

Gas Chromatography in the Analysis of Compounds Released from Wood into Wine

Maria João B. Cabrita¹, Raquel Garcia¹, Nuno Martins¹,
Marco D.R. Gomes da Silva² and Ana M. Costa Freitas¹

¹*School of Science and Technology, Department of Plant Science, Institute of Agricultural and Environmental Science ICAAM Mediterranean, University of Évora, Évora,*

²*REQUIMTE, Department of Chemistry, Faculty of Science and Technology, New University of Lisbon, Campus Caparica, Portugal*

1. Introduction

Wood has been used in alcoholic beverages for centuries, mainly as material for containers used for alcoholic beverages aging. Recently OIV (Organisation Internationale de la Vigne et du Vin) approved the use of chips (Resolution oeno 3/2005) and staves as alternatives for barrels. These practices are being rapidly spread among winemakers. The increased used of these alternatives are mainly related to low investments, similar sensorial results obtained in shorter time, simplicity of use and the possibility of avoiding contamination and off-flavours, too-often related to aged or contaminated barrels.

Besides oak, other woods are being looked at for enological purposes, such as acacia, cherry, chestnut and mulberry. Their characteristics are commonly compared to oak. In the past, chestnut (*Castanea sativa*) was widely used in the Mediterranean area, because of its availability and its cheap price. Chestnut wood has higher porosity than oak. Cherry wood (*Prunus avium*) has high porosity and oxygen permeation, and is usually used for short aging times. Acacia wood (*Robinia pseudoacacia*) is hard, with low porosity. Mulberry wood (*Morus alba* and *Morus nigra*) is tender and elastic, with medium porosity, and is characterized by a low release of compounds. The lack of properties for cooperage is now overcome by their possible use as staves or chips.

The aim of this work is to present an overview on volatile and semi-volatile composition of different kind of wood with oenological interest. Within this purpose, this work will be focused on a bibliographic review of the most used chromatographic methods for characterization of volatile and semi-volatile compounds, including also a brief description of the most common reported sample preparation methods for chromatographic analysis.

The composition of woods volatile fraction depends on the botanical species and geographic origin. Prior to its final use a toasting step is needed. This toasting process induces the formation of a great number of volatile and odoriferous compounds, and it is the main reason for significant differences among non-toasted and toasted wood. Volatiles and semi-

volatiles compounds from wood belong to several different chemical families: lactones, terpenes, norisoprenoids, aldehydes, ketones, alcohols, phenols and esters.

Because of the odourific impact of some volatiles, a number of studies dealt with their characterization in wood-aged beverages and woods itself. Volatile phenols such as guaiacol and eugenol, phenolic aldehydes such as vanillin and syringaldehyde, oak lactones, and furanic aldehydes (furfural and derivatives) have been described as the main contributors to the sensory fingerprinting of aged alcoholic beverages.

Most of the volatile compounds are formed during open-air seasoning and toasting phases of wood processing. Several furanic aldehydes and ketones come from the thermo degradation of celluloses and hemicelluloses. This is the case of hydroxy-methylfurfural (HMF) (from cellulose-derived glucose) and furfural arising from pentoses produced by partial hydrolysis of hemicelluloses. These latter compounds are responsible for almond and toasty odours. Thermal degradation of lignin determines the formation of methoxylated volatile phenols (*i.e.*, guaiacyl and syringyl derivatives), phenolic ketones, and phenolic aldehydes contributing to smoked or spiced and vanilla aromas, respectively.

To study volatiles in woods or in alcoholic beverages some preparation methods must be considered. The volatile fraction from woods can be studied from three different points of view: the volatiles existing in wood itself, the volatiles that wood can release into synthetic medium miming alcoholic beverages and the study of alcoholic beverages like wines and spirits after aging with wood contact. In practical terms, that implies using sample preparation methods for solid and liquid matrices.

Sample preparation for gas chromatography (GC) analysis of volatile compounds from woods can be performed by pressurized liquid extraction, a process that combines temperature and pressure with liquid solvent to achieve extracts rapidly and efficiently. This technique is available in an automated or a manual version as accelerated solvent extraction (ASE), and it is being currently used as a good alternative for the solid-liquid extraction used previously for studying volatiles from solid matrices. Most of the “oldest” sample preparation methods involved Soxhlet extraction with dichloromethane or methanol or simultaneous distillation-extraction procedures.

The sample preparation procedures for GC analysis of volatile compounds in wines or hydro-alcoholic mixtures in general, are usually done by LLE (liquid-liquid extraction), SPE (solid-phase extraction) or SPME (solid-phase microextraction). But, more environmental friendly sample preparation techniques like SBSE (stir bar sorptive extraction) can also be employed with good results when thermal desorption is used instead of retro-extraction, for subsequent chromatographic analysis.

The chromatographic technique more suitable for these analyses is gas chromatography-mass spectrometry (GC/MS), as the mass spectrometer allows a more powerful tool for compounds identification. When MS is coupled with two-dimensional (2D) chromatographic systems, broader capabilities can be open in order to fully characterized wine matrices. An olfactometric approach is also mandatory in order to identify chromatogram zones where peak identification should take place. Consequently gas chromatography-olfactometry (GC-O) emerges as an important technique to achieve this purpose. GC-O analysis has been widely used to identify odour-active compounds or to

screen the odour volatile composition in wines. This technique allows to obtain relatively simple olfactograms and to establish a hierarchy of the most important odorants according to their potential sensory impact. In general it implies the use of headspace technique as sample preparation method, such as purge-and-trap (P&T) or solid-phase microextraction (HS-SPME) systems.

