DETECTION OF VOLATILE COMPOUNDS FROM ROMANIAN OAK TOASTED WOOD BY GC/MS ANALYSIS

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Abstract. The toasting process changes the extractable substances in the oak wood of barrels used for wine aging. The GC/MS analysis led to the detection of 13 volatile compounds. The major wood volatile compounds detected in wood samples were furanic aldehydes, furfural and 5-methylfurfural, the two isomers of β-methyl-γ-octalactone, *cis* and *trans* (commonly known as oak lactones or whiskey lactones), vanillin and syringaldehyde. The percentage areas of oak volatile compounds detected were different depending on contact time and type of toast.

Keywords: GC/MS, oak wood, volatile compounds, toast level

INTRODUCTION

In wine technology, wood is used for transportation containers and for aging wine. Oak wood (*Quercus* genus) proved to be the best for barrels cooperage and, therefore, the most suitable for wine aging. The main oak species used in cooperage are: *Quercus alba* L. (American oak) which grows in different areas of the United States, *Quercus petraea* Liebl. (sessili oak), *Quercus robur* L. (pedunculate oak) and *Quercus pyrenaica* Willd. (Spanish oak), which grow in west of Europe. Oaks from Hungary, Russia and Romania are becoming more and more attractive. Wood is composed of cellulose, lignin, ash-forming minerals, and extractives, formed into a cellular structure (Le Floch A. *et al.*, 2015). Extractives from wood comprise several substances that belong to a wide range of chemical families. Besides botanical species, geographical origin also contributes to the final chemical composition of the extractives. Seasoning and toasting of barrel staves during cooperage give the final characteristics (Chatonnet P., D. Dubourdieu, 1998; Cadahía Estrella *et al.*, 2001; Doussot F. *et al.*, 2002; Pérez-Prieto L.J. *et al.*, 2002; Cadahía Estrella *et al.*, 2003). Oak is a pure wood, it does not contain resin canals that can transfer strong flavors to maturing beverages (Collins T.S. *et al.*, 2015). In barrel cooperage, wood seasoning is performed under natural conditions in open air for 18 to 36 months and artificial seasoning. In the barrel making process, the heat treatment (toasting) is performed by the French technique using fire (Chatonnet P. *et al.*, 1989). The toasting process is a common treatment applied to oak barrels to improve their aromatic potential. Toasting has a major influence on the quantity and the quality of the extractable substances in wines (Cutzach Isabelle *et al.*, 1997; Chatonnet P. *et al.*, 1999). The thermo degradation process during toasting leads to the formation of several compounds that can be transferred to wine during aging. The intensity and length of the applied heat affects the production of compounds during macromolecule 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 N. *et al.*, 1991, the quality and quantity of each volatile compound are strongly related to the toasting intensity, but particular characteristics of each species can also determine the change rate during toasting process.

Cerdán T.G. *et al.*, 2004, state that the main volatile compounds susceptible to migrate from oak wood to wine are the *cis* and *trans* isomers of β-methyl-γ-octalactone, furfural, vanillin, and syringaldehyde.

Until now, there is few data about the volatile composition of oak species grown in Romania and used for cooperage (Martínez-Gil Ana *et al.*, 2017). On this regard, this may be consider the first study on volatile composition on *Querqus robur* L., grown in Romania (Arad County) with different treatments of toasting (untoasted, light toast, medium toast, and heavy toast).

MATERIAL AND METHOD

The staves were samples (100 x 11 x 0.12 cm) from *Quercus robur* L. from a forest in west Romania (Arad County). After 24 months of natural seasoning in the Tonnellerie Transilvania Bois seasoning park (located in Sighetu Marmației, Maramureș County, Romania), they were submitted to different toasting processes according to the desired final product, using a revolving drum and oak fire (Table 1).

Sample preparation

5g of oak sawdust and 20 mL of dichloromethane were placed in Erlenmeyer flasks equipped with ground stopper. The extraction was carried out under continuous stirring in an ice bath for 30 minute. After separation, the organic layer was evaporated under nitrogen stream to approximately 200 µL volume of the extract. 1µL of this solution was injected to the GC-MS system. All extractions were carried out in triplicate.

