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ORIGINAL PAPER



# Volatile composition of Spanish red wines: effect of origin and aging time

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## Abstract

This study investigated the volatile profile of the red wines from different Spanish Protected Designations of Origin (PDO), sited very closely in the Castilla y León region, and from different categories (young and aged) to found the compounds that allowed differentiate them. Fifty-three volatile compounds were identified and quantified using the headspace solid-phase micro-extraction technique and gas chromatography–mass spectrometry analysis (HS-SPME-GC/MS). The best differentiation was observed between those from Ribera del Duero (RD) and those from Bierzo (BI). RD wines, which are elaborated mainly with *Tempranillo* grape variety, were characterized by having the higher content of those compounds responsible of positive fruity, floral, and oak wood aromas which could increase their sensory complexity. BI wines, elaborated with *Mencia* grape variety were characterized by having higher content of oxidation volatile compounds. According to their category, and as it was expected, young and short aged wines (oak wines) were richer in fruity aroma compounds and some cheese off flavours, and crianza and reserve wines richer positive oak wood aromas. Crianza and reserve wines were also richer in some fruity (branched ethyl esters) and floral aromas (terpenes) than young wines, improving their aroma profile.

**Keywords** Volatile compounds · HS-SPME-GC/MS · Red wine categories · Protected designation of origin · Odor active values

## Introduction

Spain is one of the most important wine producers in the world with 33.5 millions of hectoliters [1]. Its wines, and mainly those within a Protected Designation of Origin (PDO), are highly considered around the world due to their quality that usually guides to the consumers when buy a wine. Wine's category (young or aged) is another criterion that consumers usually considers when buying a wine. Castilla y León is one of the most important Spanish winemaking regions sited in the North of Spain, being Ribera del Duero, Toro, Bierzo and Cigales PDOs with the highest volumen of hectoliters of young and aged wines produced this region [1].

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The wine's aromatic characteristics are one of the most important sensory attributes taken into account to evaluate its quality, having identified more than 1000 volatile compounds. The volatile profile of wines depends on several factors such as grape variety, geographical region production, climate, vintage, viticultural practices, winemaking techniques, aging and storage conditions [2–4]. The volatile compounds that come from grapes can be found in their free or glycosylated form (aromatic precursors non-volatile compounds), but only those that are in free form have odoriferous power (primary aromas). Due to the hydrolytic processes occurred in the wine, the bound between the volatile compound and sugar moiety can break and release the free volatile compound form into the wine. On the other hand, during fermentation processes, yeasts, enzymes and lactic bacteria can hydrolyze the glycosidic bonds of the aromatic precursors and allow releasing the aromatic compound into the wine (secondary aromas). In addition, some aromatic compounds can be formed from aminoacids during the fermentation process. Finally, wines aged in oak wood barrels and/or alternatives have aromatic compounds that come from wood, which increase their aromatic complexity (tertiary aromas) [5]. The analysis of volatile compounds in wines can be carried out using different techniques such as distillation, solvent extraction or solid-phase extraction (SPE) [6–8]. However, in recent years, the volatile extraction technique of head space-solid-phase micro-extraction (HS-SPME) has been used commonly due to the advantages presented such as it is less expensive, faster and requires little manipulation of the samples compared with other techniques. Volatile compounds are generally classified in esters, fatty acids, aldehydes, ketones, terpenes, alcohols, lactones, volatile phenols, etc., with a range concentration that can vary from mg/L to µg/L or even ng/L [9–13]. Most of these compounds contribute positively to enhance the aromatic profile of wines, but others can contribute negatively depending on their concentration and odor threshold perception. In this way, the sensory impact of the volatile compounds present in the wines depends on their odor active value (OAV), because only those compounds with an OAV > 1 have been perceived by the human nose, and could have a real impact in the olfactory perception [3, 14–17]. Previous works have been carried out in white and rosé wines from the point of view of volatile and phenolic composition [18] and in red wines using different physico-chemical parameters and phenolic compounds [19]. However, a study of the aromatic composition of these red wines and its possible sensory impact in the wines in function of the region and aging time is of interest. Therefore, the aim of this study was to carry out the volatile characterization of commercial red wines from different Spanish PDOs sited very closely geographically in the Castilla y León region in the North of Spain. In addition, the volatile compounds with a potential effect on the sensory profile were selected to differentiate wines from PDOs or category.

## Materials and methods

### Wine samples

One hundred and thirty-five commercial red wines from different PDOs and categories were studied (Table 1). The wines from Ribera del Duero (RD) and Toro (TO) were elaborated with at least 75% of *Tempranillo* grape variety, and the wines from Cigales (CI) with at least 50% of this variety. The wines from Bierzo (BI) were elaborated with at least the 85% of *Mencía* grape variety. The wines from each PDO were classified in four categories: (1) “young”: wines without aging in oak barrel; (2) “oak”: wines with at least three months of aging in oak barrel; (3) “crianza”: wines with a minimum aging period of 24 months, with at least 12 of these months in oak barrels; (4) “reserve”: wines with a minimum aging period of 36 months, with at least 12 of these months in oak barrels. The remaining aging time for “crianza” and “reserve” wines must be done in the bottle. The wines from the different regions are governed by the same regulations, therefore, the minimum total aging of time and the minimum period that the wine must remain in the oak barrel is the same for all the PDOs studied.

**Table 1** Number of wines analyzed in each category for each PDO

| | Ribera del Duero | Bierzo | Toro | Cigales | Total |
|---|---|---|---|---|---|
| Young | 14 | 7 | 7 | 4 | 32 |
| Oak | 21 | 5 | 7 | 4 | 37 |
| Crianza | 21 | 7 | 4 | 4 | 36 |
| Reserve | 20 | 2 | 4 | 4 | 30 |
| Total | 76 | 21 | 22 | 16 | 135 |

### Reagents and standards

The volatile compound standards were purchased from Fluka (Buchs, Switzerland), Sigma-Aldrich (Steinheim, Germany), and Lancaster (Strasbourg, France). Helium BIP (99.9997%) was purchased by Carburos Metálicos S.A. (Valladolid, Spain). The remaining reagents were supplied by Panreac (Madrid, Spain).

## Headspace solid-phase micro-extraction (HS-SPME) and GC/MS conditions

The extraction, identification and quantification of the volatile compounds was carried out following the methodology described in Del Barrio-Galán et al., 2021 [18].

The identification of the volatile compounds was carried out using the mass spectra of the calibration standards, retention times, and the NIST library. The quantification was carried out by calibration curves, using the chemical standards of each compound to be determined in the concentration range of application of the method, and adding a known concentration of six internal standards (IS). Table 2 summarizes the quantification ions and the IS chosen for each compound, the volatile compounds identified and quantified in the red wines studied, as well as the odor threshold and odor descriptor for each compound. These compounds were grouped as ethyl esters and alcohol acetates (10), fatty acids (7), alcohols (5), terpenes (3), lactones (3), aldehydes (7) (with positive and negative sensory notes), furanic compounds (3), volatile phenols (11) (with positive and negative sensory notes) and sulphur compounds (2). Most of these compounds are commonly found in red wines and come from the different grape varieties used, the fermentation processes (alcoholic and malolactic) and winemaking techniques applied.