2. Composition and biosynthesis of the volatile fraction of woods: Effect of botanical species and toasting

For centuries, wood has been used in wine technology, either as containers for transportation either for aging wine and spirits. Over the years, many different tree species have been used in cooperage, but oak and chestnut woods proved to be the best ones to manufacture barrels and therefore the most suitable ones for wine and spirits aging.

The use of barrels is, however, expensive since barrels can only be used few times for wine aging. Besides the above mentioned issue, barrels can often be the cause of wine contaminations and off-flavours, if sanitation procedures are not correctly applied.

All woods are composed of cellulose, lignin, ash-forming minerals, and extractives formed into a cellular structure. The characteristics and amounts of these compounds and differences in cellular structures give to each wood its specific characteristics. Some are more flexible than others, some are easier to work, some are harder or softer, heavier or lighter.

Extractives from different wood species comprise several substances which belong to an extremely wide range of chemical families that are characteristics of each wood. Thus, extractives allow the identification of wood species, contributing also for the determination of other wood properties, namely permeability, density, hardness and compressibility.

Besides botanical species, geographical origin also contributes to the final chemical composition of the extractives. Technological treatments during cooperage such as seasoning and toasting give the final characteristics to the barrel (Chatonnet & Dubourdieu, 1998; Cadahía et al., 2001; Doussot et al., 2002; Pérez-Prieto et al., 2002; Cadahía et al., 2003).

Wood physical properties play a significant role in cooperage. Usually, oak is the most used specie due to its unique physical and chemical nature. Physically, oak has strength since its wide radial rays give strength when shaped for a cask. Oak is also a "pure wood" as opposed to pine or rubber trees which contain resin canals that can transfer strong flavours to maturing beverages.

Several studies have been conducted in order to evaluate the accumulation of oak volatile compounds in wines and spirits and how different factors affect the final concentration of these compounds both in barrels (Puech, 1987; Sefton et al., 1993; Yokotsuka et al., 1994; Waterhouse & Towey, 1994; Piggot et al., 1995; Escalona et al., 2002; Ferreras et al., 2002; Pérez-Prieto et al., 2002, 2003; Netto et al., 2003; Madrera et al., 2003; Garde-Cerdán et al., 2002, 2004; Gómez-Plaza et al., 2004; Jaraúta et al., 2005; Garde Cerdán & Ancín-Azpilicueta, 2006 b; Caldeira et al., 2006 a,b; Jiménez-Moreno & Ancín-Azpilicueta, 2007; Jiménez-Moreno et al., 2007; Frangipane et al., 2007) and with oak chips (Pérez-Coello et al., 2000; Arapitsas et al., 2004; Caldeira et al., 2004; Guchu et al., 2006; Frangipane et al., 2007; Bautista-Ortín et al., 2008; Rodríguez-Bencomo et al., 2008, 2009; Rodríguez- Rodríguez & Gómez-Plaza, 2011).

Other studies were made in model solutions to avoid matrix influence (Singleton & Draper, 1961; Ancín-Azpilicueta et al., 2004; Fernández de Simón et al., 2010 a; Rodríguez-Rodríguez & Gómez-Plaza, 2011) or in wood itself (Vichi et al., 2007; Natali et al., 2006; Díaz-Maroto et al., 2008).

More recently some studies have been made with other woods than oak (Flamini, et al., 2007; de Rosso et al., 2009; Fernández de Simón et al., 2009; Caldeira et al., 2010) as they becoming increaseling interesting.

Ever since OIV approved the use of alternatives for barrels, like chips and staves, researchers are looking into other kind of woods such as acacia, cherry and mulberry, which were abandoned in the past due to the lack of cooperage properties.

2.1 Effect of botanical species

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) growing in different areas of the United States, *Quercus patraea* Liebl. (sessili oak), *Quercus Robur* L. (pedunculate oak) and *Quercus pyrenaica* growing in Europe. French oaks are the most widespread wood for barrels, especially those from Allier and Limousin regions. But oaks from Hungary, Russia, Spain, Romania and Portugal are also becoming more and more attractive.

Many researchers are now dedicated to the study of chemical compounds in different kind of woods, although oak is still the most studied one. Whenever a new wood is tested it is compared with the oak effects in wines and spirits. Oak belonging to different species can be significantly different regarding volatile composition. Jordão et al. (2006) concluded that *Quercus pyrenaica* released significantly more volatile compounds than *Quercus patraea*, in a study with SPME in hydro-alcoholic oak wood solutions. Fernández de Simón et al., (2010 a) concluded that *Quercus pyrenaica* chips, althought similar to other species, have some odourific particularities, such as high levels of furanic compounds, eugenol, furaneol and *cis*-whiskylactone and low levels of vanillin. Several authors pointed out that β -methyl- γ -octalactone (whisky lactone), particularly the *cis* isomer, can be used to differentiate American from French oaks (Masson et al., 1995; Waterhouse & Towey, 1994; Masson et al., 1997; Chatonnet & Dubourdieu, 1998; Pérez-Coello et al, 1999). Several norisoprenoid compounds were found in American oak, but were almost absent in European oaks (Sefton et al., 1990). Same wood species from French oak and East European oaks can be distinguished by their contents of eugenol, 2-phenylethanol and aromatic aldehydes, mostly vanillin and syringaldehyde (Prida & Puech 2006).

