Effects of composition, storage time, geographic origin and oak type on the accumulation of some volatile oak compounds and ethylphenols in wines


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A B S T R A C T

The aim of this work was to study the effect of different parameters on the accumulation of volatile oak compounds and ethylphenols in red barrel-aged wines. For this, 510 wines, from four different geographic zones and aged for various times in different oak barrel types were analysed. The results of the statistical analysis showed that the compounds were in four groups, accounting for 82.99% of the variance. The enological parameters did not present correlation with any of these four groups. The wines that remained longer in oak barrels presented, in general, higher concentrations of the studied compounds. Three of the four geographic zones were similar to each other. The oak barrel type affected the value of the ratio cis/trans, but it did not affect the accumulation of any of the volatile oak compounds or ethylphenols.

1. Introduction

In a previous work, the effects of different parameters (enological parameters, geographic origin of wines, and oak barrel types) on the contents of volatile oak compounds and ethylphenols in wines, aged in oak barrels for at least 6 months, were studied (Garde-Cerdán et al., 2008). The results obtained were interesting, so we now attempt to confirm the results, enlarging the sampling to wines that remain in oak barrels for at least 12 and 18 months. Thus, the sampling of wines used in this second study included the entirety of ageing modalities employed in a country producing quality wines, i.e. Spain.

The compounds extracted by the wine during its ageing in barrels are of great importance for wine quality since they markedly modify the aroma of the wine (Díaz-Plaza, Reyero, Pardo, & Salinas, 2002a; Garde-Cerdán & Ancín-Azpilicueta, 2006a; Lorenzo, Pardo, Zalacain, Alonso, & Salinas, 2008). The extraction and accumulation of these volatile compounds in the wine depend on numerous factors, such as geographic origin and oak species (Cadahía, Fernández de Simón, Sanz, Poveda, & Colio, 2009; Díaz-Plaza, Reyero, Pardo, Alonso, & Salinas, 2002b; Gougeon et al., 2009), the seasoning of the staves (Martínez, Cadahía, Fernández de Simón, Ojeda, & Rubio, 2008; Sefton, Francis, Pocock, & Williams, 1993), the toasting of the barrels (Bosso et al., 2008; Hale, McCafferty, Larmie, Newton, & Swan, 1999), the number of uses of the barrels (Garde-Cerdán, Rodriguez-Mozaz, & Ancín-Azpilicueta, 2002a; Gómez-Plaza, Pérez-Prieto, Fernández-Fernández, & López-Roca, 2004), the ageing time (Garde-Cerdán & Ancín-Azpilicueta, 2006b; Garde-Cerdán, Torreaga, & Ancín-Azpilicueta, 2002b; Spillman, Iland, & Sefton, 1998) and the composition and geographic origin of the wine (Garde-Cerdán, Torreaga, & Ancín-Azpilicueta, 2004; Garde-Cerdán et al., 2008; Ortega-Heras, González-Sanjosé, & González-Huerta, 2007).

A not insignificant problem is that, in wines aged in oak barrels (mainly in barrels that have been re-used), ethylphenols could be formed and these are undesirable compounds for quality since they confer unpleasant odours to wine. These compounds have a microbiological origin; some yeasts capable of contaminating wood (Brettanomyces/Dekkera genera) decarboxylate cinnamic acids and form these phenols in wines (Chatonnet, Dubourdieu, Boidron, & Pons, 1992).

For these reasons, the aim of this work was to study the influences of the wine composition, ageing time, geographic origin and oak barrel type on the accumulation of volatile oak compounds and ethylphenols in red wines aged in oak barrels. For this, 510 wines, from four different Spanish geographic zones, and aged in different oak barrels types for at least 6, 12 and 18 months, were used. Due to the great number of samples, a multivariate statistical treatment was applied to the treatment of the data.
2. Material and methods

2.1. Samples

The selection of samples was based on the information afforded by the Spanish Ministry of Agriculture, Fisheries and Food (MAPA, 2004) about domestic trade and wine production volume, which affirmed that 95% of the Spanish Origin Designations (O.D.) produced more than 30,000 hl. Around 72% of all commercialised red wines belong to four Spanish O.D. (Rioja, La Mancha, Ribera del Duero and Valdepeñas). The other Spanish O.D. selected in this study were chosen from information given by the MAPA, but also trying to extend it in relation to the different geographic wine production areas. Due to the great number of samples and the exhaustive consumption study of red wines obtained through AcNielsen consulting (AcNielsen, 2004), all O.D. have been group according to the following zones: zone 1, Navarra; Ribera del Duero and Rioja; zone 2, La Mancha and Valdepeñas; zone 3, Jumilla and Valencia; zone 4, Penedés and Somontano.