GC-MS analysis

Analysis of aroma compounds from oak sawdust was carried out using a Shimadzu QP 2010 PLUS Mass Spectrometer coupled with Gas Chromatograph (Shimadzu) equipped with a Carbowax type column from Agilent, with a dimension of 30 m x 0.32 mm ID and 0.50 µm film thicknesses. The carrier gas was He (6.0) with a flow rate of 1.7 mL/min. The working parameters were: injector temperature 250°C, the ion source temperature 220°C, and the interface temperature 250°C. The column temperature program was conducted as follows: 40°C was the initial temperature for 5 min., increasing at a rate of 4°C/min. to 220°C, and holding 220°C for 15 min. The electron impact (EI) was set at 70eV. A mass range of 35–500 *m/z* was recorded at one scan per second.

Table 1

Toasting characteristics

Oak toast	Toasting Temperature (°C)	Toasting Time (hours)
LT (light toast)	180-190	2
MT (medium toast)	190-200	3
HT (heavy toast)	210-220	4

RESULTS AND DISSCUSION

The GC/MS analysis led to the detection of 13 volatile compounds. The most abundant compound was furfural. The major wood volatile compounds detected in wood samples were furanic aldehydes, furfural, and 5-methylfurfural, the two isomers of β-methyl-γ-octalactone, *cis* and *trans* (commonly known as oak lactones or whiskey lactones), vanillin, and syringaldehyde. The percentage areas of oak volatile compounds detected were different depending on contact time and type of toast (Table 2).

Polysaccharide-derived compounds, such as 5-methylfurfural and 5-hydroxymethylfurfural / maltol result from caramelized cellulose and hemicellulose wood composition, especially from hexose sugars, found in the more crystalline cellulose (Caldeira I. *et al.*, 2006). Hexose sugars provide resistance to acid hydrolysis at relatively low temperatures (150–240°C) used during oak toasting, hence these compounds are expected at much lower intensities in toasted oak compared to furfural concentrations (Herrero Paula *et al.*, 2016; Jin W. *et al.*, 2013).

Both compounds were detected in untoasted wood, but the percentage area is much higher in toasted wood. Increasing the time and temperature of toasted wood, decreases the percentage area of furfural and 5-methylfurfural detected in samples (Table 2). Those compounds possess a light caramel, sweet, butterscotch and faint almond like aromas (Cutzach Isabelle *et al.*, 1997).

Table 2

Volatile compositions (% area) detected in *Quercus robur* L. wood (Romanian oak) in different toasting levels

Compound name \ Sample	Retention time (min)	Flavor / Odor descriptor *	Untoasted wood	Light toast	Medium toast	Heavy toast
			Area %			
2-propanone	17.3	sweet/ caramellic	-	0.19	0.32	0.22
furfural	22.9	fruity/ sweet almond	15.12	74.40	74.85	68.67
acetyl furan	24.2	nutty/ balsamic	-	0.48	0.27	0.24
5-methylfurfural	26.3	brown/ caramellic	4.05	11.75	6.38	5.77
2(5H)furanone	31.6	-/ buttery	-	0.52	0.29	0.34
cis-β-methyl-γ-octalactone	35.2	creamy soft/ fresh wood	2.92	0.22	0.11	0.26
trans-β-methyl-γ-octalactone	37.01	herbal/coconut like	21.44	1.53	0.74	1.70
methyl-2-furoate	38.2	caramellic/ fungal	-	0.28	0.16	0.15
2-hydroxy butyrolactone	42.1	creamy/ milky	-	0.28	0.33	0.83
(5-formylfuran-2-yl) methyl acetate	42.7	-/ baked bread	-	0.30	0.19	0.35
5-hydroxy-methylfurfural	50.7	herbal, hay, tobacco/ fatty, buttery	20.71	0.30	5.45	6.28
isovanilin	52.9	vanilla/ sweet vanila	20.38	5.38	1.04	2.25
syringic aldehyde	54.1	spicy, smoky/ wood	-	-	-	3.46

The furfural percentage area was clearly the most intense signal observed in volatiles, which indicates that furfural is generated and volatilized in high quantities during the toasting process; those results are in accordance with those revealed by Farrell R.R. *et al.*, 2015. Rodríguez-Rodríguez P. and Encarna Gómez-Plaza, 2012, concluded that during ageing furfural and 5-methylfurfural were extracted rapidly by wine, reaching a maximum level at the beginning of ageing and a decrease of concentrations of those compounds may be observed in wines after that.

