

VOLATILE COMPOUNDS FROM OAK, CHERRY, CHESTNUT AND ACACIA CHIPS: INFLUENCE OF TOASTING LEVEL

COMPOSIÇÃO VOLÁTIL DE APARAS DE CARVALHO, CEREJEIRA, CASTANHEIRO E ACÁCIA: INFLUÊNCIA DO NÍVEL DE QUEIMA

Nuno Martins¹, Raquel Garcia¹, Marco Gomes Da Silva³, Maria João Cabrita^{1,2*}

¹Instituto de Ciências Agrárias e Ambientais Mediterrânicas (ICAAM), Universidade de Évora, Portugal.

²Departamento de Fitotecnia, Escola de Ciências e Tecnologia, Universidade de Évora, Ap 94 7002-554, Évora, Portugal.

³REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal.

* Corresponding author: T. 351 266 769869; F. 351 266 769828, e-mail: mjbc@uevora.pt

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SUMMARY

In the present study, the volatile composition of wood chips from several botanical species potentially relevant for oenological purposes, namely acacia (unknown specie), chestnut (*Castanea sativa*), cherry (*Prunus cerasus*) and oak (*Quercus robur*) was studied by GC/MS. In order to evaluate the effect of the toasting process on volatile compounds contents we have extended our study to wood chips from the botanical species described above, subjected to different toasting levels, such as untoasted and medium toast. To achieve this goal, a preliminary step comprising the extraction of the volatile compounds by pressurized liquid extraction (PLE) has been performed followed by the analysis and identification of those compounds by GC/MS. The identification was tentatively achieved attending to the characteristic fragmentation patterns of these compounds and by comparison with those reported in the literature. The determination of linear retention indexes has allowed the confirmation of those attributions. Within this study, we were able to identify 45 compounds, arising from polysaccharides, lipids, lignin and polyphenols degradation. Additionally, 16 other compounds were identified in the different wood species under study although their origin is not fully known. In general, our results showed differences among the volatile composition of the different botanical species studied in this work and the influence of toasting degree was also observed in this study.

RESUMO

No presente estudo, os compostos voláteis de aparas de madeira de diferentes espécies botânicas potencialmente relevantes em enologia, acácia (espécie desconhecida), castanheiro (*Castanea sativa*), cerejeira (*Prunus cerasus*) e carvalho (*Quercus robur*) foram estudados por GC/MS. De forma a se poder avaliar o efeito da queima no teor em compostos voláteis, este estudo foi também efectuado em aparas de madeira das espécies acima indicadas, sujeitas a diferentes níveis de queima: não queimadas e queima média.

A primeira etapa deste estudo consistiu na obtenção dos compostos voláteis das amostras em estudo por extracção com solvente pressurizado (PLE), seguida da análise dos extractos obtidos por GC/MS. A identificação dos compostos foi efectuada por comparação com os padrões de fragmentação dos compostos em estudo, por comparação com os referidos na literatura. A determinação dos índices de retenção linear permitiu a confirmação da identificação. Foram identificados 45 compostos, provenientes da degradação dos polissacarídeos, lípidos, lignina e polifenóis. Foram ainda identificados 16 compostos, embora a sua origem não seja totalmente conhecida. Os resultados demonstram que as diferentes espécies botânicas em estudo apresentam diferenças na composição volátil. O efeito da queima na composição volátil foi também observado.

Key words: wood chips, volatile compounds, PLE, GC/MS.

Palavras-chave: aparas de madeira, compostos voláteis, PLE, GC/MS.

INTRODUCTION

After an extensive research on volatile compounds of oak, researchers are now interested in other wood species, namely chestnut, acacia and cherry. The increasing interest on other woods than oak are linked to the possible use of wood fragments instead of barrels.

Botanical species and technological treatments during cooperage such as seasoning and toasting, plays a relevant role in final volatile composition of woods (Chatonnet and Dubourdiou, 1998; Canas *et al.*, 1999; Cadahía *et al.*, 2001; Doussot *et al.*, 2002; Pérez-Prieto *et al.*, 2002; Cadahía *et al.*, 2003; Arfelli

et al., 2007; Canas *et al.*, 2011; Alañón *et al.*, 2012).

