Environmental Engineering and Management Journal February 2020, Vol. 19, No.2, 229-234
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

STUDY OF VOLATILE COMPOUNDS OF ROMANIAN RED WINES AGED WITH OAK CHIPS

Georgiana-Diana Dumitriu Gabur[1], Carmen Teodosiu[1]*, Valeriu V. Cotea[2], Rafael Andres Peinado[3], Iulian Gabur[4], Nieves Lopez de Lerma[3]

[1]"Gheorghe Asachi" Technical University of Iasi, Romania, "Cristofor Simionescu" Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. D. Mangeron Blvd., 700050 Iasi, Romania
[2]University of Agricultural Sciences and Veterinary Medicine "Ion Ionescu de la Brad" Iasi, Romania Department of Viticulture and Oenology, 3 Mihail Sadoveanu Alley, 700490, Iași, Romania
[3]University of Córdoba, Spain, Department of Agricultural Chemistry, Agrifood Campus of International Excellence ceiA3, Campus de Rabanales, Edificio Marie Curie, 14071, Córdoba, Spain
[4]University of Agricultural Sciences and Veterinary Medicine "Ion Ionescu de la Brad" Iasi, Romania Department of Plant Sciences, 3 Mihail Sadoveanu Alley, 700490, Iași, Romania

Abstract

Wine aroma plays an essential role and can be considered one of the most important attributes of the overall wine quality. Generally, aroma is a remarkable complex chemical matrix comprising compounds from various chemical classes (alcohols, esters, acids, aldehydes, lactones, phenols, terpenes, ketones, norisoprenoids, etc.). Although some studies tackle wine aroma in general, the chemical changes attributed to wine aroma during the ageing process are still poorly understood.
In this study, the profiles of minor volatile compounds of wine obtained from *Fetească neagră* grape variety, aged for 1.5 and 3 months by using stir bars sorptive extraction and gas chromatography coupled to mass spectrometry (SBSE-GS-MS) were investigated. Red wines were aged using medium toast oak wood chips with the following dimension 0.5 × 1.5 × 0.2 cm (width × length × thickness). The analysis identified 20 minor volatile compounds in samples. These compounds belong to four major chemical groups, namely esters, volatile phenols, carbonilics and oak compounds. Samples aged for 3 months registered an increase, when compared to 1.5 months samples, for all identified and quantified compounds. However, heptanal and octanal concentrations decreased. Principal components analysis of the minor volatile compounds differentiated wines according to their ageing time. The first principal components (PC1) explained 78.80% and PC2 14.03% of the total variance. Sensory profile of Feteasca neagră aged with oak chips was characterized by high notes of woody, toasty, vanilla, smoky and cacao and an attenuation of ripe fruit and herbaceous attributes.

Key words: oak chips, red wines, SBSE-GC-MS analysis, volatile compounds

Received: January, 2019; Revised final: November, 2019; Accepted: November, 2019; Published in final edited form: February, 2020

1. Introduction

Since the end of last century, innovation in winemaking allowed the development of alternative methods as ageing by using oak wood, especially in red wine production. Traditionally, wine ageing was performed in oak barrels. This represents an essential stage to produce high quality wines. However, the use of barrels requires long periods of wood-wine contact time, is not cost efficient, and is limited by their lifetime (5-6 years). Moreover, barrels cleaning is particularly challenging as undesirable microorganism such as *Brettanomyces* and *Dekkera* may cause severe contaminations and negative environmental impacts.

* Author to whom all correspondence should be addressed: e-mail: cteo@tuiasi.ro

The combined effect of the mentioned drawbacks makes traditional ageing systems very laborious, costly and environmental unfriendly due to the enormous volume of trees required for the barrels (Garde-Cerdán and Ancín Azpilicueta, 2006).

Alternative techniques, such as oak wood chips, offer a promising solution to traditional barrel ageing. Nowadays, oak chips have become a common winemaking practice in the world. Oak chips are cost efficient and produce chemical and sensory properties similar to wines produced in barrels (Dumitriu et al., 2016, 2017, 2019; García Carpintero et al., 2014; Wilker and Gallander, 1988). Wines aged with oak chips are known to present a deeper colour and higher levels of volatile oak extraction (Del Álamo Sanza et al., 2004).

