5	2.75×10^6	4.56×10^5
Ethyl decanoate	2.24×10^6	3.47×10^5	1.20×10^6	1.52×10^5	5.04×10^5	1.61×10^5	1.08×10^6	3.41×10^5
Dibutyl maleate	1.26×10^6	2.22×10^5	nd	–	nd	–	nd	–
Total average peak area	1.39×10^8 A		6.77×10^7 B		1.48×10^7 B		6.21×10^7 B	

Data given as area units of chromatograph peaks, mean of three analyses. Average peak areas followed by different letters are significantly different; $P < 0.05$
nd, Not detected

compounds responsible for the aroma of alcoholic beverages.

The evolution of peak areas obtained shows that for Portuguese oak (*Quercus pyrenaica*) wood chips, the increase of the values with the toasting process was less evident than for the French oak wood chips. According to Vivas et al.,[51] the quality and quantity of each volatile compound are narrowly related to the toasting intensity, but the particular characteristics of each species can also determine the rate of modification during the toasting process.

Considering the peak areas obtained for individual volatile compounds from all toasted oak wood species (Table 4), it can be pointed out that in general the values increase significantly with the toasting process. Furan derivatives [furfural, 5-methylfurfural, and 2-(3*H*)-furanone], hexanal, ethyl decanoate, and dibutyl maleate displayed the greatest influence of the toasting process. These compounds showed the highest increment, especially furfural (from 1.68×10^6 to 1.08×10^8 average peak area in Portuguese oak wood chips), 5-methylfurfural (not detected in unheated Portuguese oak wood and with a average peak area of 9.11×10^6 in medium toasting) and 2-(3*H*)-furanone (not detected in unheated French oak wood chips and with a average peak area of 1.79×10^6 in medium toasting). The increase of the values is in accordance with previous studies.[2,4,19]

The important increase in furan derivatives, furfural, 5-methylfurfural, and 2-(3*H*)-furanone in toasted oak wood, as opposed to the unheated oak, reflects sugar degradation during the toasting process. Because the hemicelluloses are the most thermosensitive polymers in wood,[52] they are preferentially degraded during heat treatment, thus leading to furfural and contributing to make furfural the main furanic derivative in toasted oak wood.[53,54]

In this study, the variation of *cis*-3-methyl-γ-octalactone (Table 4) did not show a great increment with heat treatment. Therefore, for Portuguese oak wood, the average peak area ranged from 1.20×10^6 in unheated wood to 2.04×10^6 for medium toasting, followed by a decrease of average peak area values with strong toasting (1.98×10^4 average peak area). There are conflicting accounts in the literature concerning the effect of heating wood on the concentration of oak lactones in wood extracts. Hence Marsal and Sarre[55] reported a decrease of oak lactone levels extracted from toasted wood, when compared with extracts of unheated wood, whereas another author[56] reported an increase in oak lactone concentrations as a result of charring. Additionally, Sefton et al.[18] reported that the oak lactone levels were not significantly affected when wood samples were heated to 175°C.

In this study, it became evident that the toasting process had a significant influence on the volatile composition of the two botanical species studied. The differences in extractable compounds for each wood species could not be simply explained by different heat treatments. In fact, the physical properties and the structure of wood, such as the proportion of latewood to earlywood and the abundance of fibers, may influence heat conduction and reactions upon heating. Furthermore, the degradation of cellulose and other polyoses and lignin is considerably different for different wood species.[52] All these factors influence the results of the SPME/GC-MS analysis.

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