The main botanical species used in cooperage is oak (genus *Quercus*) and in a lesser extension, chestnut (genus *Castanea*). The oak species more used in cooperage are *Quercus alba* (American oak), *Quercus patraea* Liebl. (sessile oak), *Quercus robur* L. (pedunculate oak) and *Quercus pyrenaica*. In 2005, OIV approved (Resolution Oeno 3/2005) the use of oak and chestnut wood fragments, like chips and staves. Then, researchers were looking into other kind of woods which were abandoned in the past due to the lack of cooperage properties. The chemical compounds released from acacia, chestnut, cherry,

mulberry and oak untoasted woods into alcoholic extracts, shows that each wood has a different and characteristic volatile compound profiles (Flamini *et al.*, 2007, Rosso *et al.*, 2009, Fernández de Simón *et al.*, 2009b).

Among all variables that can influence wood characteristics and their impact on wine or spirits sensory changes, heating is the most important. Toasting has a significant influence on wood's chemical compounds, modifying both the quantity and the quality of the extractable substances (Cutzach *et al.*, 1997; Chatonnet, 1999). The toasting process drastically enhances the gain in volatile compounds arising from the thermal degradation of oak wood (Cutzach *et al.*, 1997; Chatonnet, 1999; Doussot *et al.*, 2002), so it is expectable the same influence on other wood species. The extent of the chemical changes during thermal treatment depends considerably on the chemical structure of the wood species apart from many other factors, such as the type and the duration of thermal treatment (Windeisen and Wegener, 2008).

When heat is applied to wood during toasting process, chemical bonds are disrupted within biopolymers such as cellulose, hemicellulose, lignin, polysaccharides, polyphenols and lipids, resulting in degradation or compositional changes by pyrolysis and thermolysis (Fernández de Simón *et al.*, 2009b; van Jaarsveld *et al.*, 2008), which induce a notable modification of wood chemical composition.

Volatile phenols, phenolic aldehydes, phenyl ketones and some phenyl alcohols are mainly formed from lignin thermodegradation. In particular, high levels of mono and dimethoxylated phenols, benzoic and cinnamic aldehydes were identified in toasted wood. Lignin is a complex polymer synthesized from phenylpropanoid monomers, and with thermal processing yields a range of products, of which the most characteristic ones are methoxy phenols (Asghari and Yoshida, 2010).

Heat degradation of polyosides leads to the production of furanic aldehydes, pentacyclic and hexacyclic ketones. Lactones, formed from wood lipids, increase their concentration at the beginning of toasting, although they can be destroyed by a lengthy toasting process (Giménez-Martínez *et al.*, 1996; Chatonnet, 1999; Cadahía *et al.*, 2003). This thermo degradation process leads to the formation of several compounds that can be transferred to wine and spirits during aging or maturation, hence, extensive information about the volatile composition of wood used in cooperage would be of great interest to the wine industry.

In order to study volatile fraction of wood species and the influence of the toasting process in a very complete way, three approaches should be considered: the volatiles existing in wood itself, the volatile that are extracted into an hydroalcoholic solution in order to avoid matrix effect, and finally the volatiles of wines fermented or matured with these woods.

Sample preparation methods and chromatography techniques within this purposed has been recently reviewed by Cabrita *et al.* (2012).

In this work the volatile fraction from woods were studied by GC/MS in acacia (unknown specie), chestnut (*Castanea sativa*), cherry (*Prunus cerasus*) and oak (*Quercus robur*) chips, subjected to different toasting levels, in order to compare untoasted and medium toasted woods.

To achieve that goal we have used a method based on Pressurized Liquid Extraction (PLE) for the extraction of volatile compounds from wood samples. The PLE, also known as "Accelerated Solvent Extraction" (ASE) was introduced in 1996 (Richter *et al.*, 1996) and is one of the most useful techniques for extraction of non-polar and medium polar solutes from solid and semi-solid samples. Among the extraction methods that use organic solvents, PLE has been proposed as an improved exhaustive extraction method that requires only small volumes of solvents and allows faster and systematic extractions of compounds.