The ageing process may cause losses of fruit and floral aromas characteristic to young wines and produce new "ageing" aromas (Petrozziello et al., 2018). Aged young red wines are described to contain notes attributed to "red fruit"- red and black currant, cherry, "floral" - rose, violet, "nutty" - almond, hazelnut, "sweet" - caramel, honey, "balsamic" and "resinous" - pine, eucalyptus aromas (Rogerson et al., 2001). Additionally, wines have rich flavors of blackcurrants and intense aromas of dried prunes. At the end of the ageing period, wines could be described as having deep flavors of intense fruit and mellow spices, with just a hint of pepper and cloves from the oak chips. Overall, wine aroma can be considered a crucial attribute of wine quality, playing a vital role in consumer selection and preferences. Generally, wine aroma is a remarkable complex chemical matrix where compounds from all chemical classes interact and provides to wine specificity and typicity. Nevertheless, the effect of the ageing process on wine aroma is poorly understood and needs comprehensive studies to be elucidated.

*Feteasc*ă *neagr*ă vine variety is one of the oldest Romanian varieties, whose origin is indisputable. This variety appeared through popular selection made in time by local winemakers, from the wild forest vine (*Vitis silvestris*) which was cultivated by the Dacian peoples in the area between the Carpathians and the Nistru River. According to OIV, in Romania, in 2015, *Feteasc*ă *neagr*ă was cultivated only in Romania on 2845 ha (OIV, 2015).

In this study we investigated the profiles of minor volatile compounds of *Feteasc*ă *neagr*ă wines, aged for 1.5 and 3 months, with medium toast degree by using stir bars sorptive extraction and gas chromatography coupled to mass spectrometry (SBSE-GS-MS).

2. Material and methods

2.1. Winemaking protocol

Wine was obtained from a red single-variety (cv. *Feteasc*ă *neagr*ă, *V. vinifera*) processed on a pilot scale in a cellar of Department of Viticulture and Oenology, University of Agricultural Sciences and Veterinary Medicine "Ion Ionescu de la Brad" Iași, Romania.

The maceration-fermentation process was made at 10-12°C for 7 days. Then, the grape skins were pressed to extract the remaining juice. The pressed wine was blended with the free run wine, and the mixture was pumped off into stainless steel tanks to complete alcoholic and malolactic fermentations. The wine obtained was divided and placed in glass vessels. The wines were aged with oak wood chips for 1.5 and 3 months. Wood species used in this experiment are *Quercus petraea*, from France. The dimension chips in centimeters were 0.5 × 1.5 × 0.2 (width × length × thickness). The chemical parameters of the initial wines were: total acidity, as tartaric acid, 5.82 g/L, pH 3.69, volatile acidity, as acetic acid, 0.52 g/L, and alcoholic strength by volume, 14.95 % v/v.

2.2. Minor volatile compounds

Aroma extraction was determined according to Tredoux et al. (2008) with minor changes. Stir bars (0.5 - mm film thickness, 10 - mm length, Gerstel GmbH, Mülheim an der Ruhr, Germany) coated with PDMS were used. The wine samples were diluted tenfold with a hydroethanolic solution (12% ethanol (v/v) and pH 3.5).

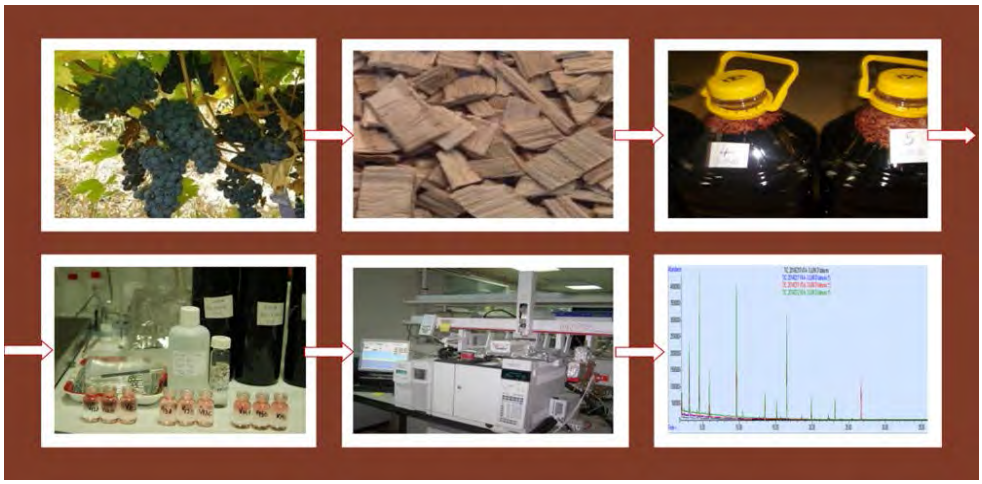

Fig. 1. Experimental design of identification and quantification of minor aroma compounds