For this study, 510 aged red wines were analysed, and the total number of wine brands was 170 (3 bottles of each brand, with each bottle belonging to different lots). Of these wines, 315 were of zone 1, 93 of zone 2, 51 of zone 3, and 51 of zone 4. Aged red wines were classified, according to their ageing time, into three different categories: aged-6 (red wines with an ageing of at least 6 months in oak barrels), aged-12 (red wines with an ageing time of at least 12 months in barrels), and aged-18 (exceptional quality red wines with at least 18 months ageing in oak barrels). The total amount of samples analysed in this study was: 267 aged-6 wines, 189 aged-12 wines, and 54 aged-18 wines. 390 wines were aged in American oak barrels, 54 were aged in American and French oak barrels, and 66 were aged in French oak barrels. Of the 390 wines aged in American oak barrels, 213 were aged-6 wines, 153 were aged-12 wines and 24 were aged-18 wines; of the 54 wines aged in American and French oak barrels, 30 were aged-6 wines, 18 were aged-12 wines and 6 were aged-18 wines; of the 66 wines aged in French oak barrels, 24 were aged-6 wines, 18 were aged-12 wines and 24 were aged-18 wines.

2.2. Enological parameters

The parameters evaluated to analyse the wine composition were pH, total acidity and alcoholic degree. These parameters were determined according to the official methods established by ECC (1990).

2.3. Analysis of volatile oak compounds and ethylphenols by gas chromatography

The volatile compounds cis-oak lactone, trans-oak lactone, guaiacol, eugenol, furfural, 5-methylfurfural, 4-ethylphenol, and 4-ethylguaiacol (Sigma-Aldrich, Madrid, Spain) were analysed, following the method described by Marín, Zalacain, De Miguel, Alonso, and Salinas (2005), based on the SBSE technique, by GC–MS. The compounds were extracted by introducing the poly-methylsiloxane-coated stir bar (0.5 mm film thickness, 10 mm length, Twister, Gerstel, Mülheim and der Ruhr, Germany) into 10 ml of sample, to which 100 µl of internal standard γ-hexalactone solution, at 1 µl/ml in absolute ethanol (Merck, Darmstadt, Germany), was added. Samples were stirred at 700 rpm at room temperature for 60 min. The stir bar was then removed from the sample, rinsed with distilled water and dried with a cellulose tissue, and later transferred into a thermal desorption tube for GC–MS analysis.

In the thermal desorption tube, the volatile compounds were desorbed from the stir bar under the following conditions: oven temperature at 330 °C; desorption time, 4 min; cold trap temperature, –30 °C; helium inlet flow 45 ml/min. The compounds were transferred into the Hewlett-Packard LC 3D mass detector (Palo Alto, USA) with a fused silica capillary column (BP21 stationary phase 50 m length, 0.22 mm i.d., and 0.25 µm film thickness) (SGE, Ringwood, Australia). The chromatographic programme was set at 50 °C (held for 5 min), raised to 180 °C at 2.5 °C/min (held for 2 min) and to 230 °C (5 °C/min) and held for 20 min. For mass spectrometry analysis, electron impact mode (EI) at 70 eV was used. The mass range varied from 35 to 500 U and the detector temperature was 150 °C. Identification was achieved by using the NIST library and by comparison with the mass spectrum and retention index of chromatographic standards designed by us and data found in the bibliography. Quantification was based on 5-point calibration curves of respective standards (R² > 0.94) in a 12% ethanol (v/v) solution at pH 3.6.

2.4. Statistical analysis

A factor analysis was applied, using statistical software SPSS 14.0. The number of variables was 9 (cis-oak lactone, trans-oak lactone, guaiacol, eugenol, furfural, 5-methylfurfural, 4-ethylphenol, 4-ethylguaiacol, and ratio cis/trans). All variables were mean-centred and scaled to unit variance prior to the analysis. The factor analysis was used to concentrate the information in a reduced number of new variables (named factors) that represent the original variables and collect the major part of total variability (Hair, Anderson, Tatham, & Black, 1995). The principal components method has been used as a factor extraction method and, after that, a varimax rotation was carried out to obtain a better interpretation of the factors.