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 profile (Flamini et al., 2007, de Rosso et al., 2009, Fernández de Simon et al., 2009). Acacia had significant aromatic aldehydes, particularly vanillin, syringaldehyde and dihydroxy-benzaldehyde but no eugenol (de Rosso et al., 2009) or methoxyeugenol (Flamini et al., 2007) were found. Chestnut and oak showed the highest content of volatile compounds namely vanillin, eugenol, methoxyeugenol, syringaldehyde, α -terpineol, and oak presented high amouts of *cis*- and *trans*- β -methyl- γ -octalactones. In cherry, several

aromatic compounds were found although in low abundance, but mulberry was the poorest, with small amounts of eugenol and absence of methoxyeugenol (de Rosso et al., 2009). Cherry is also characterized by methoxyphenols, particularly, high content of trimethoxyphenol (Flamini et al., 2007). Chestnut and oak woods are known to release significant amounts of eugenol and methoxyeugenol into wines. High amounts of vanillin are released from chestnut and high levels of syringaldehyde are released from acacia and oak woods.

2.2 Effect of toasting level

Oak wood chemical composition mainly depends on the species, its provenience and the various treatments that wood undergoes in cooperage, such as seasoning, region of seasoning and toasting (Marco et al., 1994; Chatonnet & Dubourdieu, 1998; Cadahía et al., 2001; Doussot et al., 2002; Pérez-Prieto et al., 2002; Cadahía et al., 2003).

Seasoning prevents the wood from shrinking after barrel production while firing is applied to stabilise the curved shape of the barrel (van Jaarsveld et al., 2009) and both these steps play a crucial role in wood flavour development.

Wood seasoning in cooperage is usually performed under natural conditions in open air during a variable period of time (18 to 36 months), but artificial seasoning can also be performed. However, natural seasoning has a more positive effect on the odourific profile of wood. During this process the wood volatile compounds profiles, which include lactones, phenolic aldehydes or volatile phenols, show significant differences.

Nevertheless, among all variables that can influence the impact of woods in 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 et al., 1999). The toasting process drastically enhances the gain in volatile compounds arising from the thermal degradation of oak wood (Cutzach et al., 1997; Chatonnet et al., 1999; Doussot et al., 2002).

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., 2009; van Jaarsveld et al., 2009), 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.

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 et al., 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. Table 1 resumes information regarding main volatile compounds formed from wood biopolymer during toasting process.

Common name	IUPAC name	m/z fragment	LRI Apolar column	LRI Polar column	Aroma notes
DERIVED FROM POLYSACCHARIDES					
Furanic aldehydes					
Furfural	2-Furancarboxaldehyde	95, 96	834 ^(a) 811 ^(h)	1444 ^(b)	Bread, sweet almond ⁽ⁱ⁾ , slightly toasty, caramel ^(h)
5-Methylfurfural	5-Methyl-2-furancarboxaldehyde	109, 110	965 ^(a)	1551 ^(b)	Almond, caramel ⁽ⁱ⁾ , spicy, toasty ^(h)
5-Hydroxymethylfurfural	5-Hydroxymethyl-2-furancarboxaldehyde	97 ,126	1235 ^(a)	2466 ^(b)	Odourless ⁽ⁿ⁾
Maltol	3-Hydroxy-2-methyl-4H-pyran-4-one	71, 126	1111 ^(a)	1938 ^(b)	Toasty ⁽ⁿ⁾
Furaneol	4-Hydroxy-2,5-dimethyl-3(2H)-furanone	85, 128	1083 ^(a)	2013 ^(b)	Caramel-like ^(o)
Acids					
Acetic acid	Ethanoic acid	43 ,45,60	602 ^(g)	1464 ^(f)	vinegar ^(f)
DERIVED FROM LIGNIN AND POLYPHENOLS					
Volatile phenols					
Eugenol	2-Methoxy-4-(prop-2-enyl) phenol	77,103, 164	1359 ^(a)	2139 ^(b)	Clove,honey ⁽ⁱ⁾ spicy, cinnamon ^(h)
Isoeugenol (<i>cis</i> and <i>trans</i>)	<i>cis</i> - and <i>trans</i> -1-Methoxy-4-(prop-2-enyl) phenol	77,149, 164	1408 ^(a) 1451 ^(a)	2226 ^(b) 2314 ^(b)	Spicy ^(m) clove,woody ^(h)
Phenol	Hydroxybenzene	66,94	983 ^(a)	1978 ^(b)	Ink ⁽ⁿ⁾
3,4-Dimethylphenol	1-Hydroxy-3,4-dimethylbenzene	107	1193 ^(a)	2192 ^(b)	
<i>o</i> -Cresol	2-Methylphenol	107 /108	1059 ^(a)	1980 ^(b)	Leather, spicy ^(m)
<i>p</i> -Cresol	4-Methylphenol	107 /108	1079 ^(a)	2056 ^(b)	
<i>m</i> -Cresol	3-Methylphenol	107 /108	1086 ^(a)	2064 ^(b)	
Guaiacol	2-Methoxyphenol	109/ 124	1089 ^(a)	1833 ^(b)	Smoke,sweet, medicine ⁽ⁱ⁾
4-Methylguaiacol	4-Methyl-2-methoxyphenol	123/ 138	1191 ^(a)	1928 ^(b)	Spicy,phenolic, lightly green ^(h)
4-Ethylguaiacol	4-Ethyl-2-methoxyphenol	137 /152	1274 ^(a)	2002 ^(b)	Phenolic ^(i,m) leather ^(m) smoked ⁽ⁱ⁾
4-Propylguaiacol	4-Propyl-2-methoxyphenol	137 /166	1461 ^(a)	2083 ^(b)	Leather animal ^(m)