**Table 2** Odor threshold, aromatic descriptors, quantification ions and internal standards used (IS) of each compound

| | Odor threshold (μg/L)[a] | Aromatic descriptor[a] | Quantification ion (m/s) | IS[b] |
|---|---|---|---|---|
| Ethyl esters and acetates | | | | |
| Ethyl butyrate | 20 | Fruity | 88 | 1 |
| Ethyl-2-methylbutyrate | 18 | Fruity. strawberry. anise | 57 | 1 |
| Ethyl isovalerate | 3 | Apple. sweet | 88 | 1 |
| Ethyl hexanoate | 5 | Fruity. green apple. strawberry. anise | 88 | 2 |
| Ethyl octanoate | 2 | Sweet. fruity. pear. pinneapple | 127 | 2 |
| Ethyl decanoate | 200 | Fruity. grape | 88 | 2 |
| Propyl acetate | Not found | Not found | 61 | 1 |
| Isobutyl acetate | 1600 | Fruity. apple. banana | 43 | 1 |
| Isoamyl acetate | 30 | Banana. fruity. sweet | 70 | 3 |
| Hexyl acetate | 670 | Apple. cherry. pear. floral | 56 | 1 |
| *β*-phenylethyl acetate | 250 | Floral. rose. honey | 104 | 3 |
| Fatty acids | | | | |
| Isobutyric acid | 200,000 | Cheese. fatty | 88 | 3 |
| Butyric acid | 173 | Spicy. sour. cheese. butterlike | 60 | 3 |
| Isovaleric acid | 33.4 | Rancid | 60 | 3 |
| Hexanoic acid | 3000 | Cheese. fatty | 60 | 3 |
| Octanoic acid | 500 | Fatty acid. rancid. cheese | 60 | 3 |
| Decanoic acid | 1000 | Fatty. rancid | 73 | 3 |
| Dodecanoic acid | 1000 | Dry. metallic | 129 | 3 |
| Alcohols | | | | |
| 1-hexanol | 8000 | Green. grass | 56 | 1 |
| *Trans*-3-hexenol | 400 | Green. floral | 41 | 1 |
| *Cis*-3-hexenol | 400 | Green | 67 | 1 |
| Benzyl alcohol | 200,000 | Citrusy. sweet | 85 | 4 |
| 2-Phenylethanol | 14,000 | Rose, flowery | 91 | 4 |
| Terpenes | | | | |
| Linalool | 25 | Flower. lavander. grape-like. citric | 121 | 4 |
| α-Terpineol | 1000 | Floral. sweet | 59 | 3 |
| Citronellol | 100 | Sweet. citrus-like | 69 | 3 |
| Lactones | | | | |
| *Trans*-whiskey lactone | 32 | Wood. sweet fruit. coconut | 99 | 4 |
| *Cis*-whiskey lactone | 74 | Wood. coconut | 99 | 4 |
| γ-nonalactone | 30 | Coconut. peach | 85 | 2 |
| Aldehydes | | | | |
| Isobutyraldehyde | 6 | Dried fruit. wet old wood, papery, sweet fusel | 72 | 5 |
| 2-methylbutanal | 16 | Dried fruit. wet old wood. papery. sweet fusel | 58 | 5 |
| 3-methylbutanal | 4.6 | Dried fruit. wet old wood. papery. sweet fusel | 58 | 5 |
| *Trans*-3-octenal | 3 | closed room, pungent | 70 | 5 |
| Vanillin | 60 | Vanilla | 151 | 4 |
| Methyl vanillate | 3000 | Vanilla | 151 | 4 |
| Ethyl vanillate | 990 | Vanilla | 151 | 4 |
| Acetovanillone | 1000 | Vanilla | 166 | 4 |
| Furanic compounds | | | | |
| Furfural | 14,100 | Bread. almonds. nuts. caramel | 96 | 5 |
| 5-Methyl furfural | 20,000 | Toasted almond | 110 | 5 |
| Furfuryl alcohol | 2000 | Cocoa, smoky, nut, burnt | 98 | 6 |
| Phenols | | | | |
| Guaiacol | 9.5 | Smoke. sweet. medicine | 121 | 6 |

**Table 2** (continued)

| | Odor threshold (µg/L)[a] | Aromatic descriptor[a] | Quantification ion (m/s) | IS[b] |
|---|---|---|---|---|
| 4-methylguaiacol | 65 | Burnt. ash. smoke | 138 | 4 |
| Eugenol | 6 | Clove. cinnamon | 164 | 4 |
| *Trans*-isoeugenol | 6 | Spices | 164 | 6 |
| Syringol | 350 | Smoke | 154 | 6 |
| 4-methylsyringol | | | 168 | 4 |
| 4-allylsyringol | 1200 | Spices. smoke | 194 | 4 |
| 4-ethylguaicol | 33 | Medicine. wood. clove. smoky | 137 | 4 |
| 4-ethylphenol | 440 | Phenolic. medicine. horsey | 107 | 4 |
| 4-vinylguaiacol | 40 | Spices. clove. curry | 150 | 4 |
| 4-vinylphenol | 180 | Medicine, phenolic, paint | 120 | 6 |
| Sulphur compounds | | | | |
| Methyl thioacetate | 50 (beer) | Sulfurous, cheesy. rotten eggs/cooked vegetables | 90 | 1 |
| Methional | 250 (beer) | Onion, mashed potatoes, cooked potato | 104 | 5 |

[a]References of odor threshold and aromatic descriptors: [3, 11, 15–17, 20, 30, 32, 33, 35, 36]

[b]1: methyl-2-methylbutyrate (17.7 mg/L); 2: methyl octanoate (45 mg/L); 3: heptanoic acid (185 mg/L); 4: $^{13}$C-benzyl alcohol (20 mg/L); 5: hexanal (16.3 mg/L); 6: 3,4-dimethylphenol (20 mg/L)

### Odor active values (OAVs)

OAV was calculated for stablish, quantitatively, the contribution of each volatile compound to the aroma of the wines studied. This value was calculated using the following equation consulted in the scientific literature: OAV = concentration (µg/L) / odor threshold (µg/L) [3, 17].

### Statistical analyses

One-way analysis of variance (ANOVA), followed by the Tukey's test (post hoc comparison test that allowed to determine statistically significant differences between the means with a confidence level of 95% ($p < 0.05$)), and principal component analysis (PCA) was carried out to the standardized data using the Statgraphics Centurion XVIII version statistical package.

## Results and discussion

### Characterization of the wines from different PDO

Table 3 shows the concentration and the odor active value (OAV) of each compound according to the PDO and category criteria. Quantitatively, alcohols, fatty acids, furanic derivatives, ethyl esters and alcohol acetates were the majority groups.

Statistically significant differences were found in the content of the wines from different PDOs (Table 3). Thus, the wines from RD and TO had the highest content of ethyl esters and alcohol acetates, mainly due to the differences found in isoamyl acetate, ethyl octanoate, ethyl hexanoate and ethyl decanoate, which were the most abundant compounds in this group. These volatile compounds are responsible of fruity aromas of wines [20–22], and are characterized by apple, strawberry, green apple, and banana fruity aromas. Considering the OAVs, octanoate and hexanoate ethyl esters, and isoamyl acetate were the compounds with the highest values having a real impact in the sensory profile of the wines. These results were in accordance with those obtained by other authors [3, 16, 23] who indicated the importance of these compounds in the sensory profile of red wines.

No significant differences were found in the total content of fatty acids, and only punctual differences were found in the concentration of isobutyric and isovaleric acids. Sensorially, only isovaleric acid had OAVs > 1, which could supply unpleasant rancid notes to the wines [3]. In this way, the wines from BI could had higher rancid notes than those from RD and CI.