The most important volatile compounds with a high sensory impact on oak-aged wines are the oak lactones (Polášková P. *et al.*, 2008). The main aroma constituents of raw oak are the *cis* and *trans* isomers of oak lactone (*cis*-β-methyl-γ-octalactone and *trans*-β-methyl-γ-octalactone). As it results from table 2, in untoasted wood, percentage area was higher for untoasted samples, while, as the heat treatment increases, the percentage area of those compounds decreases. An excessive amount of *cis*-β-methyl-γ-octalactone and *trans*-β-methyl-γ-octalactone molecules in oak barrels stave could be detrimental to the aromatic quality of wine; therefore the loss of oak lactones during toasting is beneficial (Masson E. *et al.,* 2000).

Our results are similar with those reported by Duval C.J. *et al.*, 2013, and Farrell R.R. *et al.*, 2015. Toasting treatments had different effects on lactones level, such as: no effect, decreasing at high temperature, increasing then decreasing, or decreasing then increasing. Chatonnet P., 1991, states that the smelling potential of the toasted wood is influenced by the *cis/trans* isomer of β-methyl-γ-octalactone ratio, because the *cis* isomer is 2 to 12 times more odorous (notes of wood and coconut) than the *trans* isomer when evaluated in pure solution. Oak lactone associated sensory descriptors are fresh oak and coconut. The *cis* isomer is a more powerful aromatic than the *trans* isomer (Farrell R.R. *et al.*, 2015). An increase in barrel toast may reduce the amounts and the sensory impact of oak lactones in wine. The *cis* and *trans* forms of β-methyl-y-octalactone have woody and coconut odours and, along with vanillin, are among the major aroma compounds of uncharred oak wood (Câmara J.S. *et al.*, 2006).

Vanilla and isovanillin are lipid-compounds, generated by lignin heat degradation, but they are also present in raw oak (Farrell R.R. *et al*, 2015). Lignin is considered to be the most thermally stable wood polymer, which degrades at 280º–500ºC, but some degradation of lignin has been shown to occur at relatively low temperatures (e.g. 165ºC, Jin W. *et al.*, 2013). Vanillin concentration is considered to reflect the intensity of the toasting process.

Our results show a higher percentage area of isovanilin in untoasted wood, but in toasted samples the percentage area of this compound varies with the level of temperature (Table 2). Our findings are similar with other research, which concluded that isovanillin content in wood samples increases with medium toast levels, but it may decrease with very high toast (Zhang B. *et al.*, 2015). Vanillin concentration in wines could be related to smoky, cinnamon, coffee or dark chocolate descriptors (Chira K., P.L. Teissedre, 2013a). Vanillin and whisky lactone are the volatile compounds that are implicated in the overall woody aroma, these compounds being influenced by toasting (Chira K., P.L. Teissedre, 2013b).

The increase in toasting intensity enhanced the content of the aging markers in aged beverages such as vanillin and syringaldehyde (Bortoletto Aline Marques, A.R. Alcarde, 2015). Chatonnet P., 1991, states that the smelling potential of the toasted wood is influenced by the *cis*/*trans* isomer of β-methyl-γ-octalactone ratio, because the *cis* isomer is 2 to 12 times more odorous (notes of wood and coconut) than the *trans* isomer when evaluated in pure solution. Boidron J.N. and P. Chatonnet, 1988, suggest that, due to their threshold level, vanillin and the isomers of β-methyl-γ-octalactone have a major influence on wine aroma, while furfural and 5-methylfurfural have a minor impact.