MATERIAL AND METHODS

Chemicals

Dichloromethane, chromatographic grade, and anhydrous sodium sulphate were from Panreac (Barcelona, Spain), diatomaceous earth (ASE® Prep DE) was from Dionex and 3-Octanol was purchased from Extrasintese (Genay, France). The alkanes mixture, from C7 to C30 was from Supelco Analytical (Bellefonte, USA).

Samples

Wood samples from acacia, chestnut, oak and cherry were provided as chips, untoasted (UT) and medium toast (MT, 2 hours at 200°C) by JM Gonçalves Cooperage industry. Woods were seasoned in the open air during 25 months for cherry and acacia, 22 month for chestnut and 32 month for oak. Toasting characteristics are protected by industry secret. Botanical species were: oak (*Quercus robur*) chestnut (*Castanea sativa*), acacia (unknown specie), and cherry (*Prunus cerasus*). Acacia is usually *Robinia pseudoacacia* L., False Acacia or Black Locust, commonly named acacia instead of robinia.

Sample Extraction

Extraction of oak chips was performed by using an Accelerated Solvent Extractor ASE 100 (Dionex, ASE 100). About 3g of exactly weighed wood chips, dispersed in 1.5g of diatomaceous earth, was placed into the sample cell, which was filled with dichloromethane and raised to 150°C. After the selected temperature had been reached, a three times pressurized static extraction phase (7 min) at 20 MPa were carried out.

The obtained extracts (ca 30 mL) were added to sodium sulfate, filtered, and concentrated to approximately 2 mL in an evaporative rotavapor (BUCHI Rotavapor R-114). 3-Octanol (1 mL of 0.08mg/mL solution) was added as internal standard before concentration. Extraction procedure was based on Natali *et al.* (2006).

The chips wood samples were previously grounded in a coffee mill into powder, and after this procedure, were extracted as described above. Samples were prepared in triplicate.

GC/MS analysis

A Thermo Finnigan Trace GC gas chromatograph (Thermo Finnigan, Austin, TX), equipped with a Thermo Finnigan Polaris Q mass selective detector was used. Samples (1 μ L) were injected in the splitless mode and volatiles were separated using a fused silica capillary column, ZB-Wax 30 m, 0,25 mm i.d and 0,25 μ m film thickness (Zebron Capillary GC column; Phenomenex USA) under the following working conditions: GC grade helium as carrier gas at a flow rate (constant flow) of 1.0 mL/ min; column temperature program, 40°C (held 1 min) heated at 4 °C/ min to 100 °C and then heated at 8 °C/min to 250°C (held for 10 min). The injection temperature was 250°C. Detection was carried out by positive ion electron impact (EI) mass spectrometry in the full scan mode, using an ionization energy of 70 eV and a transfer line temperature of 250°C.

The mass acquisition range was m/z 40-450 and the scanning rate 1 scan s⁻¹. Chromatographic peaks were identified by comparing their mass spectra with those reported in the literature and in commercial libraries NIST 2.0 and Wiley 7. The linear retention index values were calculated in the polar column described and also in a apolar column, Rtx-5 (Crossbond 5% diphenil – 95% dimetil polysiloxane) 30 m, 0.25 mm i.d and 0.25 μ m film thickness (RESTEK, USA). For each compound, the linear retention indexes calculated were compared with that reported by other authors. Semi-quantitation was carried out from total ion current peak areas according to the internal standard method. Results were expressed as mg of 3-octanol per 100 grams of wood.

RESULTS AND DISCUSSION

Identification of volatile compounds

The GC/MS analysis of wood extracts revealed the presence in these woods of several molecules already described in literature. But some compounds not usually referred in literature were also identified. Table I gives the compounds that were identified in at least one sample under study, together with the retention index for columns, their fragmentation pattern and the aromatic notes usually associated with these compounds.

TABLE I

Volatile and semi-volatile compounds found in at least one wood sample

Compostos voláteis e semi-voláteis encontrados em, pelo menos, uma das amostra de madeira.