Significant differences were also found in the content of total C6 alcohols, being the wines from CI which presented the highest content, mainly due to the differences found in 1-hexanol and *cis*-3-hexenol. These compounds were characterized by supply cut grass and herbaceous notes to the wines [15–18, 20–22]. However, in the studied wines, the OAV was lower than 1 and they do not affect the sensory profile. 2-phenylethanol was the most important alcohol and was the only one which presented an OAV > 1. Similar results were obtained by Jiang et al. [3] in a similar study, which observed that this compound had an important effect on the

**Table 3** Volatile compounds concentration (μg/L),odor active values (OAV) of the red wines according to their PDO and category, and ANOVA results [a]

| | Protected designation of origin | | | | | | | | Category | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | RD | | BI | | CI | | TO | | YOUNG | | OAK | | CRIANZA | | RESERVE | | MANO-VA[c] |
| | μg/L | OAV [b] | μg/L | OAV | μg/L | OAV | μg/L | OAV | μg/L | OAV | μg/L | OAV | μg/L | OAV | μg/L | OAV | PDO x CAT-EGORY |
| Ethyl esters and acetates | | | | | | | | | | | | | | | | | *p*-value |
| Ethyl butyrate | 274.8 | 13.74 | 247.2 | 12.36 | 264.7 | 13.24 | 283.6 | 14.18 | 276.9 | 13.85 | 259.4 | 12.97 | 263.2 | 13.16 | 286.8 | 14.34 | 0.147 |
| Ethyl-2-meth-ylbutyrate | 20.8 | 1.16 | 24.7 | 1.37 | 21.3 | 1.18 | 16.6 | 0.92 | 9.0a | 0.50 | 13.0a | 0.72 | 28.0b | 1.56 | 35.0c | 1.94 | 0.013 |
| Ethyl isovaler-ate | 38.9 | 12.97 | 37.4 | 12.47 | 37.6 | 12.53 | 27.3 | 9.10 | 15.8a | 5.27 | 24.4a | 8.13 | 50.3b | 16.77 | 57.0b | 19.00 | 0.011 |
| Ethyl hex-anoate | 445.7c | 89.14 | 254.7a | 50.94 | 319.5ab | 63.90 | 387.2bc | 77.44 | 416.6 | 83.32 | 396.2 | 79.24 | 370.1 | 74.02 | 383.1 | 76.62 | 0.384 |
| Ethyl octanoate | 508.7b | 254.35 | 298.7a | 149.35 | 416.9ab | 208.45 | 503.1b | 251.55 | 591.3b | 295.65 | 553.5b | 276.75 | 349.6a | 174.80 | 357.7a | 178.85 | 0.002 |
| Ethyl decanoate | 186.6b | 0.93 | 90.8a | 0.45 | 164.0ab | 0.82 | 176.1b | 0.88 | 273.8b | 1.37 | 221.1b | 1.11 | 93.6a | 0.47 | 76.9a | 0.38 | 0.000 |
| Propyl acetate | 30.1 | | 21.3 | | 31.3 | | 29.0 | | 30.1 | | 24.4 | | 30.6 | | 29.9 | | 0.849 |
| Isobutyl acetate | 61.3b | 0.04 | 53.1ab | 0.03 | 47.1a | 0.03 | 62.5b | 0.04 | 59.7 | 0.04 | 58.8 | 0.04 | 60.3 | 0.04 | 55.0 | 0.03 | 0.304 |
| Isoamyl acetate | 862.0b | 28.73 | 721.1ab | 24.04 | 453.4a | 15.11 | 1031.9b | 34.40 | 1398.8b | 46.63 | 844.2a | 28.14 | 585.5a | 19.52 | 450.7a | 15.02 | 0.697 |
| Hexyl acetate | 8.3 | 0.01 | 5.1 | 0.01 | 10.3 | 0.02 | 11.5 | 0.02 | 17.4b | 0.03 | 7.2a | 0.01 | 6.2a | 0.01 | 3.5a | 0.01 | 0.213 |
| β-phenylethyl acetate | 55.2ab | 0.22 | 58.1ab | 0.23 | 40.3a | 0.16 | 85.1b | 0.34 | 98.2b | 0.39 | 60.1a | 0.24 | 44.1a | 0.18 | 32.7a | 0.13 | 0.795 |
| Total | 2497.6b | | 1817.1a | | 1808.8a | | 2641.2b | | 3190.5c | | 2463.2b | | 1899.5a | | 1779.0a | | 0.013 |
| Fatty acids | | | | | | | | | | | | | | | | | |
| Isobutyric acid | 1709.3ab | 0.74 | 2144.2b | 0.93 | 1506.2a | 0.65 | 1941.7ab | 0.84 | 2047.1c | 0.89 | 1984.9ab | 0.86 | 1527.5a | 0.66 | 1603.2ab | 0.70 | 0.008 |
| Butyric acid | 1310.9 | 7.58 | 1447.5 | 8.37 | 1176.2 | 6.80 | 1460.6 | 8.44 | 1489.7b | 8.61 | 1424.9b | 8.24 | 1101.9a | 6.37 | 1367.5b | 7.90 | 0.002 |
| Isovaleric acid | 693.5a | 20.76 | 883.7b | 26.46 | 634.4a | 18.99 | 776.9ab | 23.26 | 748.3 | 22.40 | 757.0 | 22.66 | 712.7 | 21.34 | 698.6 | 20.92 | 0.063 |
| Hexanoic acid | 2666.7 | 0.89 | 2082.4 | 0.69 | 2134.2 | 0.71 | 2334.7 | 0.78 | 2797.6c | 0.93 | 2656.1bc | 0.88 | 2030.0a | 0.68 | 2367.6ab | 0.79 | 0.000 |
| Octanoic acid | 2086.4 | 4.17 | 1964.0 | 3.93 | 1984.6 | 3.97 | 2297.6 | 4.60 | 2363.4b | 4.73 | 2314.8b | 4.63 | 1820.1a | 3.64 | 1851.2a | 3.70 | 0.001 |
| Decanoic acid | 366.5 | 0.37 | 305.2 | 0.31 | 354.2 | 0.35 | 363.3 | 0.36 | 451.3b | 0.45 | 345.3a | 0.35 | 343.6a | 0.34 | 277.3a | 0.28 | 0.001 |
| Dodecanoic acid | 14.6 | 0.01 | 7.0 | 0.01 | 9.7 | 0.01 | 9.6 | 0.01 | 22.3c | 0.02 | 11.4b | 0.01 | 9.5ab | 0.01 | 4.8a | 0.00 | 0.000 |
| Total | 8848.0 | | 8834.3 | | 7799.1 | | 9184.9 | | 9919.9b | | 9494.6b | | 7545.1a | | 8170.2a | | 0.000 |
| Alcohols | | | | | | | | | | | | | | | | | |
| 1-hexanol | 1644.2b | 0.21 | 1204.0a | 0.15 | 2425.6d | 0.30 | 2025.8c | 0.25 | 1863.8 | 0.23 | 1718.1 | 0.21 | 1732.7 | 0.22 | 1603.4 | 0.20 | 0.000 |
| *Trans*-3-hex-enol | 55.3 | 0.14 | 52.0 | 0.13 | 60.1 | 0.15 | 57.4 | 0.14 | 60.4 | 0.15 | 53.8 | 0.13 | 56.1 | 0.14 | 52.5 | 0.13 | 0.001 |
| *Cis*-3-hexenol | 317.9b | 0.79 | 98.0a | 0.25 | 328.8b | 0.82 | 340.0b | 0.85 | 289.2 | 0.72 | 325.1 | 0.81 | 266.4 | 0.67 | 269.6 | 0.67 | 0.000 |