Common name	IUPAC name	m/z fragment	LRI Apolar column	LRI Polar column	Aroma notes
4-Vinylguaiacol	4-Vinyl-2-methoxyphenol	135/ 150	1314 ^(a)	2165 ^(b)	Clove ⁽ⁱ⁾
Syringol	2,6-Dimethoxyphenol	139/ 154	1353 ^(a)	2237 ^(b)	Smoke, burned wood ^(f)
4-Methylsyringol	4-Methyl-2,6-dimethoxyphenol	168	1449 ^(a)	2322 ^(b)	Smoke, burned, flowery ^(f)
4-Ethylsyringol	4-Ethyl-2,6-dimethoxyphenol	167	1528 ^(a)	2381 ^(b)	
4-Allylsyringol	4-Allyl-2,6-dimethoxyphenol	194	1605 ^(a)	2511 ^(b)	Spicy smoky ^(m)
4-Propylsyringol	4-Propyl-2,6-dimethoxyphenol	167	1612 ^(a)	2452 ^(b)	
4-Ethylphenol	1-Ethyl-4-hydroxybenzene	107 ,122		2201 ^(f)	Animal, horse, stable ^(f)
2-Phenylethanol	Hydroxyethylbenzene	91	1113 ^(a)	1888 ^(b)	Floral, roses ^(h)
Phenolic aldehydes					
Vanillin	4-Hydroxy-3-methoxybenzaldehyde	151 /152	1399 ^(a)	2518 ^(b)	Vanilla ⁽ⁱ⁾
Benzaldehyde	Phenylmethanal	77, 106	962 ^(a)	1493 ^(b)	Bitter almonds ^(h)
Conyferaldehyde	3-Methoxy-4-hydroxycinnamaldehyde	178	1747 ^(a)	3096 ^(b)	Vanilla, woody ⁽ⁿ⁾
Syringaldehyde	4-Hydroxy-3,5-dimethoxybenzaldehyde	181, 182	1643 ^(a)	2904 ^(b)	Vanilla ⁽ⁱ⁾
Sinapaldehyde	3,5-Dimethoxy-4-hydroxycinnamaldehyde	208	2002 ^(a)	3458 ^(b)	Vanilla ⁽ⁿ⁾
Phenolic esters					
Ethyl vanillate	4-Hydroxy-3-methoxy benzoic acid, ethyl ester	151 , 167,196	1648 ^(g)		Flower, vanilla, fruit, sweet, ⁽ⁱ⁾
Methyl vanillate	4-Hydroxy-3-methoxy benzoic acid, methyl ester	151 ,182	1518 ^(a)	2565 ^(b)	Caramel, butterscotch, vanilla ⁽ⁱ⁾
Phenyl ketones					
Acetovanillone	1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone	151 /166	1487 ^(a)	2595 ^(b)	Vanilla ⁽ⁱ⁾
Propiovanillone	1-(4-Hydroxy-3,5-dimethoxyphenyl)-propanone	151 /180	1501 ^(a)	2661 ^(b)	Vanilla ⁽ⁿ⁾
Butyrovaniillone	1-(4-Hydroxy-3-methoxyphenyl)-butanone	151 /194	1590 ^(a)	2770 ^(b)	Caramel, sweet, Buttery ⁽ⁱ⁾

Common name	IUPAC name	m/z fragment	LRI Apolar column	LRI Polar column	Aroma notes
Acetosyringone	2-(4-Hydroxy-3-methoxyphenyl)-acetaldehyde	181/196	1744 ^(a)	2953 ^(b)	
Propiosyringone	1-(4-Hydroxy-3,5-dimethoxyphenyl)-propanone	181/210	1753 ^(a)	3010 ^(b)	Vanilla ⁽ⁿ⁾
Isoacetosyringone	2-(4-Hydroxy-3,5-dimethoxyphenyl)-acetaldehyde	167	1712 ^(a)	2927 ^(b)	
Isopropiosyringone	1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propanone	167	1785 ^(a)	2979 ^(b)	
Alcohols					
Coniferyl alcohol	4-(1- <i>trans</i>)-3-Hydroxy-prop-1-enyl-2-methoxyphenol	137	1745 ^(a)	3213 ^(b)	
Benzyl alcohol	Hydroxy methylbenzene	79,108		1879 ^(p)	Sweet, floral ^(m)
DERIVED FROM LIPIDS					
Lactones					
β-Methyl-γ-octalactone (<i>cis</i>)	<i>cis</i> -4-Methyl-5-butyldihydro-2(3 <i>H</i>)-furanone	99	1325 ^(a)	1928 ^(b)	Sweet, coconut (i) woody ^(k,l)
β-Methyl-γ-octalactone (<i>trans</i>)	<i>trans</i> -4-Methyl-5-butyldihydro-2(3 <i>H</i>)-furanone	99	1292 ^(a)	1861 ^(b)	Sweet, coconut (i) woody ^(k,l)
γ-Butyrolactone	Dihydro-2(3 <i>H</i>)-furanone	86	913 ^(a)	1593 ^(b)	Cheese ^(m)
Acids					
Propionic acid	Propanoic acid	45,74	668 ^(g)		Fruity, floral ^(q)
Butyric acid	Butanoic acid	60,73,88	827 ^(g)	1627 ^(d)	Sweaty, cheesy unpleasant ^(h)
3-Methyl butyric acid	3-Methylbutanoic acid		834 ^(h)	1675 ^(r)	Cheesy, sweaty ^(h)
Valeric acid	Pentanoic acid	60,73,101			Strawberry ^(q)
Caproic acid	Hexanoic acid	60,73	982 ^(g)	1865 ^(d)	Faintly cheesy sweaty ^(h)
Caprylic acid	Octanoic acid	60,73,144	1163 ^(h)		Sweaty, penetrating ^(h)
Capric acid	Decanoic acid	60,73,172			Rancid ^(p)
Lauric acid	Dodecanoic acid	60,73,200			Soap ^(f)
Myristic acid	Tetradecanoic acid	43,60,73			Coconut oil
Palmitic acid	Hexadecanoic acid	43,60,73		2820 ^(d)	