Data for the volatile compounds were processed by analysis of variance with the wine composition, storage time, geographic zone and oak barrel type as independent variables. Volatile compounds and the score factors obtained in the factor analysis have been used as dependent variables. It was previously verified that all the assumptions, which the statistical method needed, were fulfilled. The method used was the LSD (least significant difference) test for multiple comparisons (α < 0.05).

3. Results and discussion

3.1. Characteristics of the wines

Table 1 shows the enological parameters of wines analysed. For the different geographic zones, the average pH values of aged-6 and aged-12 wines were similar. However, differences between the aged-6 and aged-12 wines and the aged-18 wines were observed. The wines from zone 3 showed higher average alcoholic degrees than did the wines from other zones, probably because this zone has a lower average annual rainfall (www.winesfromspain.com; MAPA, 2004), thus favouring the concentration of sugars in the grape. The average total acidities were quite similar in all the wines, independently of the zone and of the type of wine, and it was around 5 g tartaric acid/l (Table 1).

3.2. Content of volatile oak compounds and ethylphenols in the wines

The concentrations (in the wines) of the analysed compounds are shown in Table 2. cis- and trans-Oak lactones were the only compounds that were present in all of the wines. The average concentration of the cis isomer, in the wines of the four different zones and different types (aged-6, aged-12, and aged-18), was above its...
perception threshold (0.046 mg/l) (Wilkinson, Elsey, Prager, Tana-
ka, & Sefton, 2004), while the average concentration of the trans
isomer was, in all the samples, below its perception threshold
(0.46 mg/l) (Chatonnet, Boidron, & Pons, 1990). These two lactones
produce woody and coconut-like aromas in the wine, which add
quality. In the case of guaiacol, the average concentration for the
aged-12 and aged-18 wines was above its perception threshold
(0.075 mg/ml) (Boidron, Chatonnet, & Pons, 1988), while the con-
tentration of eugenol in all the wines was below its perception thresh-
hold (0.5 mg/l) (Boidron et al., 1988). These two volatile phenols add
smoky and spicy aromas to the wine. The average concentration of
furfural for the aged-6, aged-12 and aged-18 wines and for the four
different zones was below its perception threshold (20 mg/l) (Boi-
dron et al., 1988), although in some samples it was above this
threshold. In the case of 5-methylfurfural, none of the samples pre-
sented concentrations above its perception threshold, due to the
high value of this (45 mg/l) (Boidron et al., 1988). These two com-
pounds, which possess a grilled almond aroma, enhance the per-
ception of oak lactones (Reazin, 1981). The total average value of 4-
ethyl phenol (4-EP) and 4-ethyl guaiacol (4-EG) in aged-6, aged-
12 and aged-18 wines was above the values at which these com-
pounds can contribute negatively to wine quality (0.620 mg/l and
0.140 mg/l, respectively) (Chatonnet et al., 1992).

The total average of the ratio cis/trans was higher in the aged-
and aged-12 wines than in the aged-18 wines (Table 2) because, in
these last ones, the use of French oak barrels was more frequent
than in the aged-6 and aged-12 wines (Fig. 1a). This confirms re-
ports by other authors that American oak gives a greater quantity of
cis-oak lactone to the wine than do European oaks (Díaz-Plaza
et al., 2002b; Garde-Cerdán et al., 2002a; Gómez-Plaza,
2004; Waterhouse & Towey, 1994). The total average of the ratio
4-EP/4-EG of the aged-6 wines was below that of the aged-
and aged-18 wines (Table 2). This ratio for the aged-12 and
aged-18 wines was within the range found by Pollnitz, Pardon,
and Sefton (2000), i.e. between 3.5 and 10.1.