**Table 3** (continued)

| | Protected designation of origin | | | | | | | | Category | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | RD | | BI | | CI | | TO | | YOUNG | | OAK | | CRIANZA | | RESERVE | | MANO-VA[c] |
| | μg/L | OAV [b] | μg/L | OAV | μg/L | OAV | μg/L | OAV | μg/L | OAV | μg/L | OAV | μg/L | OAV | μg/L | OAV | PDO x CAT-EGORY |
| Total $C_6$ alcohols | 2017.5b | | 1353.8a | | 2813.8c | | 2422.7bc | | 2213.4 | | 2096.4 | | 2055.6 | | 1925.3 | | 0.000 |
| Benzyl alcohol | 443.7 | 0.00 | 272.2 | 0.00 | 254.8 | 0.00 | 382.0 | 0.00 | 477.3 | 0.00 | 286.6 | 0.00 | 442.0 | 0.00 | 332.5 | 0.00 | 0.987 |
| 2-Phenyletha-nol | 29,423.5bc | 2.10 | 23,402.7a | 1.67 | 27,498.4ab | 1.96 | 34,067.8c | 2.43 | 29,209.8ab | 2.09 | 32,780.2b | 2.34 | 27,641.2a | 1.97 | 25,926.7a | 1.85 | 0.063 |
| Terpenes | | | | | | | | | | | | | | | | | |
| Linalool | 63.9b | 2.56 | 32.9a | 1.32 | 67.3b | 2.69 | 47.1ab | 1.88 | 28.5a | 1.14 | 36.9a | 1.48 | 62.9b | 2.52 | 103.0c | 4.12 | 0.001 |
| α-Terpineol | 5.7 | 0.02 | 7.0 | 0.03 | 6.1 | 0.02 | 7.4 | 0.03 | 4.0a | 0.02 | 4.0a | 0.02 | 8.1b | 0.03 | 9.1b | 0.04 | 0.006 |
| Citronellol | 4.1 | 0.04 | 4.6 | 0.05 | 3.4 | 0.03 | 4.3 | 0.04 | 5.3b | 0.05 | 4.2b | 0.04 | 4.5b | 0.05 | 2.4a | 0.02 | 0.041 |
| Total | 73.8b | | 44.5a | | 76.6b | | 58.6ab | | 37.9a | | 45.0a | | 75.6b | | 114.5c | | 0.001 |
| Lactones | | | | | | | | | | | | | | | | | |
| *Trans*-whiskey lactone | 92.2b | 2.88 | 44.0a | 1.38 | 51.7ab | 1.62 | 57.4ab | 1.79 | 19.3a | 0.60 | 78.1b | 2.44 | 98.9b | 3.09 | 97.8b | 3.06 | 0.544 |
| *Cis*-whiskey lactone | 166.7b | 2.25 | 67.6a | 0.91 | 115.9ab | 1.57 | 116.1ab | 1.57 | 10.1a | 0.14 | 127.4b | 1.72 | 199.0c | 2.69 | 208.4c | 2.82 | 0.151 |
| γ-nonalactone | 7.0c | 0.23 | 4.5a | 0.15 | 5.5ab | 0.18 | 5.9bc | 0.20 | 6.3 | 0.21 | 6.4 | 0.21 | 6.6 | 0.22 | 5.8 | 0.19 | 0.010 |
| Total whiskey lactones | 258.7b | | 111.8a | | 167.5ab | | 173.5ab | | 29.4a | | 205.4b | | 298.0c | | 306.2c | | 0.290 |
| Aldehydes | | | | | | | | | | | | | | | | | |
| Isobutyralde-hyde | 16.4a | 2.73 | 33.8b | 5.63 | 22.1a | 3.68 | 24.4ab | 4.07 | 14.1a | 2.35 | 20.3ab | 3.38 | 26.2b | 4.37 | 23.4b | 3.90 | 0.024 |
| 2-methylbu-tanal | 4.9a | 0.31 | 12.9b | 0.81 | 5.8a | 0.36 | 6.2a | 0.39 | 4.7a | 0.29 | 6.4ab | 0.40 | 8.2b | 0.51 | 6.5ab | 0.41 | 0.130 |
| 3-methylbu-tanal | 24.2 | 5.26 | 23.1 | 5.02 | 20.4 | 4.43 | 23.5 | 5.11 | 18.8a | 4.09 | 26.3b | 5.72 | 25.7b | 5.59 | 22.3ab | 4.85 | 0.001 |
| Total negative sensory aldehydes | 45.5a | | 69.8b | | 48.3a | | 54.1ab | | 37.6a | | 53.0ab | | 60.1b | | 52.2ab | | 0.347 |
| Vanillin | 31.6 | 0.53 | 10.7 | 0.18 | 21.4 | 0.36 | 25.6 | 0.43 | 8.4a | 0.14 | 39.6b | 0.66 | 29.5ab | 0.49 | 24.7ab | 0.41 | 0.797 |
| Methyl vanillate | 13.0b | 0.00 | 5.1a | 0.00 | 5.1a | 0.00 | 3.8a | 0.00 | 10.2 | 0.00 | 10.8 | 0.00 | 8.5 | 0.00 | 7.5 | 0.00 | 0.008 |
| Ethyl vanillate | 74.9b | 0.08 | 58.7ab | 0.06 | 46.3a | 0.05 | 51.8ab | 0.05 | 42.8a | 0.04 | 56.9ab | 0.06 | 86.6c | 0.09 | 73.1bc | 0.07 | 0.578 |
| Acetovanillone | 29.6b | 0.03 | 16.4a | 0.02 | 22.7ab | 0.02 | 19.6a | 0.02 | 21.1a | 0.02 | 27.4ab | 0.03 | 22.5ab | 0.02 | 29.6b | 0.03 | 0.431 |
| Total positive sensory aldehydes | 149.2b | | 91.1a | | 95.6a | | 100.9a | | 82.6a | | 134.8b | | 147.2b | | 135.2b | | 0.598 |