Common name	IUPAC name	m/z fragment	LRI Apolar column	LRI Polar column	Aroma notes
DERIVED FROM CAROTENOIDS					
Norisoprenoids					
β-Ionone	4-(2,6,6-Trimethyl-cyclohex-1-enyl)-but-3-en-2-one	43, 177,192		1614 ^(c)	Violet ^(m)
3-Oxo- <i>α</i> -ionol	9-Hydroxymegastigma-4,7-dien-3-one	108	1648 ^(a)	2518 ^(b) 2658 ^(d) 1937 ^(c)	
Blumenol C	4-(3-Hydroxybutyl)-3,5,5-trimethyl-cyclohex-2-en-1-one	41, 43 ,108		2002 ^(c)	
Blumenol A (vomifoliol)	6,9-Dihydroxymegastigma-4,7-dien-3-one	189, 207 , 224		2180 ^(c)	
Vitispirane	2,6,6-Trimethyl-10-methyliden-1-oxospiro[4,5]dec-7-ene		1286 ^(e)	1327 ^(c)	Floral, fruity, earthy, woody
3-Oxo-retro- <i>α</i> -ionol	9-hidroximegastigma-4,6-dien-3-one (<i>cis</i> and <i>trans</i>)			2001 ^(c) 2081 ^(c) 2797 ^(d)	

^(a)DB5 column, Fernandez de Simon et al., 2009 ; ^(b)Carbowax column, Fernandez de Simon et al., 2009; ^(c)DB1701 (medium polar) column, Sefton et al., 1990; ^(d)Stabilwax column, Natali et al., 2006 ^(e)HP5 column, Jordão et al.,2006; ^(f)DBWax column, Caldeira et al.,2008; ^(g)HP5 column, Vichi et al., 2007; ^(h)SPB1 column, Diaz-Maroto et al., 2008; ⁽ⁱ⁾Rodriguez-Bencomo et al., 2009; ^(j)Mosedale & Puech, 1998; ^(k)Piggott et al., 1995; ^(l)Garde-Cerdán & Ancín-Azpilicueta , 2006a ^(m)Sáenz-Navajas et al., 2010; ⁽ⁿ⁾Togores, 2004; ^(o)Gomes da Silva & Chaves das Neves, 1999; ^(p)Zhao et al, 2011 ^(q)Cormier et al. 1991; ^(r)Barata et al., 2011

Table 1. Main volatile compounds formed from wood biopolymer during toasting process. LRI denotes linear retention indexes; *m/z* denotes mass fragment ions and base peak is presented in bold.

The intensity and length of the applied heat affects the production of compounds during macromolecules degradation and define the toasting levels. Designations like untoasted, light, medium and heavy toast are common, but there is no industry standard for toast level.

According to Vivas et al. (1991) the quality and quantity of each volatile compound are strongly related with toasting intensity, but particular characteristics of each species can also determine the rate of modification during toasting process. For instance, when comparing volatile composition of *Q. pyrenaica* and *Q. petraea* wood chips, the increase amount of compounds with the toasting process was less evident in the Portuguese oak (Jordão et al., 2006). These authors pointed out that physical properties and structure of wood may influence heat conduction and reactions upon heating. Caldeira et al., (2006 b) also found that as toasting intensity increases, concentration of the majority of volatile compounds found in wood matrix rises. In several oak species, as well as in Portuguese chestnut,

increasing toasting level led to an increase of furanic aldehydes, volatile phenols, 4-hydroxybut-2-en-lactone and vanillin (Caldeira et al., 2006 b)

It is also relevant that the response of a wood to a particular seasoning and toasting condition is determined by the size of the wood piece, as it affects their structural properties, and hence, the flavour characteristics. Moreover, each piece size shows different extraction kinetics when in contact with wines (Fernández de Simón et al., 2010 b).

Indeed, when heat is applied to wood, a depolymerization of the lignin takes place producing phenolic aldehydes. Therefore, their concentration increases with toast level. Toasting also produce the cleavage of α - β bonds of cinnamic aldehydes and their thermo-oxidation and thermo-decarboxylation, leading to the formation of dimethoxyphenyl units such as syringol, and in heavy toast, to simple phenols as phenol and *o*-cresol (Nonier et al., 2006).

Toasting is such an important parameter that the characteristic profile of a toasted wood is completely different from the untoasted wood. The particular characteristics of macromolecules, lignin, cellulose, hemicellulose and lipids in each wood have a great influence on the volatiles composition of toasted woods. Fernández de Simón et al., (2009) concluded that toasting led to an increase in almost all the compounds when compared to untoasted woods. These increases were more evident in acacia, chestnut and ash woods, concerning lignin, lipids and carbohydrate derivatives. Cherry and ash woods were found to be richer than toasted oak in lignin derivatives, but much poorer in lipid and carbohydrate derivatives.