3.3. Multivariate statistical analysis

Factor analysis was applied to reduce the number of variables.
This gave four significant factors with eigenvalues greater than 1,
accounting for 82.99% of the total variance (Table 3). The loadings
for each variable on the four selected factors are displayed in Table 4.
As the data are autoscaled, each loading is the correlation between
the variable and the respective factor. Factor 1 was associated with
cis-oak lactone, trans-oak lactone and eugenol; factor 2 grouped to-
gether the ethylphenols, 4-ethyl phenol and 4-ethyl guaiacol; factor
3 was associated with furfural, 5-methylfurfural and guaiacol, and
factor 4 was associated with the ratio cis/trans (Table 4). Factor 1 ex-
plained 34.92%, factor 2 explained 18.29%, factor 3 explained 15.98%,
and factor 4 explained 13.81% of total variance (Table 3). These re-
results, obtained for the 510 aged-6, aged-12, and aged-18 wines, coin-
cide totally with that found in the previous work carried out with
267 aged-6 wines (Garde-Cerdán et al., 2008).

Each one of the factors obtained summarises the information from a
group of variables, which are all correlated with each other. The
fact that these volatile compounds show correlated values leads
us to believe that these are characteristics that may influence these
wines. The information found in this study will allow us to research the
possible causes of the variation of the 4 significant factors in
function of the wine composition, storage time, geographic zone
and type of wood used for the ageing of the wines. The value that a
sample shows in each of the 4 factors is called the Score Factor.

3.4. Effect of the wine composition on the accumulation of volatile oak
compounds and ethylphenols in the wines

None of the enological parameters studied (pH, alcoholic de-
gree, and total acidity) presented correlation with the four score
factors. When the 510 wines (aged-6, aged-12, and aged-18) were
studied together, the enological parameters did not affect the accu-
mulation of volatile oak compounds or ethylphenols in the wines.
In the previous work, in which the aged-6 wines were studied, it
was observed that the alcoholic degree affected the presence of
these compounds in the wines (Garde-Cerdán et al., 2008). The fact
that influence of enological parameters was not observed in this
case could be due because all sampling was more heterogeneous.
Moreover, other factors, such as oak barrel type or storage time,
could neutralise the possible effect of the wine composition.

3.5. Effect of storage time in oak barrels on the accumulation of
volatile oak compounds and ethylphenols in the wines

The accumulation of cis-oak lactone, trans-oak lactone, and
eugenol (factor 1) increased with the ageing time of the wines in
the barrels (Fig. 2a). This difference was especially noted between
the aged-6 and aged-12 wines in regard to the aged-18 wines. These
compounds, once extracted from the oak wood by the wine, are
stable. Thus, their concentration increases with time, as other
authors have found (Garde-Cerdán et al., 2002b; Pérez-Prieto,
López-Roca, Martínez-Cutillas, Pardo-Mínguez, & Gómez-
Plaza, 2003). In the case of the ethylphenols (factor 2), differences
were not observed in their accumulation between the aged-6 and
aged-12 wines (Fig. 2b). The accumulation of these compounds
was greater in the aged-18 wines, which could be because the
yeasts that form them are slow-growing species (Suárez, Suárez-
Lepe, Morata, & Calderón, 2007). On the other hand, the accumula-
tion of furfural, 5-methylfurfural, and guaiacol (factor 3) increased
with the ageing time until 12 months, and later on it diminishes
Table 2
Maximum, minimum and average values (expressed in mg/l) of the volatile compounds in the red barrel-aged wines analysed.