**Table 3** (continued)

| | Protected designation of origin | | | | | | | | Category | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | RD | | BI | | CI | | TO | | YOUNG | | OAK | | CRIANZA | | RESERVE | | MANOVA[c] |
| | µg/L | OAV [b] | µg/L | OAV | µg/L | OAV | µg/L | OAV | µg/L | OAV | µg/L | OAV | µg/L | OAV | µg/L | OAV | PDO x CATEGORY |
| Furanic compounds | | | | | | | | | | | | | | | | | |
| Furfural | 109.6 | 0.01 | 213.2 | 0.02 | 142.5 | 0.01 | 107.8 | 0.01 | 46.7a | 0.00 | 145.1b | 0.01 | 190.5b | 0.01 | 125.8ab | 0.01 | 0.787 |
| 5-Methyl furfural | 38.9 | 0.00 | 52.5 | 0.00 | 41.2 | 0.00 | 42.9 | 0.00 | 7.4a | 0.00 | 44.9ab | 0.00 | 70.8b | 0.00 | 40.6ab | 0.00 | 0.634 |
| Furfuryl alcohol | 4825.4b | 2.41 | 3461.6ab | 1.73 | 2665.3a | 1.33 | 2928.9a | 1.46 | 3513.1a | 1.76 | 3446.9a | 1.72 | 4490.6b | 2.25 | 4783.7b | 2.39 | 0.223 |
| Total | 4973.8b | | 3727.4ab | | 2849.0a | | 3079.5a | | 3567.1a | | 3636.8a | | 4752.0b | | 4950.1b | | 0.268 |
| Phenols | | | | | | | | | | | | | | | | | |
| Guaiacol | 12.2 | 1.28 | 9.1 | 0.96 | 12.3 | 1.29 | 13.0 | 1.37 | 5.1a | 0.54 | 9.4b | 0.99 | 14.4c | 1.52 | 18.9d | 1.99 | 0.747 |
| 4-Methylguaiacol | 5.8 | 0.09 | 2.2 | 0.03 | 3.4 | 0.05 | 4.2 | 0.06 | 1.3a | 0.02 | 5.4b | 0.08 | 5.8b | 0.09 | 6.1b | 0.09 | 0.896 |
| Eugenol | 29.9 | 4.98 | 51.5 | 8.58 | 26.7 | 4.45 | 34.3 | 5.72 | 4.1a | 0.68 | 30.3ab | 5.05 | 57.0b | 9.50 | 40.9b | 6.82 | 0.008 |
| *Trans*-isoeugenol | 39.6b | 6.60 | 12.8a | 2.13 | 31.1b | 5.18 | 29.5b | 4.92 | 16.1a | 2.68 | 30.8b | 5.13 | 33.7b | 5.62 | 51.6c | 8.60 | 0.046 |
| Syringol | 31.1b | 0.09 | 7.2a | 0.02 | 11.3ab | 0.03 | 14.9ab | 0.04 | 9.8a | 0.03 | 23.9b | 0.07 | 27.6b | 0.08 | 27.5b | 0.08 | 0.997 |
| 4-methylsyringol | 12.8b | | 3.4a | | 3.3a | | 4.3a | | 1.8a | | 6.3a | | 13.3b | | 13.8b | | 0.138 |
| 4-allylsyringol | 32.6b | 0.03 | 9.4a | 0.01 | 11.8a | 0.01 | 14.5a | 0.01 | 8.9a | 0.01 | 17.1a | 0.01 | 35.7b | 0.03 | 32.1b | 0.03 | 0.458 |
| Total positive sensory phenols | 166.7b | | 97.6a | | 101.3ab | | 116.9ab | | 47.9a | | 125.3b | | 191.0c | | 194.1c | | 0.427 |
| 4-ethylguaicol | 8.5 | 0.26 | 4.1 | 0.12 | 3.6 | 0.11 | 3.4 | 0.10 | 0.7 | 0.02 | 7.7 | 0.23 | 7.6 | 0.23 | 9.5 | 0.29 | 0.959 |
| 4-ethylphenol | 65.1 | 0.15 | 7.0 | 0.02 | 12.9 | 0.03 | 14.0 | 0.03 | 2.0a | 0.00 | 64.4b | 0.15 | 47.6b | 0.11 | 48.1b | 0.11 | 0.982 |
| 4-vinylguaiacol | 11.7 | 0.29 | 4.3 | 0.11 | 3.1 | 0.08 | 5.5 | 0.14 | 3.4 | 0.09 | 10.6 | 0.27 | 9.0 | 0.23 | 10.7 | 0.27 | 0.963 |
| 4-vinylphenol | 10.3 | 0.06 | 8.4 | 0.05 | 4.8 | 0.03 | 5.1 | 0.03 | 1.2 | 0.01 | 11.8 | 0.07 | 9.2 | 0.05 | 11.5 | 0.06 | 0.739 |
| Total negative sensory phenols | 95.6 | | 23.8 | | 24.5 | | 27.8 | | 7.2a | | 94.7b | | 73.4b | | 79.8b | | 0.986 |
| Sulphur compounds | | | | | | | | | | | | | | | | | |
| Methyl thioacetate | 7.5ab | 7.5 | 12.0c | 0.24 | 5.9a | 0.12 | 10.6bc | 0.21 | 10.0b | 0.20 | 9.6b | 0.19 | 7.7ab | 0.15 | 5.8a | 0.12 | 0.114 |
| Methional | 16.8b | 0.07 | 9.0a | 0.04 | 9.1a | 0.04 | 6.7a | 0.03 | 9.9a | 0.04 | 12.1a | 0.05 | 16.1b | 0.06 | 13.7ab | 0.05 | 0.839 |
| Total | 24.3c | | 21.0bc | | 15.0a | | 17.3ab | | 20.3 | | 21.7 | | 23.9 | | 19.5 | | 0.837 |

Values with different letters in the same row by PDO or category indicate statistically significant differences at $p < 0.05$

[b]The OAV in bold in each compound indicate that have an impact in the sensory profile (OAV > 1)

[c]Multifactorial analysis of variance of the interaction of PDO and category factors

sensory profile of the wines because had higher OAV value. This compound has been characterized by supply rose-like floral notes to the wines [3, 13, 15, 23–25]. Considering these studies, our results showed that the wines from RD and TO could present higher floral notes than those from BI.

Terpenes are volatile compounds largely described by their positive effect on the varietal aroma profile of the wines, contributing with floral notes [15–18, 20–26]. The wines from RD and CI showed higher content than the wines from BI due to the differences found in the content of linalool, which in addition, showed an OAV > 1. For this reason, it can be said that the wines from RD and CI could characterize by having higher floral notes than the wines from BI.

In the case of the lactones, the most important were the whiskey lactones (*trans* and *cis*), which come from oak wood, observing that their content were higher in RD wines than in BI wines. Similar result was found in the content of γ-nonalactone with the exception of the wines from TO, which showed similar values than RD wines. These compounds are extracted during the aging of wines in barrels and mainly depend on the toasted level of the wood [27]. Sensorially, whiskey lactones can supply wood and coconut nuances and γ-nonalactone peach nuances [16]. In this study, only whiskey lactones presented OAVs > 1, and could have an influence in the sensory profile of the wines from RD (higher) and BI (lower). Significant differences were also found in the content of other compounds which come from oak wood such as furanic derivatives, mainly due to the differences found in the content of furfuryl alcohol that is formed from furfural by enzymatic processes during aging in barrel [28]. Thus, the wines from RD showed higher content of this compound than the rest of the wines, with the exception of those from BI. This compound presented an OAV > 1 and can supply burnt aromas that differentiated the wines from RD to those from TO and CI.

Aldehydes were divided in vanillin derivatives (vanillin, methyl vanillate, ethyl vanillate and acetovanillone) and oxidation aldehydes (isobutyraldehyde, 2-methylbutanal, 3-methylbutanal). The wines from RD presented the highest total content of vanillin derivatives, mainly due to the differences found in methyl vanillate, ethyl vanillate and acetovanillone. None of these compounds showed an OAV > 1, but they could have a synergic effect with other compounds and increase vanillin notes in wines aroma or enhancing the aroma of another compound [29, 30].

The aldehydes produced during oxidation process can contribute with negative sensory attributes such as dried fruit, moldy, closed room and wet old room [31]. The wines from BI were characterized by having higher content of isobutyraldehyde and 2-methylbutanal than those from RD and CI. However, only isobutyraldehyde could have a real negative impact in the aroma perception of the wines (OAV > 1).

Volatile phenols were divided in those that supply positive aromas (guaiacol, 4-methylguaiacol, eugenol, *trans*-isoeugenol, syringol, 4-methylsyringol and 4-allylsyringol) and negative sensory notes (4-ethylguaicol, 4-ethylphenol, 4-vinylguaiacol, 4-vinylphenol). Only significant differences were found in the total content of positive volatile phenols, having the wines from RD higher content than those from BI, due to the differences found in the content of *trans*-isoeugenol, syringol, 4-methylsyringol, 4-allylsyringol. However, only *trans*-isoeugenol showed an OAV > 1, which could contribute to the sensory profile of RD wines with spice notes [32].

