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# Volatilome fingerprint of red wines aged with chips or staves: Influence of the aging time and toasting degree

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ABSTRACT

The influence on aroma compounds chips or staves and toasting degree have been analyzed in red wines aged for two periods of time. Ethyl propanoate, ethyl butanoate, ethyl octanoate, ethyl acetate, isoamyl acetate, isobutanol, 2-methyl-1-butanol, 2-phenylethanol, E-2-hexenol, octanal, nonanal, decanal, γ-nonalactone, furfural, 5-methylfurfural, 2-methoxy-4-vinylphenol and *cis*-whiskey lactone were the compounds that contribute the most to the aroma series profile. By means of principal components analysis, esters were related to the aging time; *cis*-whiskey lactone with the type of wood pieces and octanal, 5-methyl furfural and *cis*-whiskey lactone with the toasting degree. Star plot show that woody aroma compounds are dominant in wines aged with low toasting degree oak pieces, whereas medium plus toasted pieces increased the concentration of aroma compounds with fruity aroma descriptors. Wines with prominent fruity or woody aromas can be obtained depending upon the degree of toasting of wood pieces used for aging.

## 1. Introduction

Aging techniques are considered a decisive stage of refinement to produce high quality red wines. A series of physical and chemical transformations take place within wines that affect the volatile and phenolic compounds. Wine complexity in terms of analytic composition increases and the sensorial characteristic also change during this procedure.

One of the mostly often used techniques for aging red wines involves the utilization of oak barrels. During this procedure changes in the sensory characteristics occurs (Pérez-Prieto, López-Roca, Martínez-Cutillas, Pardo-Mínguez, & Gómez-Plaza, 2003) highlighting an enrichment of wood related aromatic compounds like vanilla, coconut, almonds and smoke (Dumitriu, López de Lerma, Zamfir, Cotea, & Peinado, 2017; Ortega-Heras, González-Huerta, Herrera, & González-Sanjosé, 2004; Ortega-Heras, González-Sanjosé, & González-Huerta, 2007). Nevertheless, aging in barrels shows several disadvantages such as wine immobilized in cellars over long periods of time and high labor demands and storage cellar maintenance activities. In addition, older barrels with the passage of time can be infected with *Brettanomyces* and *Dekkera*. These yeasts can cause negative sensorial impacts through the synthesis of ethyl phenols that are associated with nasty, medicine and phenolic flavors (Suárez, Suárez-Lepe, Morata, & Calderón, 2007); this way oak barrels must be renewed. Furthermore, during aging, important wine losses are produced due to the evaporation, leakage through the joints between staves or breaking barrels. As a result, the production costs increase, creating a negative financial impact for winemakers (Ruiz de Adana, López, & Sala, 2005).

Some of these reasons have prompted the development of alternative aging systems that are simpler, more economical, ecological and accessible. Commonly used techniques, also named "fast-aging", include oak chips and oak staves, which offer winemakers the opportunity to improve the wine structure and its aromatic development with substantially reduced costs and oak-influenced flavor profile, accelerating the aging process (Baiano et al., 2016a). These practices have expanded rapidly, especially in new wine-producing countries. Wine composition is influenced, on one hand by the botanical and geographical origin of the oak, and on the other hand by the size and toasting degree of the wood pieces. Others factors to take into account are the dosage and the contact time with the wine (Del Alamo Sanza &

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Nevares Domínguez, 2006). Lastly, the shape of the wood pieces is also known to have an influence on the wine composition (Bautista-Ortín et al., 2008; Delgado de la Torre, Priego-Capote, & Luque de Castro, 2014; Fernández de Simón, Cadahía, Muiño, Del Álamo, & Nevares, 2010).

During aging wood compounds are released to the wine, which highly influences its sensorial characteristics. The concentration of such substances depends significantly on the toasting level of the oak wood used and on the time of aging. In this sense, whereas light toasted and untoasted wood releases more hydrolysable ellagitannins which helps red wine color to stabilize, heavy toasting limits the phenolic synthesis, although produces volatile phenols with smoky and spicy character (Fernández de Simón et al., 2010). Lastly, vanillin, furfural, 5-methylfurfural, guaiacol, 4-methylguaiacol, and syringol were detected in higher concentrations in wines aged with medium and heavy toasting wood than those aged with wood pieces of light toasting degree (Bozalongo, Carrillo, Torroba, & Tena, 2007).

There is a large literature about this subject which is consistent with the high number of variables that allows this type of aging. Many studies involve the influence on the phenolic composition of red wines aged with different oak wood (Alañón et al., 2013; Del Alamo Sanza & Nevares Domínguez, 2006; del Alamo Sanza, Nevares Domínguez, CárcelCárcel, and Navas Gracia (2004); Dumitriu, de Lerma, Cotea, Zamfir, & Peinado, 2016). Other studies, are focused on the aroma compounds of wines aged with oak chips (Baiano et al., 2016b; Bautista-Ortín et al., 2008; Bozalongo et al., 2007; Guchu, Díaz-Maroto, Pérez-Coello, González-Viñas, & Ibáñez, 2006; Pizarro, Rodríguez-Tecedor, Esteban-Díez, Pérez-del-Notario, & González-Sáiz, 2014). Some of them, analyze the influence of the toasting degree or the aging time in the wine composition. The compounds released by chips and staves during aging to synthetic and red wines have also been analyzed (Fernández de Simón et al., 2010). In this paper, red wines were subjected to aging under three factors, i) aging time, ii) type of wood pieces and iii) toasting degree of the wood, with the aim of stablish a relation between the assayed conditions aging system and the aroma profile of the resulting wines.

## 2. Material and methods

### 2.1. Aging conditions

Red wines were produced from Fetească neagră red grapes (*V. vinifera*), harvested in the North-East Romania winemaking region in 2013. Once the alcoholic and malolactic fermentations finished, wines were supplied with 60 mg/L of sulphur dioxide and divided in five stainless steel tanks of 250 L in triplicate. The first one contained wine without oak pieces and was namely initial wine (IW). 3 g/L of medium toasted chips (CM) and medium plus toasted chips (CMP) were added to the second and third batches. The last two batches contained oak staves of medium (SM) and medium plus (SMP) toasting degree. *Quercus petraea* wood chips (0.5 cm × 1.5 cm × 0.2 cm) and staves (1 cm × 10 cm × 1 cm) were supplied from Amedee. Wines were analyzed before the oak pieces were added, at 1.5 and at 3 months of aging.