3. Analytical methodologies for quantification and identification of volatile compounds from woods

3.1 Sample preparation methods

Wine aroma is a very complex matrix comprising an enormous variety of compounds of many chemical families. Not all of them are odour active compounds, which imply the necessity of a target strategy in order to isolate the compounds of interest from the aqueous/alcoholic matrix.

Frequently, prior to analysis, samples are submitted to a preliminary preparation step, including isolation and concentration of the target compounds. The more used extraction and enrichment technique are liquid-liquid extraction (LLE), solid-phase extraction (SPE) and headspace, comprising the static/equilibration method (HS) and the dynamic method (purge & trap - P&T). These techniques have been recently reviewed by Costa Freitas et al. The quality of the subsequent analysis and results, depend largely on the isolation procedures. Different preparation methodologies might affect the final extract composition for the very same matrix. Nowadays researchers are focusing their attention not only to the extraction efficiency, of the methods used, but also to sustainable methods and thus more environmental friendly. Considering this, miniaturization has been applied and micro-LLE methods, such as dispersive liquid-liquid extraction (DLLME) (Fariña et al., 2007) or pressurized solvent extraction (Natali et al., 2006, Vichi et al., 2007), solid phase micro extraction methods (SPME) (Cai et al., 2009) and single drop microextraction (SDME)

(Martendal et al., 2007; Sillero et al., 2011) arise as prominent techniques for isolation of compounds in several liquid and solid matrices. Special attention has been given to methods which preclude the use of solvents, such as SPME (Bozalongo et al., 2007) and stir bar sorptive extraction (SBSE) (Marín et al., 2005; Tredoux et al., 2008; Rojas et al., 2009). These methods increase, in the case of gas chromatography (GC), the quality of the resulting chromatogram, allowing the detection of several volatile compounds that would, otherwise, be hidden under the solvent peak. As a definition one might state that preparation methods should be reproducible, and should provide an extract, as much as possible, similar to the original matrix.

Extracts obtained after exhaustive extraction techniques, which include solvent extraction and distillation, normally do not reflect the real matrix aroma profile, since they isolate compounds according, simultaneously, to solubility in the used solvent and volatility, considering the matrix properties (e.g. water or alcohol content). These methods provide a profile that reflects the volatile and semi-volatile composition of matrix rather than “real” aroma compounds of the matrix. Moreover, literature also agree, that only a small fraction of the isolated compounds can be correlated with sensory notes of the matrices (Plutowska & Wardencki, 2008). Consequently HS-based methods are currently the most used ones, since they allow the target isolation of the released volatiles from the matrix.

3.1.2 Extraction methods using solvents

In the analysis of wine aroma, the most used solvent extraction methods are LLE (Ortega et al., 2001; Garde-Cerdán & Ancín-Azpilicueta, 2006b), micro-wave assisted extraction (MAE) (Serradilla & de Castro, 2011), ultrasound assisted extraction (UAE) (Cocito et al., 1995; Fernandes et al., 2003), PLE (Natali et al., 2006; Vichi et al., 2007) and SPE (Morales et al., 2004; Campo et al 2007, Weldegergis et al., 2011). The type and quantity of the used organic solvent varies according to the methodology. In order to perform a classical LLE, eventually, a generous amount of solvent is used, and that is the reason why MAE, UAE and PLE became more popular, since the total amount of solvent can be significantly reduced. Pre-fractionation of the extract can also be subsequently performed (Fernandes et al, 2003) in order to simplify the extract for chromatographic analysis. Nevertheless, in all techniques, the obtained organic extract must be concentrated in order to be chromatographically analyzed. If gas chromatography hyphenated with olfactometry (GC-O) is going to be used, the organic extract should be rinsed with aqueous solutions, at different pH, in order to eliminate the presence of non-volatile compounds which are also extracted during the isolation process (Plutowska & Wardencki, 2008). The final extract has to be free of compounds which can produce artifacts during injection into the hot injector of the GC instrument, such as amino acids or fatty acids. The latter present a prolonged odor in the olfactometric port which can falsify the results of the analytes eluting subsequently. Thus a clean-up with resins should be performed. Before analysis a concentration step is also needed, in order to evaporate the excess of solvent prior to the chromatographic analysis. With this necessary step one can simultaneously promote the evaporation of the more volatile compounds and, eventually, odor components degradation, through oxidation processes, since air contact is almost unavoidable. Thus the final extract will not reproduce the original aroma matrix.