The stir bars were placed in a 10 mL glass headspace vials containing 10 mL of the diluted sample and 0.1 mL of ethyl nonanoate (0.4464 mg/L) as internal standard. The vials were sealed with a Teflon-coated crimp cap and they were stirred at 1500 rpm at 25 ºC for 100 min. After removal from the wine samples, the stir bars were softly dried with lint-free tissues and then transferred into the glass thermal desorption tubes for GC/MS analysis.

The glass thermal desorption tubes were introduced into a GC/MS equipped with a Gerstel TDS 2 thermo desorption system. The stir bars were heated to release and transfer the extracts into a cooled injection system/programmed temperature vaporizer (CIS 4 PTV) containing a tenax adsorption tube. Retention times, spectral libraries supplied by Wiley (version 7 N) and pure chemical compounds from Merck, Sigma-Aldrich, Riedel de Haen, and Fluka were used for identification, confirmation and preparation of standard solutions of the volatile compounds.

Each compound was quantified from its calibration curve, which was obtained by using standard solutions of known concentrations previously subjected to the same treatment as the samples in conjunction with the target and qualifier ions selected for each compound by the Hewlett Packard Chemstation (Palo Alto, CA).

2.3. Sensory analysis

Wine samples underwent a panel sensory analysis in order to determine the influence of ageing with oak chips on the organoleptic characteristics. The samples were in cold storage for a period of time and transferred to room temperature (20ºC) two hours before the sensory analysis.

Nine wide and well-defined tasting places were set up. Sensory testing panel was composed of 15 tasters. Before starting the analysis, the test objective and methodology were explained in details. Samples were coded by using a key consisting of three randomly select letters, keys being different for each sample.

Analysis targeted the following specific aroma descriptors: ripe fruit, woody, toasty, smoky, vanilla, cacao and licorice. Tasters were instructed to give a score of 1 to 5 (1-detectable, 2-weak perceptible, 3-moderate perceptible, 4-strong perceptible and 5-very perceptible) in increasing order of perceived intensity to each aroma descriptor.

2.4. Statistical analysis

Statistical data analyses were performed by using Statgraphics Centurion XVI of StatPoint Technologies Inc. (Warrenton, Virginia). Principal Component Analysis was carried out to analyze the relationship between the parameters analyzed and the different time periods used in the ageing of wine.

3. Results and discussions

3.1. Volatile compounds and sensory analysis

Medium toasted oak wood chips are able to change wine aroma by adding of compounds such as aldehydes (furfural and syringaldehyde), phenols (vanillin, eugenol and guaiacol), lactones (*cis* and *trans* whiskey lactone), furanic compounds (García-Carpintero et al., 2014), and therefore these compounds confer aromas of wood, smoky, spice vanilla and clove (Cano-López et al., 2008; Schumacher et al., 2013). Moreover, Cano López et al., (2008) found that the oak chip addition improves the aroma profile and modify the sensory descriptors as compared to the samples without chips.

Results on the volatile compounds found in wine samples subjected to the ageing indicate clear differences between samples aged with oak chips after 1.5 and 3 months (Fig. 2). These compounds were classified into four chemical groups, namely esters, volatile phenols, carbonilics and oak compounds (Fig. 2). As expected, increased amounts were observed for all identified and quantified compounds for samples aged 3 months, in comparison to 1.5 months samples.

Esters are known as essential compounds for the overall complex sensory properties of wines. Their content depends on several factors, such as yeast strain, fermentation temperature and aeration (Perestrelo et al., 2006). In this study we observed that, in general, esters contribute with positive aromas, exhibiting with fruity and floral notes (Fig 2A). The concentrations of ethyl octanoate (322.62 µg/L at 1.5 months and 564.36 µg/L at 3 months), ethyl butanoate (251.89 µg/L at 1.5 months and 384.28 µg/L at 3 months) and ethyl propanoate (292.72 µg/L at 1.5 months and 326.86 µg/L at 3 months) were higher as compared with those of other esters such as: ethyl decanoate (69.48 µg/L at 1.5 months and 111.65 µg/L at 3 months) and 2-phenylethyl acetate (79.17 µg/L at 1.5 months and 126.92 µg/L at 3 months).