### 2.2. Enological parameters and phenolic fractions

Common enological variables (ethanol, pH, reducing sugars, titratable and volatile acidity) were analyzed according to the official methods (CEE, 1990).

Colors parameters (absorbance at 420, 520 and 620 nm) were determined after filtering through a HA-0.45 µm paper in a spectrophotometer Perkin Elmer Lambda 25. Phenolic acids, flavanols, flavonols, tannin and polymeric pigments fractions were obtained by using tC-18 SepPak columns as described (Kim & Lee, 2001). The quantification was carried out enzymatically (Stevanato, Fabris, & Momo, 2004).

### 2.3. Major volatiles.

Commonly, major volatile compounds have concentration above 10 mg/L. These were identified and quantified in a gas HP 6890 Series II chromatograph equipped with the capillary column CP-WAX 57 CB (50 m in length, 0.25 mm in internal diameter and 0.4 µm in coating thickness) and a FID, according to the conditions described (Peinado, Moreno, Muñoz, Medina, & Moreno, 2004). To identify and quantify the analyzed compounds standards were injected under the same conditions as the samples.

### 2.4. Minor volatiles

Usually, minor volatiles compounds have concentration < 10 mg/L. These compounds were identified and quantified in a two steps process, both described previously in detail by (López de Lerma et al., 2018). The first one involves an extraction procedure by using stirs bars (0.5-mm film thickness, 10-mm length, Gerstel GmbH, Mülheim an der Ruhr, Germany). These are placed in a vial containing 10 mL of 1:10 diluted sample and 0.1 mL of ethyl nonanoate (0.4464 mg/L) as internal standard. After 100 min of stirring at 1500 rpm the stir bars were removed and transferred into a desorption tube for chromatographic analysis.

The second step involve the determination of the volatile compounds in a GC–MS equipped with a Gerstel TDS 2 thermodesorption system. Desorption tubes, containing the stirs bars, were heated at 280 °C with the aim of release the volatile compounds in a CIS 4 PTV cooling system programmed at 25 °C which contains a tenax adsorption tube. Lastly, the CIS is heated to release the volatiles in the GC–MS equipped with an Agilent-19091S capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness). Mass detector works in scan mode at 1850 V and check the mass from 39 to 300 amu.

To identify the volatile compounds, the retention times of standards injected under the same chromatographic conditions as the samples were used. Also, the Wiley spectral library was used. Quantification was made using calibrations curves of the standard.

### 2.5. Calculation of aroma series

The odorant activity value (OAV) of the volatile compounds were determined as the ratio concentration to its odor perception threshold. Aromatic series were obtained as the sum of the OAVs of the volatile compounds with similar aroma descriptors. This way nine aroma series namely, chemistry, fruity, creamy, floral, green, citric fruit, toasty, spice and woody were obtained. The same compound can be included in one or several aroma series, in agreement with its aromatic descriptors.

### 2.6. Statistical treatment

Multifactorial analysis of variance using as factors the toasting degree, type of oak pieces and the aging time was carried out to test their effects on the analyzed variables. A footprint of the wines was obtained by multivariate analysis using the aroma series. Lastly, the aroma compounds with OAV above the unity were used to perform a principal component analysis. To this end, statistical software Statgraphics Centurion XVI of StatPoint Technologies Inc. (Warrenton, Virginia) was used. All the analyses were undertaken in triplicate.

## 3. Results and discussion

### 3.1. Enological parameters and phenolic fractions

pH increased slowly during aging in all samples, whereas total acidity decreases at 3 months (Table 1), which could be probably ascribed to the precipitation of the tartaric salts (Moreno & Peinado,

**Table 1**
Enological parameters of the wines aged with oak chips or staves for 1.5 and 3 months. IW: initial wine; S: staves; C: chips; M: medium toast; MP: Medium plus toast. Multivariate analysis of variance (MANOVA) to study the influence of the type of oak wood, the aging time, the toast degree (TD) and the interaction among factors (In) in the analyzed variables. Phenolic fractions expressed in mg catechin/L.

| | IW | S-M | S-MP | C-M | C-MP | S-M | S-MP | C-M | C-MP | MANOVA | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1.5 Months | | | | 3 Months | | | | Type | Time | TD | In |
| pH | 3.68 ± 0.01 | 3.68 ± 0.01 | 3.64 ± 0.01 | 3.74 ± 0.01 | 3.65 ± 0.01 | 3.70 ± 0.01 | 3.69 ± 0.01 | 3.74 ± 0.01 | 3.66 ± 0.01 | * | ns | * | s |
| Titratable acidity (g tartaric acid/L) | 5.80 ± 0.04 | 5.90 ± 0.04 | 5.95 ± 0.05 | 5.68 ± 0.04 | 5.98 ± 0.06 | 5.80 ± 0.04 | 5.63 ± 0.03 | 5.62 ± 0.08 | 5.88 ± 0.03 | ns | * | * | ns |
| Volatile acidity (g acetic acid/L) | 0.48 ± 0.02 | 0.55 ± 0.02 | 0.60 ± 0.02 | 0.53 ± 0.03 | 0.58 ± 0.03 | 0.58 ± 0.02 | 0.58 ± 0.02 | 0.56 ± 0.02 | 0.59 ± 0.02 | ns | * | * | s |
| Ethanol (%v/v) | 15.0 ± 0.2 | 15.0 ± 0.2 | 15.0 ± 0.2 | 15.0 ± 0.1 | 15.0 ± 0.1 | 15.0 ± 0.2 | 15.0 ± 0.2 | 15.0 ± 0.1 | 15.0 ± 0.1 | ns | ns | ns | ns |
| A420 | 1.99 ± 0.02 | 1.97 ± 0.02 | 1.88 ± 0.01 | 1.96 ± 0.01 | 2.09 ± 0.01 | 1.99 ± 0.01 | 2.14 ± 0.01 | 2.04 ± 0.01 | 2.01 ± 0.01 | *** | *** | *** | *** |
| A520 | 12.4 ± 0.1 | 12.0 ± 0.2 | 11.7 ± 0.1 | 12.1 ± 0.2 | 11.8 ± 0.1 | 12.0 ± 0.2 | 12.2 ± 0.1 | 12.1 ± 0.1 | 11.7 ± 0.1 | ns | ns | ** | ns |
| A620 | 0.61 ± 0.03 | 0.51 ± 0.01 | 0.49 ± 0.01 | 0.51 ± 0.01 | 0.69 ± 0.02 | 0.51 ± 0.01 | 0.55 ± 0.01 | 0.53 ± 0.01 | 0.51 ± 0.01 | *** | ** | *** | *** |
| Total polyphenol index | 711 ± 22 | 664 ± 29 | 752 ± 26 | 703 ± 25 | 766 ± 23 | 712 ± 10 | 938 ± 5 | 860 ± 24 | 753 ± 33 | ns | *** | *** | *** |
| Phenolic acids and esters | 139 ± 6 | 109 ± 7 | 126 ± 6 | 180 ± 5 | 143 ± 4 | 101 ± 3 | 129 ± 4 | 136 ± 3 | 94 ± 3 | *** | *** | *** | * |
| Flavanols | 114 ± 5 | 118 ± 8 | 128 ± 6 | 181 ± 5 | 136 ± 4 | 149 ± 5 | 150 ± 4 | 100 ± 1 | 159 ± 5 | ** | ns | ** | *** |
| Flavonols | 109 ± 6 | 139 ± 7 | 104 ± 4 | 92 ± 5 | 212 ± 6 | 227 ± 7 | 293 ± 9 | 213 ± 7 | 227 ± 7 | ns | *** | *** | *** |
| Tannin and polymeric pigments | 175 ± 5 | 279 ± 3 | 333 ± 6 | 243 ± 7 | 240 ± 7 | 199 ± 6 | 285 ± 9 | 274 ± 10 | 217 ± 7 | *** | *** | *** | *** |