<u>Common Name</u>	<u>IUPAC name</u>	<u>RT (min)</u>	<u>m/z fragments</u>	<u>LRI apolar column</u>	<u>LRI polar column</u>	<u>Aromatic notes</u>	<u>Woods where compound is detected</u>
FROM POLYSACCHARIDES							
Furanic aldehydes							
Furfural	2-Furancarboxaldehyde	15,07	95(100), 96 (40)	834 834 ^(a)	1458 1444 ^(b)	Bread, sweet almond ⁽ⁱ⁾ , caramel ^(h)	All
5-Methylfurfural	5-Methyl-2-furancarboxaldehyde	17,67	109(100), 110 (70)	968 965 ^(a)	1563 1551 ^(b)	Almonds, caramel ⁽ⁱ⁾ , spicy, toast ^(h)	All
5-Hydroxymethyl-furfural	5-Hydroxymethyl-2-furancarboxaldehyde	30,23	97(100), 69(70), 126 (20)	1253 1235 ^(a)	2492 2466 ^(b)	Odorless ⁽ⁿ⁾	All
Maltol	3-Hydroxy-2-methyl-4H-pyran-4-one	23,98	126 (100), 71(35)	1119 1111 ^(a)	1950 1938 ^(b)	Toast ⁽ⁿ⁾	All
Alcohols							
Furfuryl alcohol (isomer)	2-Furanmethanol	19,43	97(100), 81(80), 98 (70)	(-) 866 ^(a)	1651 1669 ⁽ⁱ⁾	Yeast, toast, sugar ^(v)	All
Acids							
Acetic acid	Ethanoic acid	10,11	43(100), 45(15), 60 (5)	(-) 602 ^(e)	1291 1464 ^(f)	Vinegar ^(f)	All

Nitrogen heterocycles							
Pyridine	Pyridine	6,84	79(100), 52(95), 51(90)	(-) 753 ^(a)	1171 1193 ⁽ⁱ⁾	Cocoa, almond, bread ^(s)	All
FROM LIGNIN AND POLYPHENOLS							
Volatile phenols							
Eugenol	2-Methoxy-4-(prop-2-enyl) phenol	28,58	164(100), 77(40), 103(40)	1365 1359 ^(a)	2335 2139 ^(b)	Clove, honey ⁽ⁱ⁾ spicy, cinnamon ^(b)	All
Guaiacol	2-Methoxyphenol	22,58	81(100), 109(80), 124(95)	1093 1089 ^(a)	1849 1833 ^(b)	Smoky, sweet, medicine ⁽ⁱ⁾	Oak, acacia
Guaiacylacetone	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)	31,75	137(100), 180(30), 122(30)	1543 -	2643 -	-	Oak, acacia, chestnut
4-Propylguaiacol	4-Propyl-2-methoxyphenol	31,23	137(100), 166(30)	(-) 1461 ^(a)	2589 2083 ^(b)	Leather, animal ^(m)	Oak, acacia, chestnut
Allylsyringol (isomer)	2,6-dimethoxy-4-propen-2-yl-phenol	30,58	194(100), 91(70), 119 (50)	1613 1605 ^(a)	2525 2511 ^(b)	Spicy, smoky ^(m)	All
<i>cis</i> or <i>trans</i> Propenylsyringol	<i>cis</i> or <i>trans</i> -2,6-Dimethoxy-4-(1-propenyl)phenol	32,47	194(100), 91(50)	(-) -	2718 -	-	All
Syringyl propan-2-one	1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propanone	35,28	167(100), 210(45)	(-) -	(-) -	-	Oak, acacia, chestnut
Syringyl ethyl ether ^(z)	4-Hydroxy-3,5-dimethoxybenzoic acid, methyl ether	40,73	168(100), 167(75), 194(5), 212(80)	(-) -	(-) -	-	Oak, chestnut
Phenolic aldehydes							
Vanillin	3-Hydroxy-4-methoxybenzaldehyde	30,80	151(100), 152(85)	1407 1399 ^(a)	2555 2518 ^(b)	Vanilla ⁽ⁱ⁾	All
Benzaldehyde	Phenylmethanal	16,43	105(100), 77(65), 106(20)	(-) 962 ^(a)	1507 1493 ^(b)	Bitter almonds ^(b)	Chestnut, cherry, acacia
Coniferaldehyde	4-Methoxy-3-Hydroxy-cinnamaldehyde	37,08	178(100), 77(100)	1722 1747 ^(a)	(-) 3096 ^(b)	Vanilla, woody ⁽ⁿ⁾	All
2,4-Dihydroxybenzaldehyde ^(z)	Benzaldehyde, 2,4-dihydroxy	37,11	137, 138	1470 -	(-) -	-	Chestnut, cherry, acacia
Syringaldehyde	4-Hydroxy-3,5-dimethoxybenzaldehyde	34,54	182(100), 181(75)	1677 1643 ^(a)	2935 2904 ^(b)	Vanilla ⁽ⁱ⁾	All
Phenolic esters							
Methyl homovanillate	4-Hydroxy-3-methoxybenzoic acid, methyl ester	39,38	137(100), 196(30)	(-) 1518 ^(a)	(-) 2565 ^(b)	Caramel, butter, vanilla ⁽ⁱ⁾	Oak, chestnut
Benzoic acid, vinyl ester	Benzoic acid, vinyl ester	19,11	41(100), 148(5), 105(10)	(-) -	1635 -	-	Oak, acacia, cherry
Phenylketones							
Acetosyringone	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)	35,05	181(100), 196(70)	(-) 1744 ^(a)	2982 2953 ^(b)	Fruity, sweet ^(v)	Oak, chestnut, cherry
Alcohols							
Coniferyl alcohol	4-(1- <i>trans</i>)-3-Hydroxy-prop-1-enyl-2-methoxyphenol	39,05	137(100), 180(65), 124(65)	1817 1745 ^(a)	(-) 3213 ^(b)	-	All
Benzyl alcohol	Hydroxy methylbenzene	22,80	79(100), 77(65), 108(35)	(-) -	1864 1879 ^(p)	Sweet, floral ^(m)	Cherry