Within the volatile phenols group, differences of guaiacol and 4-vinylguaiacol amounts were observed, especially with higher values in samples aged 3 months than in those aged 1.5 months (Fig. 2B). Guaiacol concentration varied from 16.67 µg/L at 1.5 months to 21 µg/L at 3 months, while for 4-vinylguaiacol values of 50.33 µg/L at 1.5 months and 63.01 µg/L at 3 months were observed.

Similarly to previously describes compounds, the class of carbonilics compounds registered differences among the two ageing methods (1.5 or 3 months). Increased amounts were detected form furfural (slightly ‘toasty’, ‘woody’, ‘caramel’, ‘burned almonds’ odor), 5-methylfurfural (‘caramel’, ‘butterscotch’ aroma), heptanal (‘herbal’, ‘rancid’, ‘nut’), octanal (‘citrus’, ‘green’, ‘fresh’) and benzaldehyde (‘almond’, ‘smoked’, ‘cherry’ odour, ‘pistachio’ flavor) (López de Lerma et al., 2012; Peinado et al., 2004) within the category of Port wines with ‘indication of age’.

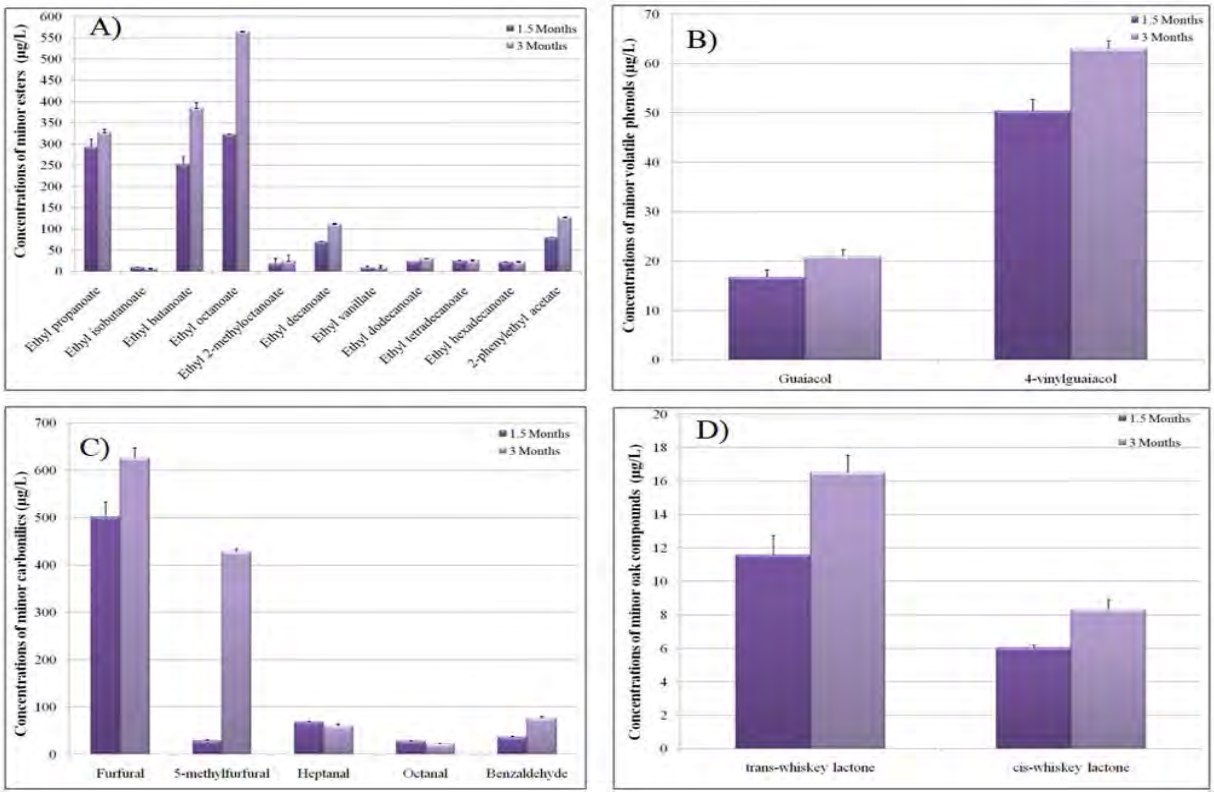

Fig. 2. Concentrations of minor volatile compounds grouped in four chemical families – A) esters, B) volatile phenols, C) carbonilics, D) oak compounds