CONCLUSIONS

The level of the toasting process of barrels staves is determining of the wine quality. In this paper, we provide the first study on volatile composition of Romanian oak staves used in cooperage in different levels of toasting. The results are similar to other authors' results. As it was expected, the percentage areas of oak volatile compounds detected were different, depending on contact time and type of toast. By increasing the time and temperature of toasted wood, the percentage area of furfural, 5-methylfurfural, *cis*-β-methyl-γ-octalactone and *trans*-β-methyl-γ-octalactone detected in wood samples decreases, however the vanillin percentage area increases. During ageing in oak barrels, the composition of wines changes due to the extraction of detected volatiles from barrel into wine, thus improving wine quality.

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REFERENCES

1. Bortoletto Aline Marques, A.R. Alcarde, 2015, Aging marker profile in cachaça is influenced by toasted oak chips. Journal of The Institute of Brewing 121(1): 70-77.
2. Boidron J.N., P. Chatonnet, 1988, Influence du bois sur certaines substances odorantes des vins (Effects of wood on aroma compounds of wine). Connaiss Vigne Vin 22: 275-294.
3. Cadahía Estrella, Brígida Fernández de Simón, Jerzy Jalocha, 2003, Volatile Compounds in Spanish, French, and American Oak Woods after Natural Seasoning and Toasting. J. Agric. Food Chem. 51 (20): 5923–5932.
4. Cadahía Estrella, Silvia Varea, Laura Muñoz, Brígida Fernández de Simón, María C. García-Vallejo, 2001, Evolution of Ellagitannins in Spanish, French, and American Oak Woods during Natural Seasoning and Toasting. J. Agric. Food Chem. 49 (8): 3677–3684.
5. Caldeira I., M.C. Clímaco, R.B. de Sousa, A.P. Belchior, 2006, Volatile composition of oak and chestnut woods used in brandy ageing: Modification induced by heat treatment. J. Food Eng. 76: 202–211.
6. Câmara J.S., M.A. Alves, J.C. Marques, 2006, Changes in volatile composition of Madeira wines during their oxidative ageing. Analytica Chimica Acta, 563 (1-2): 188–197.
7. Cerdán T.G., D.T. Goñi, C.A. Azpilicueta, 2004, Accumulation of volatile compounds during ageing of two red wines with different composition. J Food Eng 65(3): 349-356.
8. Chatonnet P., Isabelle Cutzach, Monique Pons, D. Dubourdieu, 1999, Monitoring Toasting Intensity of Barrels by Chromatographic Analysis of Volatile Compounds from Toasted Oak Wood. J. Agric. Food Chem. 47 (10): 4310–4318.
9. Chatonnet , D. Dubourdieu, 1998, Comparative Study of the Characteristics of American White Oak (*Quercus alba*) and European Oak (*Quercus petraea* and *Q. robur*) for Production of Barrels Used in Barrel Aging of Wines. Am J Enol Vitic 49: 79-85.
10. Chatonnet P., 1991, Incidences du bois de chêne sur la composition chimique et les qualités organoleptiques des vins: Applications technologiques, Bordeaux: Université Bordeaux II.
11. Chatonnet P., J.N. Boindron, 1989, Incidence du traitement thermique du bois de chêne sur sa composition chimique. 1ere partie: Définition des paramètres thermiques de la chauffe des fûts en tonnellerie. OENO One, 23, 77–87.
12. Chira K., P.L. Teissedre, 2013a, Extraction of oak volatiles and ellagitannins compounds and sensory profile of wine aged with French winewoods subjected to different toasting methods: Behaviour during storage. Food Chem 140(1-2): 168-177.