* indicate $p < 0.05$; ** indicate $p < 0.01$; *** indicate $p < 0.001$, ns: indicate $p > 0.05$; s: indicates at least $p < 0.05$.

2012). Volatile acidity depends on the toasting degree and on the aging time. Increased values of this parameter are related to non-enzymatic oxidation processes, that change ethanol into acetic acid (Ribéreau-Gayon, Glories, Maujean, & Dubourdieu, 2006).

Absorbance 420, 520 and 620 nm are usually related to brown, red and blue color components respectively. As the wine ages, blue and red components decrease whereas brown component gains in importance (Moreno & Peinado, 2012). Brown component increased significantly with the aging time and with a high toasting degree, showing chips pieces higher values than staves. The opposite is true for the blue component with the exception of the type of wood piece which is similar for chips and staves. Under the studied conditions, absorbance at 520 nm only depended significant on the toasting degree, showing the highest values with medium toasted pieces.

During aging, qualitative and quantitative composition of phenolic compounds are affected by chemical reaction as polymerization, condensation, precipitation and diffusion from oak to wine. Other factors that influence the phenolic composition are aging time, type of oak pieces, toasting degree or the botanical origin of the wood (Dumitriu et al., 2016; Fernández de Simón, Hernández, Cadahía, Dueñas, & Estrella, 2003). Under the experimental conditions, total polyphenol index increased with the aging time and show the highest values in wines aged with medium plus toasting oak pieces. Regarding to phenolic families, phenolic acids, tannins and polymeric pigments (Table 1) decreased with the aging time probably due to polymerization and precipitation reactions, whereas a high toasting degree involves an increase in the concentration of the phenolic families, except for flavanols, which is in accordance with (Dumitriu et al., 2017).

### 3.2. Influence of the studied factors in the aroma compounds concentration

Major (mg/L) and minor (μg/L) volatile compounds concentration are shown in Table 2.

Major alcohols increase slightly with the aging time which could be ascribed to cellulosic ethanolysis (Jeffery, 2012). With the exception of 2-phenylethanol, toasting degree does not influence their final content. On the other hand, only propanol and isobutanol were influenced by the type of wood piece.

Among minor volatile alcohols, the hexanol concentration can be highlighted, especially in wines aged with oak staves. E-3-hexenol, E-2-hexenol and benzyl alcohol increased with the aging time, whereas furfuryl alcohol decreased.

Acetaldehyde and acetoin are mainly produced during fermentation, although their concentrations change during aging due to oxidative phenomena (Moreno & Peinado, 2012). Both increased with the aging time and with the toasting degree of the wood. Minor carbonyls showed the lowest concentration among the volatiles analysed; however, aliphatic aldehydes possess a high impact in wine aroma due to their low odor perception threshold (Culleré, Ferreira, & Cacho, 2011). All of them depended significantly on three factors.

Esters play an important role in the fruitiness of red wines (Pineau, Barbe, Van Leeuwen, & Dubourdieu, 2009; Sumby, Grbin, & Jiranek, 2010). They are produced by yeast during the alcoholic fermentation, but tend to diminish during aging due to hydrolysis reactions (Garde-Cerdán & Ancín-Azpilicueta, 2006). The behaviour of esters does not follow a pattern, depending their behaviour on the particular compound. Ethyl propionate and ethyl butanoate increase during aging, showing the highest values in the wines aged with staves. Other esters such as ethyl isobutanoate or ethyl dodecanoate showed the highest values in the first stages of aging, decreasing significantly at three months. Ethyl octanoate or ethyl vanillate increased their concentration with the aging time and showed the highest concentration in wine aged with medium plus toasted staves. Hexyl hexanoate decreased in relation with the initial wine, showing no differences due to studied factors. Lastly, ethyl tetradecanoate and ethyl hexadecanoate did not show differences in the conditions analysed in relation with the initial wine.

**Table 2**

Concentration and aroma series (AS) of the volatile compounds determined in wines aged with oak chips or staves during 1.5 and 3 months. Multivariate analysis of variance (MANOVA) to study the influence of the type of oak wood, the aging time, the toast degree (TD) and the interaction among factors (In) in the aroma compounds concentration. IW: initial wine; S: staves; C: chips; M: medium toast; MP: Medium plus toast.