Phenylethyl alcohol ⁽³⁾	2-Phenylethanol	23,26	91(100), 92(55), 122 (10)	(-) 1110 ^(w)	1897 1931 ^(w)	Sweet, floral, spicy ^(v)	Chestnut, cherry
Acids							
Benzoic acid	Benzenecarboxylic acid	29,72	105(100), 122 (70), 77(65)	(-) 1310 ^(u)	2442 -	Balsamic ^(v)	Cherry
Homovanillic acid	Benzenecarboxylic acid, 4-hydroxy-3-methoxy	34,91	137(100), 138(50), 182 (55)	(-) -	2969 3008 ⁽¹⁾	-	Cherry

FROM LIPIDS

Lactones							
β -Methyl- γ -octalactone (<i>cis</i>)	<i>cis</i> -4-Methyl-5-butylidihydro-2(3 <i>H</i>)-furanone	22,91	40(100), 99(50), 156 (5)	(-) 1325 ^(a)	1872 1928 ^(b)	Sweet, coconut ^(j) woody ^(k,l)	Oak, chestnut, cherry
Acids							
Propanoic acid	Propanoic acid	17,42	73(100), 45(70), 74 (30)	(-) 668 ^(g)	1552 1547 ⁽³⁾	Fruit, floral ^(q)	Oak
Butanoic acid	Butanoic acid	18,86	41(100), 60 (80), 55(60), 73(35),	(-) 827 ^(g)	1620 1627 ^(d)	Sweaty, cheese unpleasant ^(h)	Cherry
Hexadecanoic acid	Hexadecanoic acid	36,66	55(100), 43(90), 73(75), 60(40)	(-) 1984 ^(s)	(-) 2820 ^(d)	Oily ^(v)	All
Aldehydes							
2-Nonenal	2-Nonenal	16,77	41(100), 55(75), 140 (5)	(-) 1142 ^(y)	1522 1510 ^(z)	Green, fatty ^(v)	Oak, chestnut, acacia

FROM CAROTENOIDS

Other furānicos							
1-(2-Furanyl)-ethanone ⁽²⁾	Ethanone, 1-(2-furanyl)	16,9	95(100), 110 (20)	(-) 912 ^(c)	1493 1483 ^(c)	-	Oak, chestnut
Others							
Toluene	Toluene	19,03	91(100), 92 (40), 65(30)	(-) 770 ^(e)	1630 -	Caramel, fruit ^(v)	All