This increase seems to be linked to the oxidative process during ageing. Furfural and 5-methylfurfural are derived from carbohydrate dehydration followed by cyclization in Maillard-type systems and are linked to wine browning during ageing. Furfural is produced from pentoses (xylose) and 5-methylfurfural arises from rhamnose (Câmara et al., 2006). Furfural and 5-methylfurfural registered the highest concentration among the two ageing methods, varying between 29 and 626 µg/L. According to Câmara et al. (2006) and in other studies, the furan compounds can be used as wine age indicators of wines. However, heptanal and octanal concentrations decreased in the same time frame (Fig. 2C).

The oak compounds, *cis* and *trans*-whiskey lactone presented higher values after 3 months of ageing (Fig. 2D). Concentrations for *cis*-whiskey lactone varied from 6.04 µg/L at 1.5 months to 8.32 µg/L at 3 months, while for *trans*-whiskey lactone from 11.59 µg/L at 1.5 months to 16.51 µg/L at 3 months. Generally, *cis*-whiskey lactone is correlated with the woody character of wines (Chatonnet et al., 1990), while the *trans* isomer has a higher sensory threshold.

Sensory evaluation is a scientific discipline used to evoke, measure, analyze, and interpret reactions to stimuli perceived through the senses (ASTM 2005)" (Lesschaeve, 2007). Giacalone (2018) defines sensory methods as a heterogeneous set of tools aimed at understanding "how different ingredients, formulations, and processing parameters are reflected in the sensory profile of the products".

The sensory analysis of the red wines obtained by adding oak chips at 2 periods of time was performed by evaluating the overall organoleptic quality to observe differences among the samples. The sensory profile of *Feteasc*ă *neagr*ă aged with oak chips was characterized by high scores assigned to woody, toasty, vanilla, smoky and cacao notes and an attenuation of ripe fruit and herbaceous attributes (Fig. 3).

3.2. Principal component analysis (PCA)

Principal components analysis (PCA) was realized to observe a reduced number of linear combinations of the variables that explain the greater variability in the data. The graphical representation of the variables analyzed in the principal components (PCs) is associated with the values of volatile compounds. Minor volatile compounds differentiated wines according to the ageing time as presented in Fig. 4. PCA results show that the first two components explain 92.83% of the variability of the data. PC1 explains 78.80% of the variance and is negatively related to the octanal and ethyl isobutanoate and positively associated to the 5-methylfurfural, ethyl decanoate, furfural and *trans*-whiskey lactone.