| Volatile aroma compounds | IW | S-M | S-MP | C-M | C-MP | S-M | S-MP | C-M | C-MP | MANOVA | | | | AS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1.5 Months | | | | 3 Months | | | | Type | Time | TD | In | |
| **Major alcohols (mg/L)** | **468 ± 11** | **512 ± 7** | **504 ± 4** | **501 ± 2** | **508 ± 2** | **537 ± 3** | **514 ± 7** | **527 ± 17** | **510 ± 5** | | | | | |
| Methanol | 199 ± 7 | 227 ± 2 | 226 ± 3 | 219 ± 2 | 228 ± 2 | 239 ± 1 | 227 ± 2 | 240 ± 5 | 229 ± 5 | ns | ** | ns | ns | 1,2 |
| Propanol | 34 ± 1 | 37 ± 1 | 37 ± 1 | 35 ± 0.3 | 36 ± 1 | 39 ± 1 | 37 ± 1 | 36 ± 1 | 37 ± 1 | * | * | ns | ns | 1 |
| Isobutanol | 46 ± 1 | 48 ± 1 | 48 ± 1 | 46 ± 1 | 47 ± 1 | 49 ± 1 | 48 ± 1 | 48 ± 1 | 47 ± 1 | ** | ns | ns | ns | 1 |
| Isoamyl alcohol | 131 ± 5 | 135 ± 6 | 131 ± 4 | 132 ± 4 | 135 ± 5 | 138 ± 4 | 136 ± 6 | 135 ± 5 | 135 ± 6 | ns | ** | ns | ns | 1 |
| 2-phenylethanol | 59 ± 2 | 66 ± 1 | 63 ± 1 | 68 ± 1 | 61 ± 1 | 73 ± 2 | 65 ± 2 | 69 ± 1 | 62 ± 1 | ns | * | *** | ns | 4 |
| **Minor alcohols (μg/L)** | **1601 ± 132** | **2345 ± 305** | **2203 ± 102** | **1841 ± 77** | **2366 ± 45** | **2812 ± 70** | **3109 ± 160** | **2760 ± 76** | **2780 ± 53** | | | | | |
| Hexanol | 1167 ± 37 | 1718 ± 32 | 1607 ± 24 | 1286 ± 62 | 1683 ± 81 | 1958 ± 15 | 2233 ± 35 | 1953 ± 58 | 1929 ± 60 | ** | * | *** | s | 5 |
| E-3-hexenol | 105 ± 1 | 146 ± 9 | 154 ± 8 | 192 ± 3 | 190 ± 6 | 186 ± 5 | 224 ± 12 | 230 ± 5 | 190 ± 7 | *** | *** | ns | s | 5 |
| E-2-hexenol | 233 ± 2 | 412 ± 9 | 378 ± 12 | 281 ± 6 | 439 ± 9 | 586 ± 14 | 583 ± 12 | 514 ± 12 | 569 ± 16 | ** | *** | *** | s | 5 |
| Furfuryl alcohol | 71 ± 4 | 62 ± 5 | 58 ± 3 | 73 ± 2 | 47 ± 3 | 59 ± 2 | 43 ± 3 | 57 ± 4 | 56 ± 4 | ns | *** | *** | s | 7 |
| Benzyl alcohol | 19 ± 1 | 7.0 ± 0.1 | 7.0 ± 0.2 | 9.0 ± 0.6 | 6.0 ± 0.3 | 23 ± 1 | 27 ± 1 | 6.0 ± 0.1 | 37 ± 2 | ** | *** | *** | s | 1,4 |
| **Major carbonyls (mg/L)** | **60 ± 2** | **96 ± 1** | **122 ± 5** | **102 ± 1** | **113 ± 5** | **154 ± 6** | **169 ± 7** | **126 ± 6** | **163 ± 6** | | | | | |
| Acetaldehyde | 30 ± 2 | 43 ± 1 | 53 ± 2 | 50 ± 2 | 56 ± 2 | 59 ± 3 | 68 ± 2 | 53 ± 2 | 56 ± 2 | ns | *** | *** | ns | 1 |
| Acetoin | 30 ± 1 | 54 ± 1 | 69 ± 2 | 52 ± 2 | 58 ± 2 | 95 ± 3 | 101 ± 5 | 77 ± 4 | 107 ± 5 | *** | *** | *** | s | 2 |
| **Minor carbonyls (μg/L)** | **30 ± 2** | **61 ± 1** | **69 ± 4** | **43 ± 2** | **56 ± 3** | **84 ± 7** | **132 ± 9** | **85 ± 4** | **101 ± 3** | | | | | |
| Heptanal | 2.3 ± 0.1 | 1.8 ± 0.2 | 1.8 ± 0.2 | 2.4 ± 0.1 | 1.9 ± 0.1 | 1.9 ± 0.1 | 1.5 ± 0.1 | 2.0 ± 0.2 | 1.6 ± 0.1 | ** | ** | *** | ns | 5 |
| Octanal | 1.1 ± 0.2 | 1.2 ± 0.1 | 2.4 ± 0.2 | 1.8 ± 0.1 | 2.8 ± 0.2 | 1.0 ± 0.1 | 2.5 ± 0.2 | 1.1 ± 0.1 | 2.2 ± 0.1 | *** | *** | ** | s | 6 |
| Nonanal | 2.3 ± 0.3 | 8.6 ± 0.5 | 8.1 ± 0.2 | 1.1 ± 0.1 | 5.9 ± 0.4 | 8.8 ± 0.5 | 11.2 ± 0.7 | 2.6 ± 0.2 | 8.3 ± 0.3 | *** | *** | *** | s | 6 |
| Decanal | 0.57 ± 0.02 | 6.5 ± 0.5 | 5.2 ± 0.3 | 1.2 ± 0.1 | 2.5 ± 0.3 | 6.1 ± 0.4 | 9.5 ± 0.7 | 2.8 ± 0.2 | 6.1 ± 0.5 | *** | *** | *** | s | 6 |
| Benzaldehyde | 24 ± 1 | 43 ± 1 | 51 ± 1 | 36 ± 1 | 43 ± 1 | 66 ± 1 | 108 ± 1 | 76 ± 4 | 83 ± 3 | *** | *** | *** | s | 7 |
| **Major esters (mg/L)** | **48 ± 2** | **56 ± 4** | **56 ± 1** | **62 ± 1** | **52 ± 1** | **64 ± 1** | **61 ± 1** | **62 ± 1** | **62 ± 2** | | | | | |
| Ethyl acetate | 32 ± 1 | 33 ± 2 | 32 ± 1 | 34 ± 1 | 28 ± 1 | 33 ± 1 | 33 ± 2 | 34 ± 1 | 32 ± 1 | ns | ns | ns | ns | 1 |
| Diethyl succinate | 16 ± 1 | 23 ± 1.6 | 24 ± 2 | 28 ± 1 | 24 ± 1 | 31 ± 1.1 | 29 ± 0.5 | 28 ± 1 | 30 ± 1 | ns | ns | ns | s | 2 |
| **Minor esters (μg/L)** | **1113 ± 69** | **1708 ± 52** | **2233 ± 25** | **1235 ± 49** | **1553 ± 36** | **2179 ± 91** | **2373 ± 41** | **1608 ± 37** | **1941 ± 57** | | | | | |