3.1.3 Solvent-less extraction methods

Extraction methods precluding the use of solvents have the main advantage of, in a single step, promoting extraction, isolation and concentration of the target compounds, without any other manipulation. At the same time, since it relies in the headspace of a sample, they will, indeed, mirroring the original sample and thus representing the true olfactory perception. This technique can be used in static or dynamic modes, or at a limit, the sample itself can be submitted to direct analysis without any previous treatment. In static mode, after reaching equilibrium, although not necessarily, sampling takes place and, normally, the more volatile compounds are successfully detected. Less volatile compounds, on the other, and depending on their individual vapour pressure, might be also detected. To overcome this drawback, dynamic sampling can be used. Here, purge & trap techniques, in which the compounds of interest are trapped in a suitable adsorbent are the most used. After sampling the trapped compounds can be directly desorbed, by means of a thermal desorber injector, or an extraction with a suitable solvent, before analysis, can be performed. Except for this latter case, the sample is completely lost after analysis, and no repeats are possible. However, no solvent peak is obtained, allowing detection of the more volatile components that, otherwise, could be co-eluting with the solvent peak. Other drawbacks of the dynamic mode should also be mentioned, namely the impact of the chemical nature of the adsorbent, on the trapped compounds. The most used trap materials are Tenax TA, Porapak Q and Lichrolut EN, since their affinity for ethanol is small (Escudero et al., 2007; Weldegergis et al, 2011). After the introduction of SPME (Belardi & Pawliszyn, 1989; Arthur & Pawliszyn, 1990), most of the HS methods started to use this method to perform aroma analysis. The obvious advantages of SPME are the fact that it does not involve critical sample manipulations. SPME is a simple and clean extraction method, comprising in a single step, all the necessary steps mandatory in aroma analysis: extraction, isolation and concentration (Rocha et al., 2007). In this technique, depending on the fibre physico-chemical properties (chemical nature and thickness), target analysis is, somehow, possible. However if a wide screening of the sample is aimed, more than one type of fibre should be tested. SPME demands a careful optimization of the experimental conditions in order to be used for qualitative and quantitative studies. The efficiency, accuracy and precision of the extraction methodology is directly dependent on extraction time, sample agitation, pH adjustment, salting out, sample and/or headspace volume, temperature of operation, adsorption on container walls and desorption conditions (Pawliszyn, 1997) besides fibre coating and thickness.

3.2 Chromatographic methods

The contact between wines and wood during the fermentation or storage process is a common practice in wine making. In order to improve the organoleptic characteristics of wine, storage in wood based barrels or the addition of wood chips is used in their natural form or after seasoning and thermal treatment by toasting or charring. The wood types for enological purposes comprises cherry, acacia, chestnut, mulberry, and especially, oak. Together with changes in colour and taste, the aroma of the resulting wine product is strongly affected (Garde-Cerdán & Ancín-Azpilicueta, 2006a). The porous nature of wood, promotes oxidation reactions, forming a wide variety of volatile compounds, otherwise not

present in the final product. Some compounds are also directly extracted into the wine during the long lasting contact between the wood and the wine. Together with endogenous volatile compounds, they contribute to the final wine bouquet. The most representative compounds, which reflect the wood influence in wine aroma, are furfural derivatives, such as furfural, 5-methylfurfural and furfuryl alcohol, phenolic aldehydes and ketones, such as vanillin and acetovanillone and a large variety of volatile phenols, such as guaiacol, 4-ethylphenol, 4-ethylguaiacol, 4-vinylphenol, 4-vinylguaiacol and eugenol and also phenolic acids (Tredoux et al., 2008; Weldergegis et al., 2011). The two oak lactones isomers, *cis*- and *trans*- β -methyl- γ -octalactone and γ -nonalactone are also present, especially if wood has been submitted to a previous seasoning or toasting process (Carrillo et al., 2006). Because they possess a very low sensory threshold, even in very low concentration, they strongly influence the final aroma. Liquid chromatographic (LC) methods, like capillary electrophoresis (CE) (Sádecká & Polonský, 2000), high performance liquid chromatography (HPLC) and ultra performance liquid chromatography (UPLC) are suitable methods to be used in order to separate, detect and quantify the above mentioned chemical classes, as recently reviewed (Cabrita et al., 2008; Kalili & de Villiers, 2011). The strong aromatic ring chromophore allows ease and sensitive detection by ultra-violet-visible (UV) detection devices or by mass spectrometry (MS). UPLC also reached better limits of detection (LOD) in the low ppb range, ten times higher for phenol compounds and furanic derivatives, when compared with HPLC methods (Chinnici et al., 2007). Considering the long-term storage in charred barrels, the presence of polycyclic aromatic hydrocarbons (PAHs) in aged alcoholic beverages has been proposed as an emerging issue. Although the transference rate, to the hydro-alcoholic mixture, of these high hydrophobic compounds is expected to be low, LODs less than 1 ppb are achievable when LC techniques are coupled with fluorimetric detection. Since the majority of the above mentioned compound classes are semi-volatile compounds, together with the endogenous compounds present in the wine, wine becomes an even more complex matrix to be analyzed as a whole. Therefore the analytical methodologies should be sufficiently powerful and sensitive to separate and detect hundreds of compounds of quite different concentrations and volatilities. The advent of gas chromatography (GC) significantly enhanced the systematic study of wine aroma, and its use, particularly when combined with mass spectrometry (MS), contributed significantly to the knowledge of wine volatile composition. Extracts from acacia, chestnut, cherry, mulberry, and oak wood, used in barrels for wine and spirits aging, have already been studied by GC/MS positive ion chemical ionization (PCI). These method, using methane as reagent gas, produce a high yield of the protonated molecular ion of volatile phenols, and allows compounds identification to be confirmed by collision-induced-dissociation (CID) experiments on $[M+H]^+$ species. MS/MS fragmentation patterns can be studied with standard compounds giving more accurate results (Flamini et al., 2007).