OTHERS

Acetate of 2-methoxy-4-allylphenyl	Acetate of 2-methoxy-4-allylphenyl	26,53	164(100), 103(60), 165(5)	(-) -	2154 -	-	All
Furancarboxylic acid*	2-Furancarboxylic acid	23,91	112 (50), 95(50)	(-) 1079 ^(e)	1943 -	-	All
Linear alcohol C14-C18 ⁽⁷⁾	-	28,84	208(100), 177(70)	(-) -	2359 -	-	All
Linear alcohol C14-C18 unsaturated ⁽⁷⁾	-	30,97	41(100), 180(60)	(-) -	2564 -	-	All
Antiarol	Phenol, 3,4,5-trimethoxy	35,84	169(30), 184 (25)	1627 -	(-) 2960 ⁽³⁾	-	Chestnut, cherry, acacia
Benzylacetone ⁽⁷⁾	2-Butanone, 4-phenyl	22,51	43(100), 148 (5)	(-) -	1844 -	-	All
Squalene	Hexamethyl-2,6,10,14,18,22-tetracosahexaene	35,73	81(100), 41(50), 123(25), 410 (5)	(-) 2790 ⁽²⁾	(-) -	-	All
Furyl hydroxymethyl ketone*	Ethanone, 1-(2-furanyl)-2-hydroxy	24,56	95(100), 97(25), 126 (10)	1220 -	1994 -	-	Oak, chestnut

16-Heptadecen-2,5,8-trione	16-Heptadecen-2,5,8-trione	41,63	127(100), 170(100), 155(65), 280	1684 -	(-) -	-	All
2,4-Nonadien-1-al ou 2,4-Octadien-1-al	2,4-Nonadien-1-al ou 2,4- Octadien-1-al	21,79	81(100), 40(70), 43(60), 124(5)	(-) -	1794 -	-	Oak, cherry, acacia
<i>trans</i> Benzalacetone	<i>trans</i> -4-Phenyl-3-buten-2- one	25,93	43(100), 146(5) , 131(5)	(-) -	2103 -	-	All

Legend: RT retention time (minutes) in ZB-Wax column; LRI linear retention indexes; m/z mass fragmentation pattern, molecular ion in bold; ^(?) tentatively identification; ^(*) Co-elution with other compounds; - not found in literature; ^(a)Column RTX5, Fernandez de Simon *et al.*, 2009a; ^(b)Column Carbowax and DB5, Fernandez de Simon *et al.*, 2009a; ^(c)Brígida de Simón, 2009; ^(d)Column DB5, Jordan *et al.*, 2002; ^(e)Column DB5, Vichi *et al.*, 2007; ^(f)Column DBwax, Caldeira *et al.*, 2008; ^(g)Column HP5, Vichi *et al.*, 2007; ^(h)Column SPB1, Diaz-Maroto *et al.*, 2008; ⁽ⁱ⁾Rodriguez-Bencomo *et al.*, 2009; ^(j)Mosedale and Puech, 1998; ^(k)Piggott *et al.*, 1995; ^(l)Garde-Cerdán and Ancín-Azpilicueta, 2006 ^(m)Sáenz-Navajas *et al.*, 2010; ⁽ⁿ⁾Togores, 2004; ^(o)Gomes da Silva and Chaves das Neves, 1999; ^(p)Zhao *et al.*, 2011 ^(q)Column ZB-Wax, Cormier *et al.*, 1991; ^(r)Barata *et al.*, 2011; ^(s)Maga and Sizer, 1973; ^(t)Column ZB-Wax, Yanagimoto *et al.*, 2004; ^(u)Column DB1, Leffingwell and Alford., 2005; ^(v)pherobase, 2011; ^(w)Column DB5 and ZB-Wax, Ferreira *et al.*, 2001; ^(x)Column DB5, Priestap *et al.*, 2003; ^(y)Zehentbauer and Reineccius, 2002; ^(z)Column ZB-Wax, Valim *et al.*, 2003; ⁽¹⁾Column ZB-Wax, Coralia *et al.*, 2001; ⁽²⁾Column HP5, Kilic *et al.*, 2004; ⁽³⁾Column Stabilwax Natali *et al.*, 2006.