| Ethyl propionate | 193 ± 5 | 284 ± 11 | 281 ± 13 | 293 ± 4 | 312 ± 6 | 482 ± 6 | 510 ± 12 | 327 ± 7 | 392 ± 9 | *** | *** | ns | ns | 2 |
| Ethyl butanoate | 250 ± 6 | 325 ± 17 | 336 ± 15 | 252 ± 18 | 346 ± 21 | 451 ± 30 | 532 ± 37 | 384 ± 23 | 416 ± 24 | *** | *** | ns | s | 2,4 |
| Ethyl isobutanoate | 2.8 ± 0.2 | 12.1 ± 0.5 | 14 ± 1 | 4.7 ± 0.2 | 7.2 ± 0.4 | 0.49 ± 0.03 | 1.2 ± 0.1 | 0.34 ± 0.02 | 1.5 ± 0.1 | *** | *** | *** | ns | 2 |
| Ethyl furoate | 6.0 ± 0.4 | 1.9 ± 0.1 | 0.60 ± 0.04 | 4.0 ± 0.2 | 0.30 ± 0.01 | 3.5 ± 0.1 | 2.00 ± 0.02 | 5.0 ± 0.2 | 3.00 ± 0.02 | *** | *** | *** | s | 4 |
| Ethyl octanoate | 334 ± 7 | 414 ± 17 | 457 ± 13 | 323 ± 3 | 457 ± 9 | 779 ± 13 | 866 ± 15 | 564 ± 13 | 703 ± 16 | *** | *** | *** | ns | 2,4 |
| Ethyl decanoate | 107 ± 5 | 126 ± 3 | 156 ± 5 | 70 ± 4 | 89 ± 2 | 164 ± 5 | 144 ± 5 | 112 ± 5 | 136 ± 4 | *** | *** | *** | s | 2 |
| Ethyl dodecanoate | 110 ± 5 | 152 ± 9 | 243 ± 4 | 23 ± 2 | 39 ± 2 | 79 ± 3 | 49 ± 3 | 31 ± 2 | 57 ± 5 | *** | *** | *** | s | 3,4 |
| Ethyl tetradecanoate | 23 ± 1 | 19 ± 1 | 20 ± 1 | 25 ± 1 | 24 ± 1 | 25 ± 1 | 26 ± 1 | 26 ± 1 | 25 ± 1 | ns | ns | ns | ns | 2 |
| Ethyl hexadecanoate | 17 ± 1 | 17 ± 1 | 15 ± 1 | 22 ± 2 | 19 ± 1 | 23 ± 1 | 25 ± 1 | 22 ± 1 | 16 ± 1 | ns | ns | ns | s | 3 |
| Ethyl vanillate | nd | 126 ± 6 | 122 ± 9 | 131 ± 9 | 123 ± 6 | 162 ± 9 | 193 ± 8 | 130 ± 6 | 164 ± 9 | ** | *** | ** | ns | 7,8 |
| **Other esters (μg/L)** | **1155 ± 62** | **1346 ± 109** | **1394 ± 66** | **994 ± 61** | **1362 ± 42** | **1844 ± 84** | **2111 ± 47** | **1404 ± 26** | **1595 ± 59** | | | | | |
| Isoamyl acetate | 1063 ± 58 | 1243 ± 23 | 1288 ± 32 | 914 ± 23 | 1260 ± 41 | 1738 ± 39 | 1988 ± 26 | 1276 ± 36 | 1476 ± 22 | *** | *** | *** | s | 2 |
| Phenylethyl acetate | 91 ± 6 | 103 ± 4 | 105 ± 5 | 79 ± 6 | 101 ± 3 | 106 ± 6 | 123 ± 6 | 127 ± 3 | 119 ± 1 | ns | ** | *** | s | 4 |
| Hexyl hexanoate | 1.3 ± 0.1 | 0.60 ± 0.02 | 0.40 ± 0.01 | 1.2 ± 0.1 | 0.60 ± 0.03 | 0.40 ± 0.01 | 0.40 ± 0.01 | 0.50 ± 0.04 | 0.50 ± 0.05 | *** | *** | *** | s | 2 |
| **γ-Lactones (μg/L)** | **609 ± 7** | **608 ± 20** | **339 ± 21** | **498 ± 35** | **665 ± 32** | **761 ± 34** | **786 ± 9** | **610 ± 12** | **556 ± 27** | | | | | |
| γ-Crotonolactone | 126 ± 5 | 226 ± 7 | 226 ± 8 | 287 ± 6 | 369 ± 12 | 230 ± 8 | 310 ± 8 | 287 ± 16 | 313 ± 12 | *** | ns | *** | s | 3,5 |
| γ-Butyrolactone | 453 ± 11 | 345 ± 12 | 76 ± 2 | 180 ± 6 | 261 ± 8 | 487 ± 11 | 427 ± 12 | 283 ± 16 | 201 ± 16 | *** | *** | *** | s | 3 |
| γ-Nonalactone | 25 ± 2 | 33 ± 1 | 33 ± 1 | 28 ± 2 | 30 ± 2 | 39 ± 1 | 46 ± 0.7 | 35 ± 2 | 37 ± 2 | *** | *** | ** | ns | 2,3 |
| γ-Decalactone | 5.0 ± 0.3 | 5.0 ± 0.3 | 4.0 ± 0.2 | 4.0 ± 0.1 | 5.0 ± 0.2 | 4.0 ± 0.1 | 4.0 ± 0.1 | 4.0 ± 0.1 | 5.0 ± 0.3 | ns | ns | ns | s | 2,3 |
| **Oak compounds (μg/L)** | **189 ± 15** | **1763 ± 80** | **2030 ± 58** | **775 ± 25** | **830 ± 14** | **2803 ± 87** | **3359 ± 115** | **1107 ± 23** | **1337 ± 31** | | | | | |
| Furfural | 143 ± 2 | 951 ± 15 | 863 ± 12 | 502 ± 4 | 514 ± 5 | 1467 ± 36 | 1609 ± 32 | 626 ± 12 | 744 ± 16 | *** | *** | * | ns | 1,7 |
| 5-methylfurfural | 45 ± 2 | 396 ± 12 | 888 ± 14 | 126 ± 5 | 199 ± 2 | 762 ± 32 | 1295 ± 36 | 252 ± 10 | 427 ± 6 | *** | *** | *** | s | 7 |
| 5-HMF | nd | 43 ± 3 | 54 ± 4 | 22 ± 3 | 31 ± 3 | 48 ± 4 | 73 ± 5 | 52 ± 4 | 62 ± 5 | *** | *** | *** | s | 7 |
| Guaiacol | 0.50 ± 0.01 | 10 ± 1 | 13 ± 2 | 17 ± 1 | 20 ± 1 | 23 ± 1 | 21 ± 1 | 21 ± 1 | 23 ± 1 | *** | *** | ** | ns | 1,7 |
| 4-vinylguaiacol | 20 ± 1 | 15 ± 0.4 | 24 ± 0.5 | 50 ± 2 | 48 ± 2 | 47 ± 2 | 50 ± 2 | 63 ± 2 | 56 ± 3 | *** | *** | ns | ns | 8,9 |
| *trans*-whiskey lactone | nd | 41 ± 3 | 24 ± 2 | 25 ± 1 | 12 ± 1 | 55 ± 3 | 34 ± 2 | 27 ± 4 | 16 ± 1 | *** | *** | *** | ns | 9 |