Considering that the human nose is still the best detector for aroma active compounds, the hyphenation of GC with olfactometry (GC-O) is mandatory, when sensorial activity, of individual compounds, and the knowledge of the relations between the perceived odour and chemical composition, of the volatile fraction, is searched. In GC-O detection is performed by an educated panel of persons and the qualitative and quantitative evaluation of the odour is carried out for each single compound eluting from the chromatographic

column. For a given compound a relationship is established between its sensorial activity at a particular concentration (if above the threshold of sensory detection) and its smell, as well as the determination of the time period of sensory activity and the intensity of the odor. This is possible if in parallel to a conventional detector, e.g. flame ionization detector (FID), MS or even a flame photometric detection (FPD) for sulfur speciation (Chin et al., 2011), an olfactometric port is attached to the instrument in order to determine the compound odor. The splitted flow carries the compounds simultaneously to both detection devices, allowing the comparison between each obtained signals. The mass structural information obtained by MS spectra allows the identification of odour active compounds. The quantitative evaluation of the intensity of the odours can be divided in three groups: detection frequency (where NIF - Nasal Impact Frequency values or SNIF - Surface of Nasal Impact Frequency are measured), dilution to threshold (CHARM method - Combined Hedonic Aroma Response Measurement and AEDA - Aroma Extract Dilution Analysis) and finally direct intensity methods (where the intensity of the stimuli and its duration are measured - OSME - Olfactometry by Finger Span Method). All these methods were carefully revised by Plutowska & Wardencki (2008).

It is easily recognizable that GC is the most appropriate instrumental approach, for wine aroma analysis. However, the enormous quantity of peaks obtained together with the similarity of retention factors of many related components means that component overlap will be the general expectation, meaning that complete separation may be largely unachievable for a given extract. In order to improve analysis, new separation technologies should be embraced. It is desirable to increase peak capacity and thus increasing the probability of locating a greater number of baseline resolved components within the chromatographic run. Together with new stationary phases (more thermal and chemically stable and enantioselective) and faster detection systems, this will largely enhance results quality. Multidimensional chromatographic (MD) methods are emerging as important alternatives to analyze such complex matrix, as wines. Whether using the heart-cutting mode (MD-GC) (Campo et al., 2007; Schmarr et al., 2007; Pons et al., 2008), enantio-MDGC (Darriet et al, 2001; Culleré et al., 2009) or comprehensive two-dimensional GC (2D-GC) approach (GC \times GC) (Ryan et al., 2005; Rocha et al., 2007; Torres et al., 2011; Weldegergis et al., 2011), MD methods allow the combination of two or more independent, or nearly independent, separation steps, increasing significantly the separation power of the corresponding one-dimensional (1D-GC) techniques and, therefore the physical separation of compounds in complex samples. When coupled with a preparative fraction collection device (selectable 1D/2D GC-O/MS with PFC) one can perform the enrichment of trace compounds with an high odourific impact (Ochiai & Sasamoto, 2011) in order to eventually proceed to further identification by NMR (Marriott et al., 2009). In order to overcome matrix complexity, a further dimensionality can be coupled to achieve separation efficiency. Methoxypyrazines were analyzed by LC-MDGC/MS (Schmarr et al., 2010a), nevertheless the complexity and price of the instrumental set-up encourages more research in this domain. 2D-LC \times LC methods (Cacciola et al., 2007; Dugo et al., 2008; Cesla et al. 2009) are also replacing the traditional 1D-LC separation modes, especially in what phenolic volatile concerns. This technique improves the separation of non-volatile polyphenols (Kivilompolo et al., 2008), and allows ease switch between LC and LC \times LC during a single analysis providing a better separation target, only, to the most complex part of the chromatogram.

Additionally to the enhanced separations achieved by 2D methods, comprehensive GC and LC also allow an easy comparison between samples, since the obtained chromatograms can be easily inspected for compound markers in quality control, certification and fraud detection. In fact, the probability of correctly determining a particular sample substance is increased, by the correlation of two or more independent data sets, in complex sample analysis. To generate these two sets of data, analysis has to be performed, individually, in two orthogonal columns phases, e.g. non-polar and a polar column for the case of GC \times GC or e.g. exclusion and a reversed-phase column in LC \times LC. Although this practice improves the quantitative data for key target components, it is often difficult, and may be tedious, to correlate the retention times for all of the peaks from the individual chromatograms. In any 2D chromatogram retention time data from the two independent stationary phases are immediately available. Thus a 2D chromatogram contains much more information than two independent 1D chromatograms. 2D analysis offers a genuine opportunity to characterize individual components based on retention time data alone, provided that high reproducibility of retention times can be achieved, reducing and eventually precluding, the requirement of MS detection for many samples. The reliability of peak position co-ordinates opens the possibility of fingerprinting comparison or statistical treatment in order to characterize the effects of distinct types of wood, the same wood from different origins, or even aging time (Cardeal et al., 2008; Vaz-Freire, 2009; Schmarr et al., 2010 b; Schmarr & Bernhardt, 2010).

4. Conclusion

Each wood species has a characteristic profile, regarding their volatile composition. Heating during processing of wood to be used in cooperage, specially toasting, has a great influence on biopolymers degradation, thus the resulting compounds. The volatile profile of an untoasted wood can be different from the same wood after toasting. Increasing toasting levels generally leads to an increase of volatile compounds but some can also suffer degradation. Compounds released from wood into wine or spirits depends on several factors such as type of wood, size of alternatives (e.g. chips and staves), time of contact, but also depends on the chemical characteristics of the beverage, specially the alcohol content.

Recent development in 2D analytical approaches, together with more sensitive and fast mass spectrometers, allow to gain insight in the volatile fraction of the wine/wood interaction system, aiming wine quality.

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