The chromatograms obtained are very complex and it was observed a series of co-elution, making difficult the identification process, thus resulting in several compounds that remained unidentified. Unequivocally we were able to identified 45 compounds, by comparing their mass fragmentation with those in commercial libraries, and with those reported in literature, also taking into account their retention indexes, structure and molecular weight. Arising from polysaccharides we identified 7 compounds, mainly furanic aldehydes (furfural, 5-methylfurfural, 5-hydroxymethylfurfural and maltol) also reported by several authors (Natali *et al.*, 2006; Vichi *et al.*, 2007). HMF is produced by dehydration of 6-carbon sugars obtained from the hydrolysis of cellulose, while furfural is a result of the dehydration of 5-carbon sugars resulting from the hydrolysis of the hemicellulosic part of woods (Asghari and Yoshida, 2010).

According to Caldeira (2004) there is a positive correlation between furanic aldehydes content and the aromatic descriptors caramel, vanilla and nuts. Hidalgo (2003) and Marín (2005) pointed out almond and toasty notes. Pyridine, not usually mentioned, was also identified, in all samples, although in small amounts. Maga (1985), Nabeta *et al.* (1986) and Chatonnet (1995) also have mentioned this aromatic nitrogenated compound.

From lignin and polyphenols degradation, we have identified 15 compounds belonging to several chemical families: volatile phenols, phenolic aldehydes, alcohols, phenylketones, phenolic esters and acids, which contribute to vanilla, spicy and smoky notes (Aiken *et al.*, 1984).

Lipids degradation during wood thermal treatments originated lactones, acids and aldehydes. β -metil- γ -octalactone is probably the most studied compound in oak woods, with coconut notes attributed to *cis* and woody notes attributed to *trans* isomers. Propanoic acid was mentioned by Caldeira *et al.* (2005) and butanoic and hexadecanoic acids were mentioned by Flamini *et al.* (2010) for oak wood.

Sixteen other compounds were identified, although their origin is not fully known.

Almost all compounds listed in Table I were already described in literature by several authors, but some compounds are not usually referred such as toluene and pyridine that we were able to identified in all samples.

Influence of the toasting on volatile compounds

Although 45 compounds were identified and additionally 54 compounds were semi quantified. Untoasted oak presented the higher amount of total volatile compounds (4556.66 mg/100g wood, expressed as 3-Octanol), follow by chestnut (3199.46 mg /100 g wood), acacia (2773.10 mg /100 g wood) and finally cherry (2138.28 mg /100 g wood) (Figure 1). When performing a Tukey-Kramer Multiple Comparison Test for $p < 0.05$, all samples are significantly different before and after toasting, and for toasted samples cherry and acacia are significantly different from oak and chestnut. For untoasted samples chestnut and cherry are different from oak.

The influence of toasting on the total volatile compounds was very significant in chestnut and cherry samples with an increment of over 200%, while in oak we observed an increment of 96% and only of 52% in acacia wood chips. In spite of this differences, all toasted samples are significantly richer on total volatile compounds when compared with untoasted samples by Tukey-Kramer Multiple Comparison Test for $p < 0.05$.

Acetic acid, furfural, 5-methylfurfural, vinyl ester of benzoic acid, maltol, eugenol, vanillin, conyferaldehyde, syringaldehyde, 4-propylguaiacol, aceto-syringone, benzyl ketone, guaiacyl ketone, methyl ether of 4-hydroxy-3,5-dimethoxy-benzoic acid, and 16-heptadecen-2,5,8 trione contents increased in all