Additionally, significant differences were found in the content of two sulphur compounds (methyl thioacetate and methional). The wines from RD had the highest content of methional, while the wines from BI and TO had higher content of methyl thioacetate than those from CI. These compounds provide unpleasant odors to cooked and/or rotten vegetables, and cooked potatoes, respectively [33]. However, these compounds do not affect negatively to the aroma perception of the wines studied (OAV < 1).

## Characterization of the wines from different categories

Significant differences were also found in the content and OAVs of several volatile compounds studied according to the wine's category (Table 3). In general, the young and oak wines were characterized by higher total content of ethyl esters and alcohol acetates than the crianza and reserve wines. These differences were mainly due to the content of octanoate and decanoate ethyl esters, isoamyl, hexyl and β-phenylethyl acetates. However, only ethyl octanoate, ethyl decanoate and isoamyl acetate had an OAV > 1, providing the highest fruity nuances in the younger wines. On contrary, the crianza and reserve wines had highest content of other volatile compounds responsible of fruity aromas, such as ethyl-2-methylbutyrate and ethyl isovalerate (branched ethyl esters). In the case of fatty acids, it was observed that the young and oak wines presented higher total content than the crianza and reserve wines. According to the OAVs of octanoic and butyric acids, the young and oak wines could have higher rancid and cheese negatives notes than the crinza and reserve wines. Within the group of alcohols, only significant differences were found in the content of 2-phenylethanol, observing that the oak wines showed higher content than the crianza and reserve wines, that could express high flowery aromas (OAV > 1), and as was mentioned in other studies which evaluated the volatile profile of different wines [3, 13, 15, 23–25].

The content of terpenes was significantly higher in crianza and reserve wines than in young and oak wines, due to the high content of linalool, which had an OAV > 1. In this way, it could be said that the wines with the longest aging time could have higher floral notes than the young ones. However, terpenes are compounds which are considered that come from grapes and can be released into the wine in their free and/or glycosylated form, and improved the varietal aroma character of the wines [15–18, 20–26]. In this way, the higher linalool content of the wines with the longest aging time could be explained due to the fact that during the aging period, the glycosidic bonds of precursor compounds were broken (by acid and enzymatic hydrolysis) and their free form was released to the wine, increasing its final concentration [13]. This result was unexpected since other studies [34, 35] have found that these compounds tend to decrease during aging due to adsorption phenomena of these compounds on the wood. As it was expected, the content of whiskey lactones was significantly higher in the wines with oak wood aging than in young wines. The OAVs of these compounds were higher than 1, so they could have an impact in the sensory profile of aged wines, supplying coconut and wood nuances [34]. As was mentioned previously, their content depends significantly of the aging time and toasted degree of barrels [35]. Thus, it was observed that the content of *trans*-whiskey lactone was equal in all aged wines, and was higher than young wines. On the other hand, the crianza and reserve wines showed the highest content of *cis*-whiskey lactone, followed by the oak wines.

Similar results were also found in the total content of vanillin derivatives, observing that the aged wines independently of the aging time presented higher content than the young wines. Although these compounds presented an OAV lower than 1), they could have a synergic effect with other compounds, as it was previously commented.

As it was also expected, the content of furanic derivative compounds was significantly higher in the crianza and reserve wines than in the young and oak wines, mainly due to the differences found in furfuryl alcohol, that could supply cocoa, smoky, nut, burnt nuances to the wines [17]. The furanic aldehydes are formed during the oak wood toasting, due to thermal degradation of the polysaccharides by the Maillard reaction, while the furfuryl alcohol is formed by enzymatic reduction of furfural during aging [34, 36].

The crianza and reserve wines also presented the highest content of positive volatile phenols, followed by the oak and young wines, mainly attributed to the differences found in eugenol, *trans*-isoeugenol, syringol, 4-allylsyringol and guaiacol. From a sensory point of view, according to the

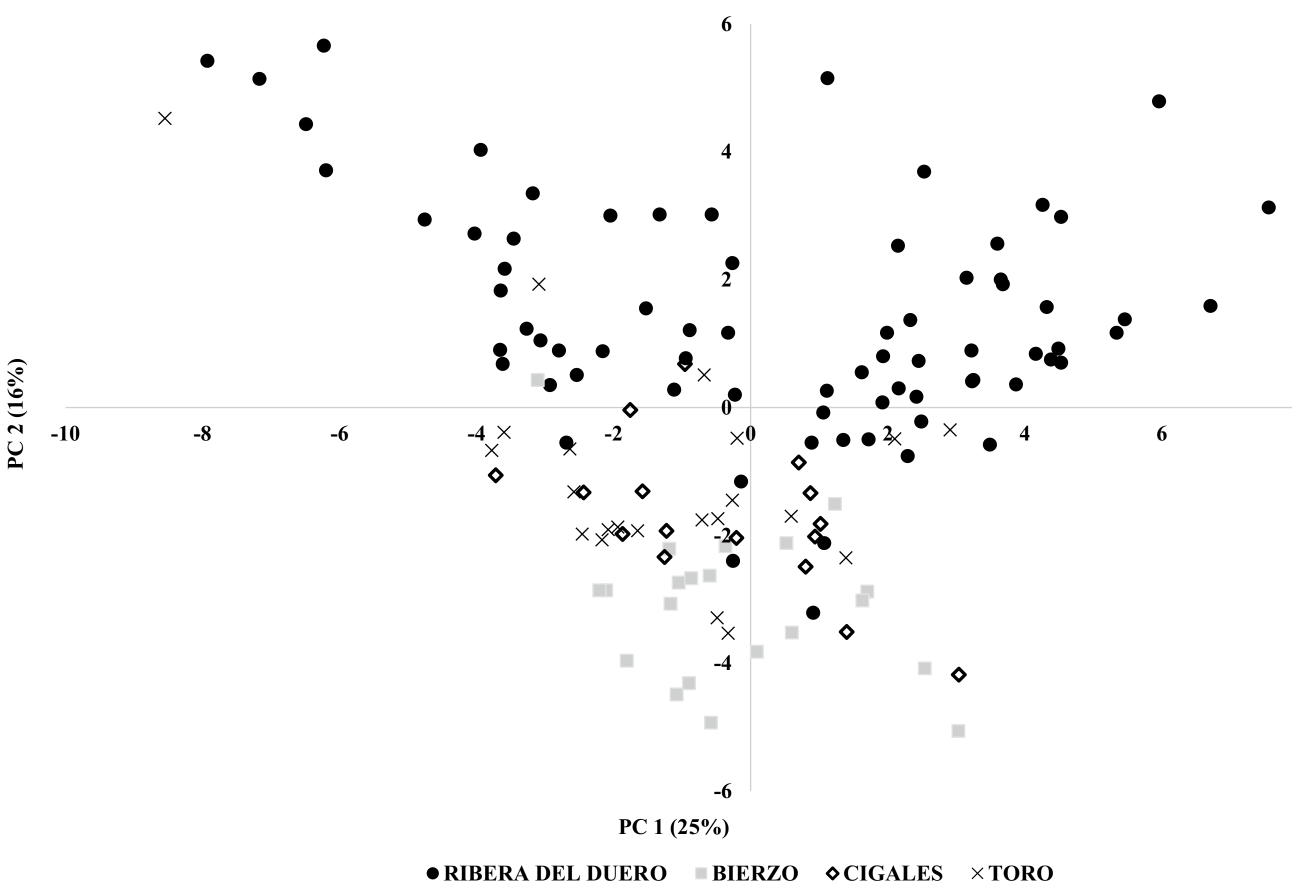


**Fig. 1** Principal component analysis (PCA) of the red wines from different PDOs defined by the first two principal components (PCs)