(*continued on next page*)

**Table 2** (*continued*)

| Volatile aroma compounds | IW | S-M | S-MP | C-M | C-MP | S-M | S-MP | C-M | C-MP | MANOVA | | | | AS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1.5 Months | | | | 3 Months | | | | Type | Time | TD | In | |
| *cis*-whiskey lactone | nd | 305 ± 19 | 164 ± 4 | 34 ± 3 | 6 ± 1 | 401 ± 21 | 278 ± 9 | 65 ± 5 | 8 ± 1 | *** | *** | *** | ns | 9 |

* indicate $p < 0.05$; ** indicate $p < 0.01$; *** indicate $p < 0.001$, ns: indicate $p > 0.05$; s: indicates at least $p < 0.05$; nd: not detected.
1-Chemistry; 2-Fruity; 3-Creamy; 4-Floral; 5-Green; 6-Citric fruit; 7-Toasty; 8-Spice; 9-Woody.

The concentration of the lactones depended on the type of wood piece and on the toasting degree, except for γ-decalactone which concentration did not depend of any of the factors.

The chemical family namely oak compounds include several types of volatiles as oak lactones, furfural and derivates and volatile phenols. Oak lactones (also known as whiskey lactones) are produced from wood lipids and are released to wine during aging, becoming markers of wood aged wines, and contributing with fruity and woody aromas (Dumitriu et al., 2017; Singleton, 1995). Both isomers showed higher concentration in wines aged with staves than in those aged with chips; in this sense, some authors identified significant differences among different wood sizes (Fernández de Simón et al., 2010). In accordance with other authors (Chira & Teissedre, 2013), their concentration increased with the aging time and showed minor values in wines aged with medium plus oak pieces. The latter fact is probably due to the thermodegradation of oak lactones during the wood heating process or to their volatilisation (Singleton, 1995). Guaiacol and 4-vinylguaiacol, come from the thermodegradation of the lignin, and high temperatures reached during oak toasting accelerates its development (Díaz-Maroto, Sánchez-Palomo, & Pérez-Coello, 2004). Both compounds depended on the oak type and aging time but only guaiacol depended on the toasting degree. Lastly, furfural 5-methylfurfural and 5-hydroxymethylfurfural result from the hemicelluloses degradation during the toasting process of the wood (Garde-Cerdán & Ancín-Azpilicueta, 2006). Their concentration depended on the three studied factors. Altogether, these compounds increased with the aging time, and the wines aged with staves the highest concentration; also, a high toasting degree involve a higher concentration of furfural and derivatives.

### 3.3. *Aroma series*

The aroma of a wine is determined not only by the volatile compounds that contains but for the interactions among them, that include positive and negative synergistic effects (Hein, Ebeler, & Heymann, 2009). The odor activity value (OAV) help us to get information about the influence of a given compound to wine aroma (Francis & Newton, 2005). This way volatile compounds with an OAV above the unity indicate a potential contribution to wine aroma.

An analytical volatilome fingerprint can be obtained by constructing aroma series, whose values are obtained as described in material and methods section. By means of this procedure, that has been previously used by several authors, (Gómez-Míguez, Cacho, Ferreira, Vicario, & Heredia, 2007; López de Lerma et al., 2018; Peinado, Moreno, Bueno, Moreno, & Mauricio, 2004) can be reduced dramatically the number of variables to take into account when differences among oenological treatments want to be analysed. Here, chemistry, fruity, creamy, floral, green, citric fruit, toasty, spice and woody (Table 3) aroma series have been obtained.

The highest values were reached with the fruity series in all wines, highlighting those aged with medium plus toasted oak pieces (Table 3). This series increased with the aging time and showed higher values in wines aged with staves. The other series to consider is the woody one, which also increased with the aging time and showed higher values in wines aged with staves but, unlike fruity series, exhibited lower values in wines aged with medium plus oak pieces. This fact could be of interested, because depending on the toasting degree, wines can be obtained with prominent fruity or woody aromas. The rest of series depended on the three studied factors, except for chemistry, creamy and spice series, which depended on the oak type and aging time.

Regarding to the individual aroma compounds, ethyl propanoate, ethyl butanoate, ethyl octanoate, ethyl acetate, isoamyl acetate, isobutanol, 2-methyl-1-butanol, 2-phenylethanol, E-2-hexenol, octanal, nonanal, decanal, γ-nonalactone, furfural, 5-methylfurfural, 2-methoxy-4-vinylphenol and *cis*-whiskey lactone showed OAV higher than the unity at least in one of the different treatment. These compounds contribute to wine aroma with fruity, floral, citric, herbaceous, spice,

**Table 3**
Aroma series of wines aged with oak chips or staves during 1.5 and 3 months. Multivariate analysis of variance (MANOVA) to study the influence of the type of oak wood, the aging time, the toast degree (TD) and the interaction among factors (In) in the volatile aroma compound concentration. IW: initial wine; S: staves; C: chips; M: medium toast; MP: Medium plus toast.