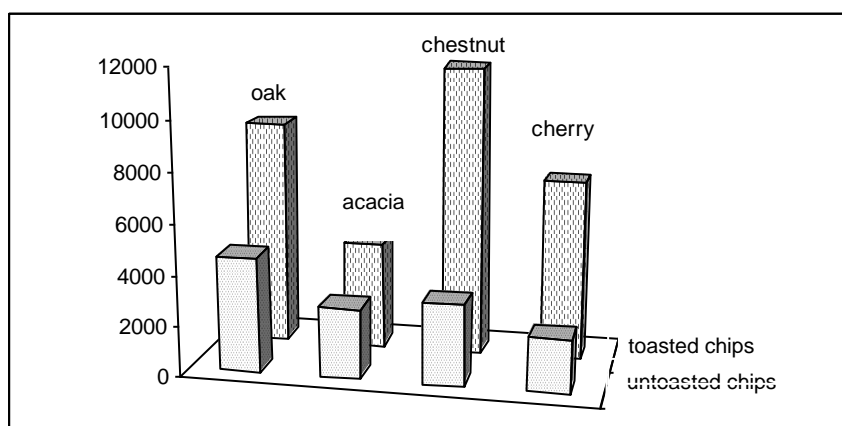


Figure 1 – Total volatile compounds (mg/100g wood, expressed as 3-octanol); Different letters denote significant difference with 95% confidence level in the Tukey-Kramer Multiple-Comparison Test.

Composição volátil total (mg/100g de madeira, expresso em 3-octanol); Letras diferentes mostram diferença significativas para um nível de confiança de 95% no teste de comparação de médias de Tukey-Kramer Multiple-Comparison.

sample submitted to a toasting treatment. Table II shows key chemical families of compounds characterized by GC/MS from oak, acacia, chestnut and cherry wood samples. The results seem to indicate that the botanical species as well as the toasting level influenced the contents of those compounds.

Untoasted woods presented small amounts of furfural, 5-methylfurfural and 5-hydroxymethylfurfural but according to Canas *et al.* (1999), Caldeira *et al.* (2006), Jordão *et al.* (2006), Nonier *et al.* (2006) and Fernández de Simon *et al.* (2009b) the content

increase with toasting. Furfural is the most abundant compound because hemicelluloses are preferentially degraded (Fernandez de Simon *et al.* 2009a). We could also observed an increase of maltol content with the toasting process for oak and chestnut, in accordance to Fernandez de Simon *et al.* (2009a). Maltol arises from hexoses degradation in the presence of nitrogen that usually is present, although in small amounts, in woods (Bourgeois and Guyonnet, 1988).

Squalene appears to exist in higher amounts in oak chips, while antiarol seems to be characteristic of

TABLE II

Key chemical families of compounds characterized by GC/MS from oak, acacia, chestnut and cherry wood samples (mg/100g wood, expressed as 3-octanol)

Famílias de compostos químicos caracterizados por GC/MS de amostras de madeira de carvalho, acácia, castanheiro e cerejeira (mg/100g wood, expresso como 3-octanol)

Compounds	Oak		Chestnut		Cherry		Acacia	
	Untoasted	Toasted	Untoasted	Toasted	Untoasted	Toasted	Untoasted	Toasted
Furanic aldehydes	55,26	397,19	41,80	270,48	nd	70,18	2,68	8,26
Volatile phenols	366,40	941,58	488,56	1485,89	77,83	334,63	382,20	197,84
Phenolic aldehydes	258,65	1563,62	266,56	3930,36	127,39	1208,42	177,16	170,38
Phenylketones	nd	55,33	8,87	167,19	nd	72,21	8,91	57,04
Lactones	18,22	14,77	1,02	1,94	1,40	3,95	nd	nd

cherry wood. Although not very often reported in literature, squalene was also found by Alañón *et al.* (2009) in dichloromethane extracts from oak chips obtained by miniaturised PLE.

CONCLUSIONS

In order to use fragments of woods alternatively to oak it is mandatory to know their chemical composi-

tion, namely volatile fraction. The knowledge of the richness of specific wood specie and the influence of the toasting process on its characteristics may be very useful for winemakers when choosing the kind of wood to be used in winemaking or wine maturation. Although this is a first step toward the fully knowledge of these woods, results shows that oak and chestnut are richer than cherry and acacia woods, and that the modifications induced by toasting are the same regardless the wood species. These

results are important because although the majority of the compounds are the same, some differences regarding quantity and relative compositions were found, imparting different flavour characteristics to the woods and, hopefully to wines made with them.

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