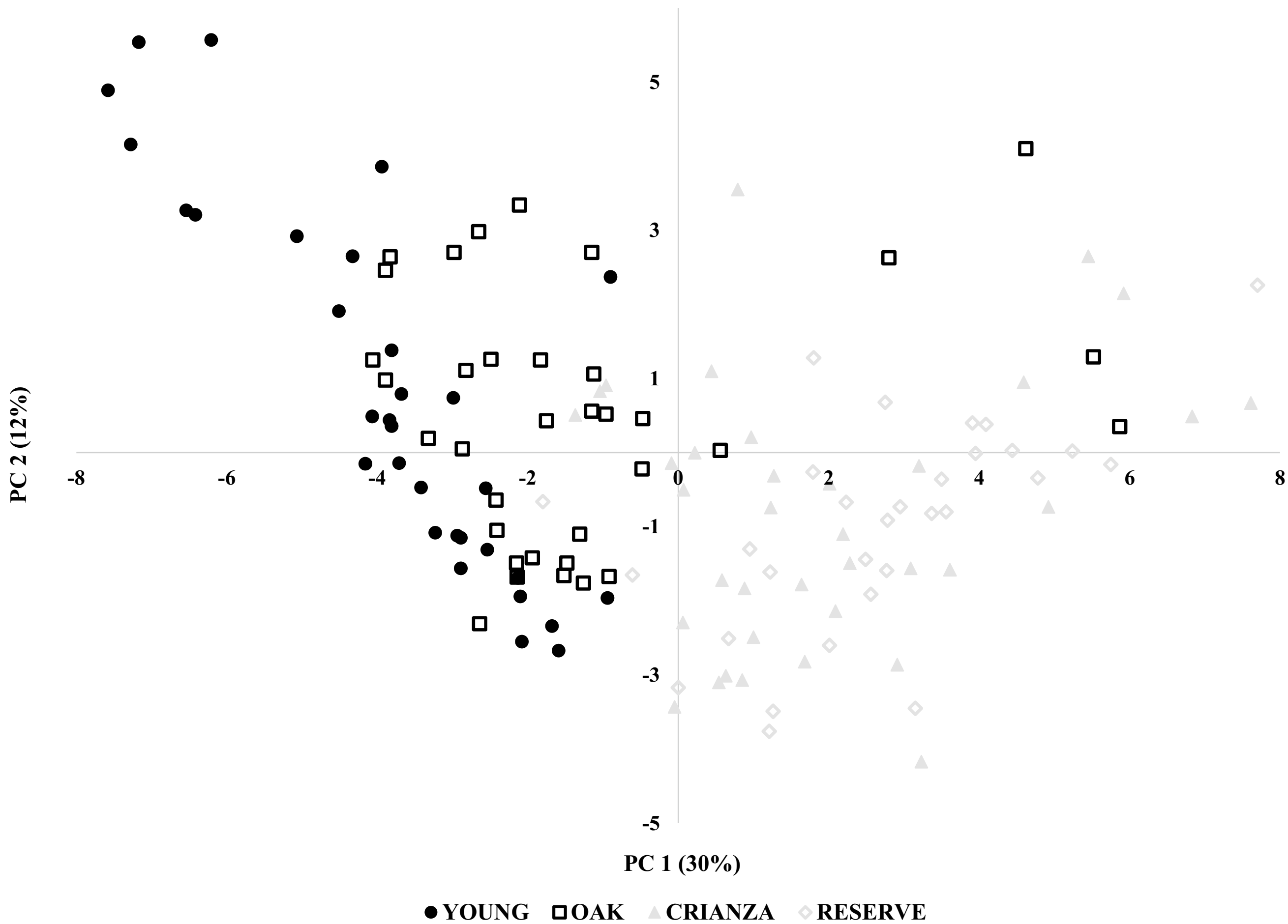


**Fig. 2** Principal component analysis (PCA) of the red wines from different categories defined by the first two principal components (PCs)

OAVs, only eugenol and *trans*-isoeugenol could had an impact in the sensory profile, providing spicy aromas.

In the case of negative volatile phenols, the wines with the longest aging time showed higher content of 4-ethylphenol than the young wines, but according to its OAV, it does not had an impact in the sensory profile. This result found for 4-ethylphenol was in agreement with a recent study carried out by Sousa et al., 2020 [37], which observed that the older wines analyzed had greater content of this compound and other that supply unpleasant nuances such as 4-vinylphenol and 4-ethylguaiacol. The total content of oxidation aldehydes was higher in the crianza wines than in the young wines. These compounds are related with the oxidation processes of the wines, and it is very common to find then in aged wines [31]. In this case, isobutyraldehyde and 3-methylbutanal have an OAV > 1, being these values highest in the aged wines.

No statistically significant differences were found in the total content of sulphur compounds, and they do not affect the sensory profile of the wines, because their OAVs were lower than 1.

## Multivariate statistical analyses

Multifactorial analysis of variance (MANOVA) have been also included in Table 3 showing the analysis of the interaction of the two factors studied in this work (PDO and category) with the aim to see differences between the category wines of the different DOs. Statistically significant effect was detected in ethyl-2-methylbutyrate, ethyl isovalerate, ethyl octanoate, ethyl decanoate; all fatty acids with the exception of isovaleric acid; 1-hexanol, *trans*-3-hexenol, *cis*-3-hexenol; linalool, α-terpineol, citronellol; γ-nonalactone; isobutyraldehyde, 3-methylbutanal; methyl vanillate; eugenol and *trans*-isoeugenol when the interaction of origin and category was considered. In general, the statistically significant differences found in these compounds coincide with those found in the one-way ANOVA. Two different principal component analysis

**Table 4** Loading values of the variables used in PCA according to the wines PDO

| | PC 1 | PC 2 |
|---|---|---|
| Ethyl hexanoate | | 0.811 |
| Ethyl octanoate | – 0.522 | 0.716 |
| Ethyl decanoate | – 0.619 | 0.536 |
| Isobutyl acetate | | 0.329 |
| Isoamyl acetate | – 0.537 | 0.550 |
| *β*-phenethyl acetate | – 0.554 | 0.334 |
| Isobutyric acid | – 0.348 | – 0.318 |
| Isovaleric acid | | – 0.446 |
| 1-hexanol | | |
| *Cis*-3-hexenol | | 0.368 |
| 2-phenylethanol | – 0.341 | |
| Linalool | 0.621 | |
| *Trans*-whiskey lactone | 0.787 | |
| *Cis*-whiskey lactone | 0.780 | |
| γ-nonalactone | | 0.730 |
| Isobutyraldehyde | | – 0.697 |
| 2-methylbutanal | | – 0.645 |
| Methyl vanillate | | 0.564 |
| Ethyl vanillate | 0.570 | |
| Acetovanillone | 0.464 | 0.360 |
| Furfuryl alcohol | 0.543 | |
| *Trans*-isoeugenol | 0.742 | |
| Syringol | 0.567 | 0.334 |
| 4-methylsyringol | 0.823 | |
| 4-allylsyringol | 0.794 | 0.309 |
| Methyl thioacetate | – 0.454 | |
| Methional | 0.522 | 0.391 |