<table>
<thead>
<tr>
<th></th>
<th>Aged-6 wines</th>
<th></th>
<th>Aged-12 wines</th>
<th></th>
<th>Aged-18 wines</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zone 1</td>
<td>Zone 2</td>
<td>Zone 3</td>
<td>Zone 4</td>
<td>Total</td>
<td>Zone 1</td>
</tr>
<tr>
<td>cis-Oak lactone</td>
<td>Average</td>
<td>1.48</td>
<td>1.07</td>
<td>0.82</td>
<td>1.15</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>Maximum</td>
<td>5.03</td>
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<td>2.47</td>
<td>3.74</td>
<td>5.03</td>
</tr>
<tr>
<td></td>
<td>Minimum</td>
<td>0.21</td>
<td>0.26</td>
<td>0.17</td>
<td>0.19</td>
<td>0.17</td>
</tr>
<tr>
<td>trans-Oak lactone</td>
<td>Average</td>
<td>0.20</td>
<td>0.16</td>
<td>0.15</td>
<td>0.18</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>Maximum</td>
<td>0.58</td>
<td>0.61</td>
<td>0.31</td>
<td>0.56</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>Minimum</td>
<td>0.05</td>
<td>0.05</td>
<td>0.03</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>Guaiacol</td>
<td>Average</td>
<td>0.07</td>
<td>0.11</td>
<td>0.08</td>
<td>0.03</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>Minimum</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>0.11</td>
<td>0.09</td>
<td>0.06</td>
<td>0.08</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>Minimum</td>
<td>0.02</td>
<td>–</td>
<td>0.02</td>
<td>0.03</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>5.17</td>
<td>3.75</td>
<td>4.56</td>
<td>3.14</td>
<td>4.56</td>
</tr>
<tr>
<td>Furfural</td>
<td>Average</td>
<td>22.7</td>
<td>14.4</td>
<td>13.1</td>
<td>11.6</td>
<td>22.7</td>
</tr>
<tr>
<td></td>
<td>Minimum</td>
<td>0.86</td>
<td>–</td>
<td>0.85</td>
<td>0.40</td>
<td>–</td>
</tr>
<tr>
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<td>Average</td>
<td>0.22</td>
<td>0.17</td>
<td>0.22</td>
<td>0.09</td>
<td>0.19</td>
</tr>
<tr>
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<td>Minimum</td>
<td>0.02</td>
<td>–</td>
<td>0.02</td>
<td>0.03</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>1.60</td>
<td>0.78</td>
<td>0.77</td>
<td>0.59</td>
<td>1.06</td>
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<tr>
<td>4-Methylfurural</td>
<td>Minimum</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>1.76</td>
<td>1.05</td>
<td>1.23</td>
<td>0.91</td>
<td>1.45</td>
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<tr>
<td>4-Ethylphenol</td>
<td>Minimum</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>5.78</td>
<td>5.58</td>
<td>4.64</td>
<td>3.50</td>
<td>5.78</td>
</tr>
<tr>
<td>4-Ethylguaiacol</td>
<td>Minimum</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>3.23</td>
<td>2.27</td>
<td>2.37</td>
<td>1.50</td>
<td>3.23</td>
</tr>
<tr>
<td>Ratio cis/trans</td>
<td>Average</td>
<td>7.39</td>
<td>7.87</td>
<td>7.15</td>
<td>6.09</td>
<td>7.23</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>1.58</td>
<td>2.14</td>
<td>1.97</td>
<td>1.60</td>
<td>2.14</td>
</tr>
<tr>
<td>Ratio 4-EP/4-EG</td>
<td>Maximum</td>
<td>2.28</td>
<td>2.12</td>
<td>1.94</td>
<td>2.07</td>
<td>2.19</td>
</tr>
<tr>
<td></td>
<td>Minimum</td>
<td>3.84</td>
<td>5.33</td>
<td>3.33</td>
<td>4.23</td>
<td>5.33</td>
</tr>
</tbody>
</table>

*a Ratio cis/trans = concentration of cis-oak lactone/concentration of trans-oak lactone.

*b Ratio 4-EP/4-EG = concentration of 4-ethylphenol/concentration of 4-ethylguaiacol.
lightly (Fig. 2c). The degradation of the furanic compounds was probably due to the reduction of their corresponding alcohols (Garde-Cerdán et al., 2004; Spillman, Pollnitz, Liacopoulos, Pardon, & Sefton, 1998), so after a certain storage time of the wines in the barrels, the conversion was greater than the extraction, and their concentration diminished. The ratio \( \frac{c_{is}}{c_{trans}} \) (factor 4) was higher in the aged-6 and aged-12 wines than in the aged-18 wines (Fig. 2d) because, for the ageing of these wines, French oak barrels were preferably used (Fig. 1a). Thus, these wines presented the ratio \( \frac{c_{is}}{c_{trans}} \) smaller than did the wines aged preferably in American oak barrels.

3.6. Effect of the geographic origin of wines on the accumulation of volatile oak compounds and ethylphenols in the wines

The accumulation of cis-oak lactone, trans-oak lactone, and eugenol (factor 1) in the wines of zone 1 was greater than that in the other zones, where significant differences among the wines were not found (Fig. 3a). The same happens with the presence of ethylphenols (factor 2) in the wines studied (Fig. 3b). Therefore, zone 1 was different from the other three zones, all three of which presented similar behaviours. Besides other factors, this could be because zone 1 presents climatic differences with respect to the other zones (www.winesfromspain.com; MAPA, 2004). The accumulation of guaiacol, furfural and 5-methylfurfural (factor 3) was lower in the wines of zone 4 than in the rest of the zones (Fig. 3c). In the case of the ratio \( \frac{c_{is}}{c_{trans}} \) (factor 4), when more American oak barrels were used (Fig. 1b), the higher was the ratio (Fig. 3d), which confirms that this ratio is a good parameter to know if the wine has been aged in one or another oak barrel type.