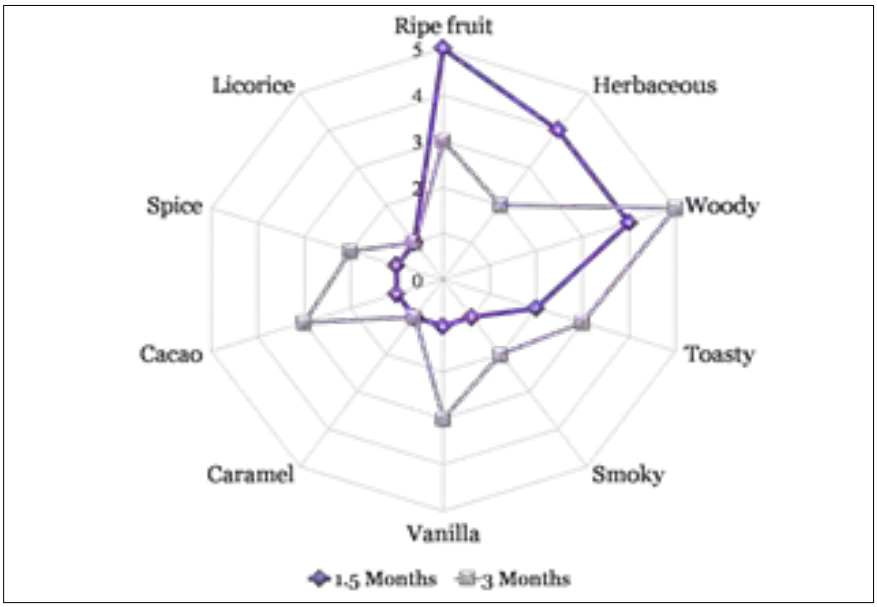

Fig. 3. The sensory profile of *Fetească neagră* aged with oak chips

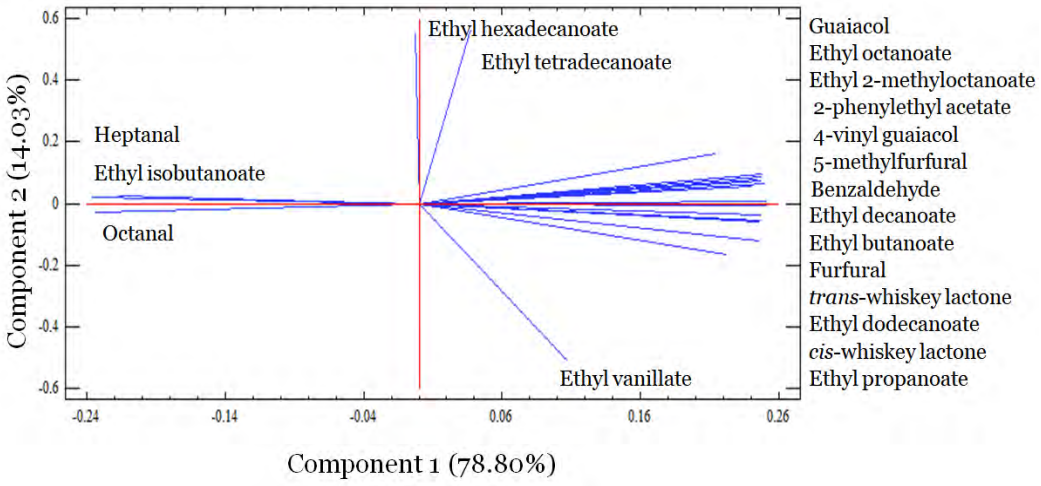

Fig. 4. PCA of wines aged 1.5 and 3 months with oak chips

The compounds that contribute highly to this differentiation were ethyl octanoate, ethyl decanoate, ethyl butanoate, furfural and ethyl dodecanoate. While PC2 explaining 14.03% of the variance is defined by ethyl hexadecanoate and ethyl tetradecanoate in the positive axis and with the ethyl vanillate in the negative axis. In the second component, it was observed that compounds with the highest weight are ethyl hexadecanoate, ethyl tetradecanoate, ethyl vanillate, ethyl propanoate and guaiacol.

4. Conclusions

The SBSE-GC-MS hyphenated techniques, combined with chemometric methods applied to the analysis of volatile compounds allows the differentiation of wines aged during 1.5 and 3 months with oak chips. The addition of oak chips has a significant influence on the aroma composition and sensory profile of *Fetească neagră* red wines. Red wines aged for 3 months showed the highest concentration of aroma compounds when comparative with aged wines for 1.5 months. Woody, vanilla, cacao, smoky and toast notes had a higher intensity in wines made in contact with oak chips for 3 months.

The ageing process with oak chips of *Fetească neagră* red wines could be a useful tool to obtain wines through cost-efficient, environmental friendly and feasible alternatives to the traditional, barrique based winemaking methods.

Acknowledgements

This study was supported by a grant of Ministry of Research and Innovation, CNCS - UEFISCDI, project number **PN-III-P1-1.1-PD-2016-0325**, "Environmental and human related impacts and risks of toxic compounds in the winemaking process" within PNCDI III". Additional funding was provided by the University of Córdoba Research Plan, call 2018, modality synergy, Córdoba, Spain.

We are also grateful to the Oenological Research Center-Romanian Academy, Iasi Branch.

References

Camara J.S., Alves M.A., Marques J.C., (2006), Changes in volatile composition of Madeira wines during their oxidative ageing, *Analytica Chimica Acta*, **563**, 188-197.

Cano-López M., Bautista-Ortín A.B., Pardo-Mínguez F., López-Roca J.M., Gómez Plaza E., (2008), Sensory descriptive analysis of a red wine aged with oak chips in stainless steel tanks or used barrels: effect of the contact time and size of the oak chips, *Journal of Food Quality*, **31**, 645-660.

Chatonnet P., Boidron J.N., Pons M., (1990), The aging of red wines in oak barrels: the formation of specific volatile components and their impact on aroma, *Science des Aliments*, **10**, 565–587.