| Aroma series | IW | S-M | S-MP | C-M | C-MP | S-M | S-MP | C-M | C-MP | MANOVA | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1.5 Months | | | | 3 Months | | | | Type | Time | TD | In |
| Chemistry | 10.7 ± 0.2 | 12.3 ± 0.3 | 12.1 ± 0.3 | 11.88 ± 0.07 | 11.39 ± 0.07 | 13.5 ± 0.3 | 13.6 ± 0.2 | 12.3 ± 0.1 | 12.3 ± 0.2 | *** | *** | ns | ns |
| Fruity | 121 ± 7 | 149 ± 7 | 160 ± 7 | 116 ± 5 | 160 ± 2 | 250 ± 12 | 281 ± 6 | 184 ± 4 | 222 ± 7 | *** | *** | *** | * |
| Creamy | 1.44 ± 0.09 | 1.89 ± 0.05 | 2.2 ± 0.1 | 1.42 ± 0.05 | 1.61 ± 0.08 | 2.23 ± 0.08 | 2.4 ± 0.1 | 1.87 ± 0.05 | 2.19 ± 0.03 | *** | *** | *** | ns |
| Floral | 6.5 ± 0.2 | 7.3 ± 0.5 | 7.2 ± 0.1 | 7.15 ± 0.03 | 6.6 ± 0.1 | 7.9 ± 0.4 | 7.1 ± 0.2 | 7.4 ± 0.1 | 6.8 ± 0.1 | *** | * | *** | ns |
| Green | 1.91 ± 0.06 | 2.5 ± 0.1 | 2.35 ± 0.04 | 2.20 ± 0.09 | 2.60 ± 0.07 | 3.07 ± 0.03 | 3.1 ± 0.1 | 2.96 ± 0.01 | 2.90 ± 0.05 | * | *** | ns | *** |
| Citric Fruit | 1.8 ± 0.1 | 9.1 ± 0.5 | 8.3 ± 0.3 | 2.1 ± 0.1 | 5.5 ± 0.4 | 8.8 ± 0.4 | 13.0 ± 0.7 | 3.7 ± 0.2 | 9.1 ± 0.3 | *** | *** | *** | *** |
| Toasty | 0.79 ± 0.06 | 2.4 ± 0.1 | 3.0 ± 0.1 | 2.49 ± 0.07 | 2.57 ± 0.03 | 4.44 ± 0.09 | 5.3 ± 0.2 | 3.26 ± 0.09 | 3.5 ± 0.1 | *** | *** | *** | ns |
| Spice | 0.49 ± 0.03 | 0.51 ± 0.03 | 0.71 ± 0.03 | 1.39 ± 0.07 | 1.3 ± 0.3 | 1.34 ± 0.05 | 1.44 ± 0.06 | 1.71 ± 0.04 | 1.56 ± 0.08 | *** | *** | ns | ns |
| Woody | nd | 5.4 ± 0.3 | 3.0 ± 0.1 | 1.22 ± 0.01 | 0.44 ± 0.04 | 7.1 ± 0.3 | 4.8 ± 0.1 | 1.7 ± 0.1 | 0.63 ± 0.04 | *** | *** | *** | ns |

* indicate $p < 0.05$; ** indicate $p < 0.01$; *** indicate $p < 0.001$, ns: indicate $p > 0.05$; s: indicates at least $p < 0.05$; nd: not detected.

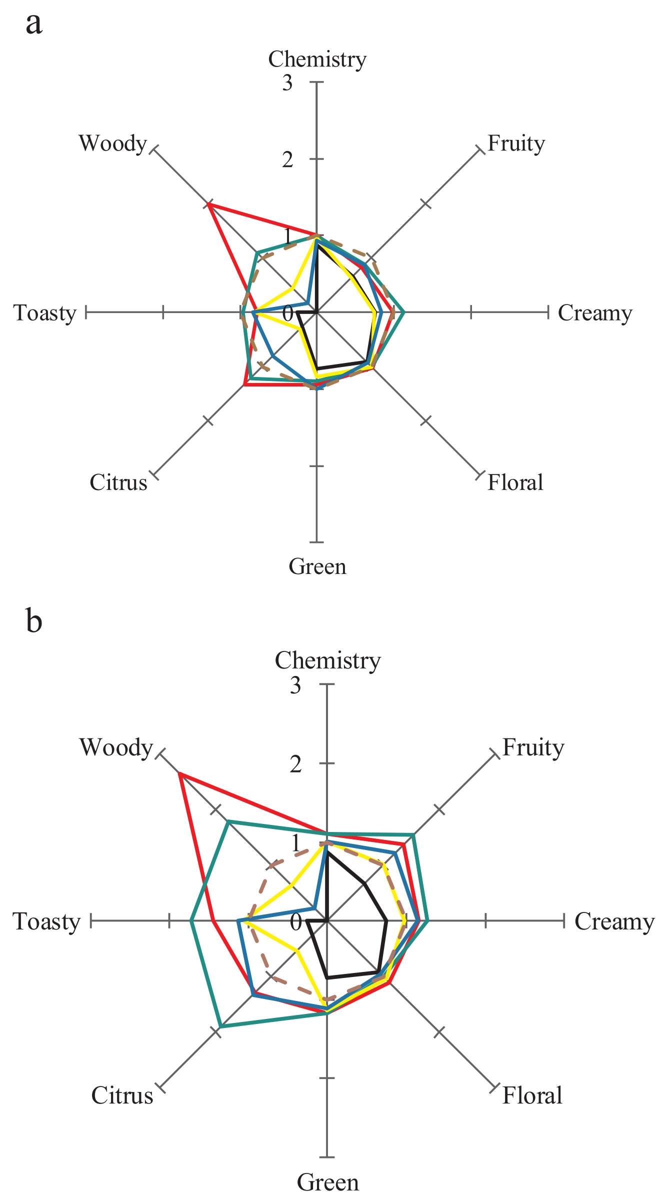


**Fig. 1.** Star plot obtained by multivariate data analysis of aroma compounds grouped in aroma series of wines aged for 1.5 (a) and 3 (b) months. Black line: initial wine. Red line: wine aged with medium toast staves. Green line: yeast strains, wine aged with medium plus toast staves. Yellow line: wine aged with medium toast chips. Blue line: wine aged with medium plus toast chips. Broken line: median value. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

toasty, and woody notes (Table 1, supplementary material) and altogether represent > 95% of the total aroma series value (Table 2 of supplementary material). Among these compounds, the following can be highlighted, ethyl propanoate, ethyl butanoate, ethyl octanoate and isoamyl acetate which contribute to fruity aromas. Other compounds of importance by its contribution to woody, citric and spice aromas were *cis*-whiskey lactone, decanal and 2-methoxy-4-vinylphenol respectively.

### 3.3.1. *Multivariate analysis*

By means of a multivariate analysis have been obtained a star plot with nine rays, one by each aroma series. Series were standardized, so the maximum length of the rays is the same for all the series being the unity the medium value of a series. With this procedure, question as what series are dominant for a given observation? and which observation are similar, i.e. are there clusters of observations? can be answered (Chambers, Cleveland, Kleiner, & Tukey, 1983).