3.7. Effect of the oak barrel type on the accumulation of volatile oak compounds and ethylphenols in wines

Table 3

<table>
<thead>
<tr>
<th>Factor number</th>
<th>Eigenvalue</th>
<th>% Of variance</th>
<th>Cumulative percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.14</td>
<td>34.92</td>
<td>34.92</td>
</tr>
<tr>
<td>2</td>
<td>1.65</td>
<td>18.29</td>
<td>53.20</td>
</tr>
<tr>
<td>3</td>
<td>1.44</td>
<td>15.98</td>
<td>69.18</td>
</tr>
<tr>
<td>4</td>
<td>1.24</td>
<td>13.81</td>
<td>82.99</td>
</tr>
</tbody>
</table>

bold values correspond to the compounds associated with the 4 different factors.

Table 4

<table>
<thead>
<tr>
<th>Factor</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Factor 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eugenol</td>
<td>0.94</td>
<td>0.08</td>
<td>0.11</td>
<td>0.12</td>
</tr>
<tr>
<td>cis-Oak lactone</td>
<td>0.94</td>
<td>0.17</td>
<td>0.14</td>
<td>0.15</td>
</tr>
<tr>
<td>trans-Oak lactone</td>
<td>0.80</td>
<td>0.17</td>
<td>0.09</td>
<td>–0.50</td>
</tr>
<tr>
<td>4-Ethylphenol</td>
<td>0.14</td>
<td>0.94</td>
<td>0.05</td>
<td>–0.06</td>
</tr>
<tr>
<td>4-Ethylguaiacol</td>
<td>0.14</td>
<td>0.94</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>5-Methylfurfural</td>
<td>0.11</td>
<td>0.02</td>
<td>0.85</td>
<td>0.07</td>
</tr>
<tr>
<td>Furfural</td>
<td>0.10</td>
<td>0.17</td>
<td>0.75</td>
<td>0.07</td>
</tr>
<tr>
<td>Guaiacol</td>
<td>0.06</td>
<td>–0.06</td>
<td>0.73</td>
<td>–0.10</td>
</tr>
<tr>
<td>Ratio cis/trans</td>
<td>0.08</td>
<td>0.02</td>
<td>0.03</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Fig. 1. Mosaic chart of the contingency table between: (a) oak barrel type and storage time, (b) oak barrel type and geographic zone. The size of each bar is proportional to the percentage of the category that represents.

Fig. 2. Relationship between each of the four score factors and the storage time in the barrels of the wines: means and 95.0% LSD intervals.
and 5-methylfurfural) did not present significant differences in function of the oak barrel type used for the ageing of the wines (Figs. 4a–c). However, the ratio \( \text{cis}/\text{trans} \) (factor 4) presented significant differences between wines aged in American oak, in combination of American and French oaks, and in French oak barrels (Fig. 4d), being inferior in this last one, as other authors have found (Díaz-Plaza et al., 2002b; Pérez-Prieto, López-Roca, Martínez-Cutillas, Pardo-Mínguez, & Gómez-Plaza, 2002; Waterhouse & Towey, 1994). These results indicate that the main difference among the wines aged in one or another oak barrel type was the ratio \( \text{cis}/\text{trans} \), and it did not depend on any of the other volatile compounds (Fig. 4).

### 4. Conclusions

The results obtained for the 510 wines aged for at least 6, 12, and 18 months in oak barrels confirm those obtained for the 267 wines aged for at least 6 months in oak barrels. Consequently, it can be said that the volatile oak compounds and ethylphenols were grouped according to their origin. Also, the accumulation of volatile oak compounds and ethylphenols was affected mainly by the storage time of the wines in the oak barrels, while the enological parameters, the geographic origin and the oak barrel type had smaller influences on the accumulation of these volatile compounds in the wines.

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References