13. Chira K., P.L. Teissedre, 2013b, Relation between volatile composition, ellagitannin content and sensory perception of oak wood chips representing different toasting processes. Eur Food Res Tech 236(4): 735-746.
14. Collins T.S., Miles J.L., Boulton R.B., Ebeler S.E., 2015, Targeted volatile composition of oak wood samples taken during toasting at a commercial cooperage. Tetrahedron 71(20): 2971-2982.
15. Cutzach Isabelle, P. Chatonnet, R. Henry, D. Dubourdieu, 1997, Identification of volatile compounds with a “toasty” aroma in heated oak used in barrel making. J. Agric. Food Chem 45: 2217–2224.
16. Doussot F., B. De Jéso, S. Quideau, P. Pardon, 2002, Extractives Content in Cooperage Oak Wood during Natural Seasoning and Toasting; Influence of Tree Species, Geographic Location, and Single-Tree Effects. J. Agric. Food Chem. 50 (21): 5955–5961.
17. Duval C.J., N. Sok, J. Laroche, K. Gourrat, A. Prida, S. Lequin, D. Chassagne, R.D. Gougeon, 2013, Dry vs soaked wood: Modulating the volatile extractible fraction of oak wood by heat treatments. Food Chem. 138: 270–277.
18. Farrell R.R., M. Wellinger, Alexia N. Gloess, D.S. Nichols, M.C. Breadmore, R.A. Shellie, C. Yeretzian, 2015, Real-Time Mass Spectrometry Monitoring of Oak Wood Toasting: Elucidating Aroma Development Relevant to Oak-aged Wine Quality, Nature Scientific Reports 5: 17334.
19. Herrero Paula, María Pilar Sáenz-Navajas, J.M. Avizcuri, Laura Culleré, P. Balda, Elena C. Antón, V. Ferreira, Ana Escudero, 2016, Study of Chardonnay and Sauvignon blanc wines from D.O.Ca Rioja (Spain) aged in different French oak wood barrels: Chemical and aroma quality aspects. Food Res. Int. 89: 227–236.
20. Jin W., K. Singh, J. Zondlo, 2013, Pyrolysis Kinetics of Physical Components of Wood and Wood-Polymers Using Isoconversion Method. Agriculture 3: 12–32.
21. Le Floch A., M. Jourdes, P.L. Teissedre, 2015, Polysaccharides and lignin from oak wood used in cooperage: Composition, interest, assays: A review. Carbohydrate Res 417: 94-102.
22. Martínez-Gil Ana, Estrella Cadahía, Brígida Fernández de Simón, G. Gutiérrez-Gamboa, I. Nevares, María del Álamo-Sanza, 2017, Quercus humboldtii (colombian oak): characterization of wood phenolic composition with respect to traditional oak wood used in oenology. Ciência Téc. Vitiv. 32(2): 93-101.
23. Masson E., R. Baumes, Christine Le Guernevé, J.L. Puech, 2000, Identification of a Precursor of β-Methyl-γ-octalactone in the Wood of Sessile Oak (*Quercus petraea* (Matt.) Liebl.). J. Agric. Food Chem. 48: 4306-4309.
24. Pérez-Prieto L.J., J.M. López-Roca, A. Martínez-Cutillas, F. Pardo Mínguez, Encarna Gómez-Plaza, 2002, Maturing Wines in Oak Barrels. Effects of Origin, Volume, and Age of the Barrel on the Wine Volatile Composition. J. Agric. Food Chem. 50 (11): 3272–3276.
25. Polášková P., J. Herszage, S. Ebeler, 2008, Wine flavor: chemistry in a glass. Chem. Soc. Rev. 2478–2489.
26. Rodríguez-Rodríguez P., Encarna Gómez-Plaza, 2012, Dependence of Oak-Related Volatile Compounds on the Physicochemical Characteristics of Barrel-Aged Wines, Volatiles in Barrel-Aged Wines. Food Technol. Biotechnol. 50 (1): 59–65.
27. Vivas N., Y. Glories, B. Doneche, E. Gueho, 1991, Observations sur la flore fongique du bois de chêne (Quercus sp.) au cours de son séchage naturel. Annales des Sciences Naturelles, Botanique et Biologie vegetale, 13 (11), 149-153.
28. Zhang B., J. Cai, C.Q. Duan, M.J. Reeves, F. He, 2015, A Review of Polyphenolics in Oak Woods. Int. J. Mol. Sci. 16: 6978-7014.