The loadings of the variables of PC2 marked in bold were those that allowed the wine differentiation by PDO.Loadings with values < ± 0.3 are not showed

**Table 5** Loading values of the variables used in PCA according to the wines category

| | PC 1 | PC 2 |
|---|---|---|
| Ethyl-2-methylbutyrate | 0.666 | – 0.348 |
| Ethyl isovalerate | 0.678 | – 0.264 |
| Ethyl octanoate | – 0.637 | 0.543 |
| Ethyl decanoate | – 0.712 | 0.454 |
| Isoamyl acetate | – 0.605 | 0.465 |
| Hexyl acetate | – 0.586 | 0.440 |
| *β*-phenethyl acetate | – 0.570 | 0.340 |
| Isobutyric acid | | |
| Butyric acid | – 0.365 | |
| Hexanoic acid | – 0.507 | 0.493 |
| Octanoic acid | – 0.708 | |
| Decanoic acid | – 0.629 | |
| Dodecanoic acid | – 0.566 | 0.346 |
| Phenylethyl alcohol | | |
| Linalool | 0.561 | |
| α-terpineol | 0.585 | |
| Citronellol | – 0.314 | |
| *Trans*-whiskey lactone | 0.750 | |
| *Cis*-whiskey lactone | 0.764 | |
| Isobutyraldehyde | 0.353 | – 0.359 |
| 2-methylbutanal | 0.317 | – 0.319 |
| 3-methylbutanal | | |
| Vanillin | 0.437 | |
| Ethyl vanillate | 0.499 | |
| Acetovanillone | 0.416 | 0.702 |
| Furfural | 0.515 | |
| 5-methylfurfural | 0.446 | |
| Furfuryl alcohol | 0.427 | |
| Guaiacol | 0.770 | |
| 4-methylguaiacol | 0.530 | 0.660 |
| Eugenol | 0.365 | |
| 4-ethylphenol | 0.398 | 0.452 |
| *Trans*-isoeugenol | 0.715 | 0.395 |
| Syringol | 0.545 | 0.722 |
| 4-methyl-syringol | 0.710 | 0.328 |
| 4-allyl-syringol | 0.671 | 0.372 |
| Methyl thioacetate | – 0.374 | |
| Methional | 0.407 | 0.346 |

The loadings of the variables of PC1 marked in bold were those that allowed the wine differentiation by category

Loadings with values < ± 0.3 are not showed

(PCA) was carried out using only the variables with statistically significant differences in ANOVA and MANOVA to clarify the results obtained and to identify possible patterns related to the wine differentiation. The first PCA (Fig. 1) included the variables which were statistically significant in the ANOVA for PDO factor; the second PCA (Fig. 2) was represented with those significant variable in the ANOVA for category factor. Figure 1 shows the plot of the first two principal components (PCs), which explained the 41% of the total variance according to the PDO criterion. The PC 2 allowed a relative separation of the wines from RD (located on the top of the plot) to the rest of the wines (located on the bottom of the plot). The best separation was found between the wines from RD and BI, which are elaborated with different grape varieties (*Tempranillo* and *Mencía,* respectively). The other wines elaborated with *Tempranillo* grape variety (TO and CI) were not clearly separated from the *Mencía* wines. The loadings of the variables of PC2 marked in bold (Table 4) were those that allowed the wine differentiation by PDO, in the case of Fig. 1. The variables with positive loading values and closer to 1 were that most contributed to the separation of the RD wines. Thus, the ethyl esters and alcohol acetates (mainly ethyl hexanoate, ethyl octanoate, ethyl decanoate and isoamyl acetate), and several compounds released from oak wood (γ-nonalactone and methyl vanillate) were the compounds that most contributed to RD wine differentiation, probably due to the higher number of samples with aging analyzed of this PDO. On the other hand, those compounds with negative loadings close to − 1 value were, principally, correlated with the separation of the wines from BI (Table 4). These compounds were isobutyraldehyde and 2-methylbutanal (oxidation aldehydes). Therefore, the wines from RD were characterized by fruity aromas, while the wines from BI were characterized by oxidation compounds.

Considering wine category, the two first PCs explained the 43% of the total variance (Fig. 2). PC 1 allowed, in general, to separate the young and oak wines (located on the left of the plot) to those with the longest aging time (crianza and reserve, located on the right of the plot). In this case, the loadings marked in bold in PC1 in Table 5 allowed the wine differentiation according to its category, in the case of Fig. 2. As can be seen, several ethyl esters and acetates (ethyl octanoate, ethyl decanoate, isoamyl acetate, hexyl acetate and β-phenethyl acetate) and fatty acids (mainly hexanoic, octanoic, decanoic and dodecanoic acids) were more associated with the young and oak wines, due to their negative loading values more closely to − 1. On the other hand, the compounds with high positive loading values were more associated with the separation of the crianza and reserve wines, mainly related with compounds released from the oak wood such as whiskey lactones, vanillin derivatives, furanic derivatives and the majority of volatile phenols. Terpenes such as linalool and α-terpineol, and branched ethyl esters were also associated with the separation of the crianza and reserve wines. Therefore, in general, the young and oak wines were characterized by the presence of compounds related to fruity notes, while the wines with longest aging time (the crianza and reserve wines) were differentiated by the branched ethyl esters, terpenes and oak related compounds. The differentiation between crianza and reserve wines was not possible probably, because the compounds that are released from the wood to the wine depend not only on the aging time, but also on the toasting degree, the origin and grain of the wood [38, 39]. As it can be seen in the plane, the PCA showed that there were several oak wines that were included in the plane area of the crianza and reserve wines. This fact could mainly be due to that although these wines must to have a minimum of 3 months of aging, there is a lot of variability and there were wines that can be aged for a longer period and with different origin, grain and toasting of wood.

## Conclusions

The chemical characterization of the volatile fraction of the red wines carried out in this study allowed to find important quantitatively differences between the wines from different PDOs, which are very closely geographically, and/or categories. These quantitative differences allowed to provide new information on the possible aromatic potential of wines from these PDOs of one of the most important wine producing region of Spain. According to their PDO, the greatest differences were found between the wines from RD (elaborated with *Tempranillo* as principal grape variety) and the wines from BI (elaborated mainly with *Mencía* grape variety). The RD wines were characterized by their higher content of fruity, floral and some oak wood volatile compounds being wines with a high sensory complexity. On contrary, the BI wines were characterized by their higher content of an oxidation volatile compound. The wines from TO were also characterized by the higher content of fruity volatile compounds and CI wines by the floral notes. According to their category, the young and oak wines were characterized by having highest contents of compounds that supply fruity nuances and some cheese off flavor nuances, while the crianza and reserve wines were characterized by highest content of volatile compounds from oak wood, which supply spices, toasted, nuts and smoked nuances. Unexpectedly, the wines with longest aging time were also characterized by highest content of compounds responsible of floral nuances such as linalool, and other compounds responsible of fruity aromas such as ethyl isovalerate, increasing their aromatic complexity. The PCA analysis allowed to obtain a relative separation between the wines studied by PDO and category. This result could probably be conditioned by the different number of samples analyzed in each PDO and category. The results were also conditioned by the mixing of the wines which could be elaborated with different percentages of different grape varieties, in the case of PDO factor. And in the case of the category factor, by mixing wines aging with oak wood from different origins, toasted and grain.

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## Declarations

**Conflict of interest** The authors declare that they have no conflict of interest.

**Compliance with ethics requirements** The authors declare that this study does not containy experiments with human participants or animals performed.

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