Del Álamo-Sanza M., Nevares-Dominguez I., Cárcel-Cárcel L.M., Navas-Gracia L., (2004), Analysis for low molecular weight phenolic compounds in a red wine aged in oak chips, *Analytica Chimica Acta*, **513**, 229-237.

Dumitriu G.D., Lopez De Lerma N., Cotea V.V., Zamfir C.I., Peinado R.A., (2016), Effect of ageing time, dosage and toasting level of oak chips on the color parameters, phenolic compounds and antioxidant activity of red wines (var. 'Fetească neagră'), *European Food Research and Technology*, **242**, 2171-2180.

Dumitriu G.-D., López de Lerma N., Zamfir C.-I., Cotea V.V., Peinado R.A., (2017), Volatile and phenolic composition of red wines subjected to aging in oak cask of different toast degree during two periods of time. *LWT - Food Science and Technology*, **86**, 643–651.

Dumitriu (Gabur) G.-D., Peinado R.A., Cotea V.V., López de Lerma N., (2019), Volatilome fingerprint of red wines aged with chips or staves: influence of the aging time and toasting degree, *Food Chemistry*, **310**, 125801.

Garde-Cerdán T., Ancín-Azpilicueta C., (2006), Effect of oak barrel type on the volatile composition of wine, Storage time optimisation, *LWT-Food Science and Technology*, **39**, 199–205.

Giacalone D., (2018), *Sensory and Consumer Approaches for Targeted Product Development in the Agro-Food Sector*, In: *Case Studies in the Traditional Food Sector*, Cavicchi A., Santini C. (Eds.), Elsevier Ltd., Cambridge, MA, 91-128.

García-Carpintero G.E., Sánchez-Palomo E., González Viñas M.A., (2014), Volatile composition of Bobal red wines subjected to alcoholic/malolactic fermentation with oak chips, *LWT - Food Science and Technology*, **55**, 586-594.

Lesschaeve I., (2007), Sensory evaluation of wine and commercial realities: review of current practices and perspectives, *The American Journal of Enology and Viticulture*, **58**, 252-258.

López de Lerma N., Bellicontro A., Mencarelli F., Moreno J., Peinado R.A., (2012), Use of electronic nose, validated by GC–MS, to establish the optimum off-vine dehydration time of wine grapes, *Food Chemistry,* **130***,* 447–452.

OIV, (2015), *Grapevine varieties' area by country, International Organization of Vine and Wine*, On line at: http://www.oiv.int/public/medias/5882/grapevine-varieties-area-by-country-2015.pdf.

Peinado R.A., Moreno J., Bueno J.E., Moreno J.A., Mauricio J.C., (2004), Comparative study of aromatic compounds in two young white wines subjected to pre-fermentative cryomaceration, *Food Chemistry,* **84,** 585–590.

Perestrelo R., Fernandes A., Albuquerque F.F., Marques J.C., Câmara J.S., (2006), Analytical characterization of the aroma of Tinta Negra Mole red wine: Identification of the main odorants compounds, *Analytica Chimica Acta*, **563**, 154-164.

Petrozziello M., Torchio F., Piano F., Giacosa S., Ugliano M., Bosso A., Rolle L., (2018), Impact of increasing levels of oxygen consumption on the evolution of color, phenolic, and volatile compounds of nebbiolo wines, *Frontiers in Chemistry*, **6**, doi: 10.3389/fchem.2018.00137.

Rogerson F.H., Castro N., Fortunato Z., Azevedo A., Freitas V., (2001), Chemicals with sweet aroma descriptors found in Portuguese wines from the Douro region: 2,6,6-Trimethylcyclohex-2-ene-1,4-dione and diacetyl, *Journal of Agriculture and Food Chemistry*, **49**, 263-269.

Schumacher R., Alañón M.E., Castro-Vázquez L., Pérez-Coello M.S., Díaz-Maroto M.C., (2013), Evaluation of oak chips treatment on volatile composition and sensory characteristics of Merlot wine, *Journal of Food Quality*, **36**, 1-9.

Tredoux A., de Villiers A., Májek P., Lynen F., Crouch A., Sandra P., (2008), Stir bar sorptive extraction combined with GC-MS analysis and chemometric methods for the classification of South African wines according to the volatile composition, *Journal of Agricultural and Food Chemistry*, **56**, 4286-4296.

Wilker K.L., Gallander J.F., (1988), Comparison of Seyval blanc wine aged in barrels and stainless steel tanks with oak chips, *American Journal of Enology and Viticulture,* **39**, 38-43.