For wines aged with staves for 1.5 months (Fig. 1A) most of series showed values around the median, except for the woody and citrus series which showed the highest values. However, wines aged with chips showed values lesser than those obtained with staves with no series above the median. At 3 months (Fig. 1B), the aroma series of the wines aged with staves increased markedly, highlighting the woody series in wines aged with medium toasted staves and the toasty, citrus and fruity series in wines aged with medium plus toasted staves. Wines aged with chips showed values below the median for the woody series although medium toasted chips show higher values than medium plus toasted chips, as is the case of staves. The opposite was true for fruity and citrus series. In this sense, (Návojská, Brandes, Nauer, Eder, & Frančáková, 2012) reported that wines aged with high toasting oak pieces show lower contents of both whiskey lactone isomers, responsible of woody notes, and increase the concentrations of furfural and derivates.

### 3.3.2. Principal component analysis

Principal component analysis is a statistical tool aimed to reduce the numbers of variables with the little loss of information as possible. New factors or components are a lineal combination of the input variables. The interpretation of the obtained components must be done by the analyst. Here, have been selected as initial variables the 17 aroma compounds with OAV above the unity, previously described. 3 principal components were obtained that account for the 84% of the observed variability (Fig. 2). The first principal component is related to the aging time and accounts for 60% of the variability (Fig. 2). Positive values of the component are related to a high aging time. This component was mainly influenced by ethyl propanoate, ethyl butanoate, ethyl octanoate, isoamyl acetate, γ-nonalactone, E-2-hexenol, decanal and furfural. Other compounds with high contribution were nonanal, 5-methylfurfural and *cis*-whiskey lactone (Table 4). All the aroma compounds showed positive values, so it can be assumed that their concentration increased with the aging time. The vertical axis of the Fig. 2 shows the weighted value of the second and third components that accounted for 24% of the variability and is related to the toast degree and the type of wood piece. Both components were mainly influenced by ethyl acetate, octanal, 2-methoxy-4-vinylphenol and *cis*-whiskey lactone. 2-phenylethanol and isobutanol contribute in a lesser extent.

**Table 4**
Weight of the volatile compounds used as classifying variables in the principal components analysis for each one of the selected components.

| | Aging time | Toasting degree and type of oak piece |
|---|---|---|
| Ethyl acetate | 0,0446 | −0,2614 |
| Ethyl propanoate | 0,2931 | 0,0799 |
| Ethyl butanoate | 0,2982 | 0,1009 |
| Ethyl octanoate | 0,2919 | 0,0928 |
| Isoamyl acetate | 0,2965 | 0,0442 |
| γ-nonalactone | 0,2945 | 0,0414 |
| Isobutanol | 0,2084 | −0,1857 |
| Isoamyl alcohols | 0,2093 | −0,0048 |
| 2-phenylethanol | 0,1442 | −0,1856 |
| E-2-hexenol | 0,2805 | 0,1183 |
| Octanal | 0,0455 | 0,3805 |
| Nonanal | 0,2577 | −0,0079 |
| Decanal | 0,2816 | −0,0291 |
| Furfural | 0,2980 | −0,0956 |
| 5-methylfurfural | 0,2628 | −0,0269 |
| 2-metoxy-4-vinilphenol | 0,1384 | 0,2709 |
| *cis*-whiskey lactone | 0,2276 | −0,3073 |

## 4. Conclusions

17 aroma compounds contribute to the sum of aroma series with > 95% highlighting those with fruity, and woody notes. In general, the concentration of volatiles increased with the aging time and with the use of wood pieces of medium plus toast degree. Also, wines aged with staves showed higher volatile concentration than those aged with chips. The principal components analysis put in evidence that ethyl propanoate, ethyl butanoate ethyl octanoate, isoamyl acetate and furfural are related positively with the aging time; also, *cis*-whiskey lactone is related to the use of low toasting degree oak pieces and to the use of staves. Lastly, start plot showed that woody series is dominant in wines aged with the lowest toasting degree oak pieces whereas in wines aged with medium plus toasting pieces highlighted the aroma compounds with fruity descriptors. Although further verification is needed, this fact is of interest because its provides the basis to relate fruity or woody aromas with the toasting degree of the wood pieces.

## Declaration of Competing Interest

The authors declare that they have no known competing financial

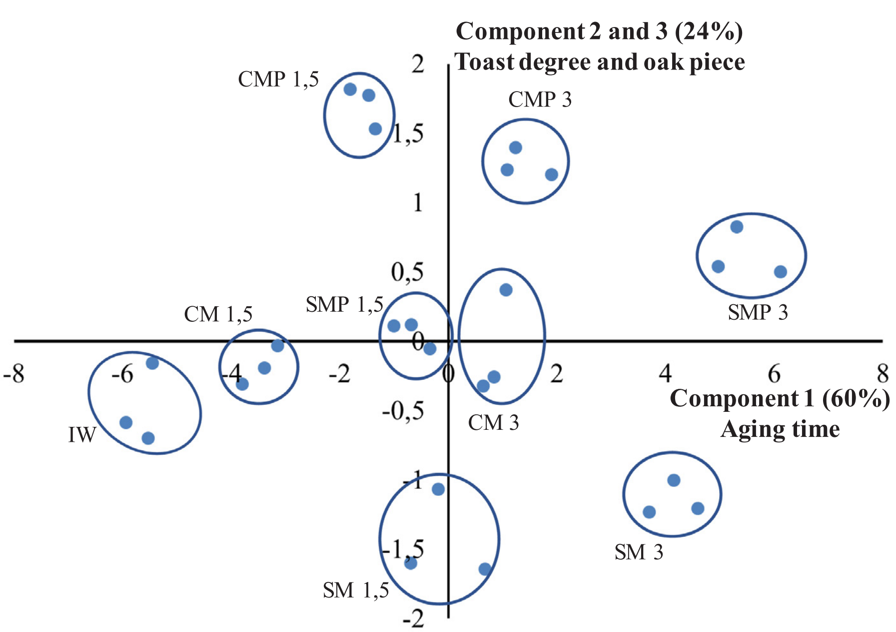


**Fig. 2.** Principal component (PC) analysis using the aroma compounds with odor activity values above the unity as classifying variables. PC1 is related to the aging time (a); PC2 is related to the toasting degree (a); PC3 is related to type of oak piece (b). IW: initial wine. CM and CMP: wines aged with medium toast or medium plus toast chips. SM and SMP: wines aged with medium toast or medium plus toast staves. 1.5 and 3 indicate the months of aging.

interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2019.125801.

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