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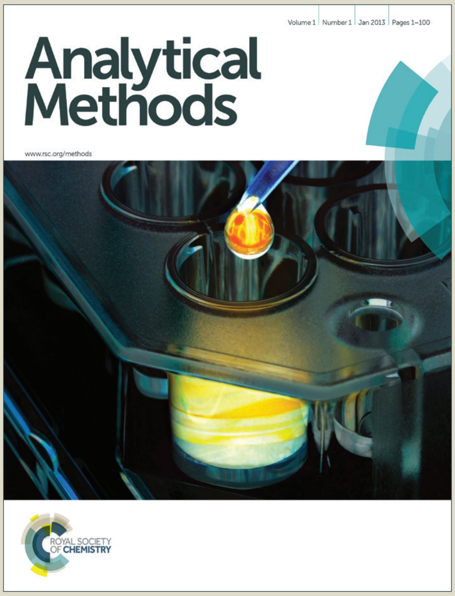
Accepted Manuscript



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# Comparison of the volatile profile of vine-shoots and oak chips by headspace–gas chromatography–mass spectrometry (HS–GC–MS)

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Profiling and identification analysis of the volatile fraction formed by heating vine-shoots or oak chips powder have been obtained by headspace–gas chromatography–mass spectrometry (HS–GC–MS). For this purpose, vine-shoots collected from eighteen varieties of vineyards and five types of oak chips have been heated at different temperatures in a headspace autosampler to compare the volatile compounds formed from both types of wood. This strategy allowed obtaining a representative profile of volatile compounds from each sample. Multivariate statistical analysis of the resulting data by application of Venn diagrams and principal component analysis showed the strong influence of the temperature on the composition of the volatile compounds obtained from vine-shoots and oak chips. Finally, identification of the compounds in the volatile fraction of vine-shoots and tested oak chips was carried out. The main families of compounds have been identified as a function of both the heating temperature and type of wood. Semiquantitative analysis of compounds with oenological interest in the volatile fraction formed by heating vine-shoots and oak chips was used to evaluate similarities and differences between both materials.

## 1. Introduction

Traditionally, wine and spirits are aged in oak barrels by virtue of the beneficial characteristics that oak wood transfers to these beverages. Barrel ageing allows color to be stabilized and astringency reduced as a result of oxidation of certain compounds by the atmospheric oxygen transferred through wood pores.[1,2] A wide variety of compounds (e.g. phenols, lactones, coumarins, polysaccharides, hydrocarbons, fatty acids, terpenes, carotenoids, steroids, norisoprenoids and furans) is known to be transferred in this process from the wood barrel to wine. Among the transferred compounds, volatile phenols and benzoic aldehydes are particularly relevant since they are responsible for desirable sensory properties of wine and spirits.[3–5]

Natural oak wood only contains small amounts of these compounds. For this reason, wood is first modified by a natural or artificial seasoning in which ellagitannins are decreased.[6] After drying, the wood is thermally treated by toasting or charring,[7] the former treatment standing as the most critical for aroma production due to the severe modification of the chemical composition of wood, which involves a significant increase of desirable volatile compounds. Depending on the toasting degree, pyrolysis and hydrothermolysis degrade wood constituents to some extent, not only ellagitannins, which are easily hydrolyzed,[8,9] but also polymers such as lignin, cellulose and hemicellulose (the most important polymers in natural oak).[10] Hydrolysis of these polymers leads to toasty flavor compounds such as furfural, 5-hydroxymethylfurfural and derivatives (dried fruit and burned almonds aroma), phenolic aldehydes (responsible for sugar flavor) such as vanillin (vanilla aroma), and a wide variety of volatile phenols (responsible for smoky, medicinal and burnt wood aromas) such as guaiacol, vinylguaiacol and derivatives, or eugenol (spices, cloves character).[3–5] Oak lactones, such as *cis*- and *trans*-β-methyl-γ-octalactone (known as whisky lactones), and nonanoic lactone are present in natural oak, but their contents may either increase or decrease by both seasoning and toasting. The transferred compounds contribute to the final bouquet of wine and, although they are present at low concentrations (µg/L or less), they exert a strong influence on wine aroma because of their low sensory thresholds.

Numerous oak wood varieties have been studied in depth, being American oak (*Quercus alba*) and French oak (*Q. robur*and *Q. petraea*) species the most commonly used for oenological purposes. [11] American oak is characterized by lower levels of phenols and higher amounts of whisky lactone than European species.[12,13] Some studies have also confirmed differences between the two European species,[14] with *Q. petraea* possessing characteristics similar to those of American oak, while *Q. robur* is characterized by high levels of ellagitannins, but often negligible amounts of whisky lactones.[13] Contribution of *cis*- and *trans*-β-methyl-γ-octolactones to the coconut, woody fresh odor descriptors is dissimilar, the former being the strongest odorant.[15–17] Apart from oak wood, there is a present trend to the use of some other types of wood such as that from chesnut, acacia, cherry or mulberry for ageing of wine and spirits. Alternative ageing methods such as addition of either oak or chesnut chips have proven to be profitable for the involved industry by decreasing ageing time. In addition, this alternative has led to an increase in the available types of commercial wine with different flavor characteristics.[2,3,11]

Vine-shoots have been characterized as a potential source of phenols usually detected in wines.[18,19] The phenolic composition of extracts from vine-shoots was similar to that observed in extracts from oak wood. The aim of this research was to characterize the volatile fraction formed by heating different varieties of vine-shoots and oak chips. The heating temperature was selected according to treatments applied to oak wood. The application of the protocol would allow obtaining a qualitative profile of the volatile fraction from vine-shoots. This fraction was analyzed in eighteen varieties of vine-shoots and compared with that obtained from five commercial varieties of oak chips by using multivariate statistical analysis. For this purpose, a headspace (HS) autosampler–gas chromatograph with an ion-trap mass detector (HS–GC–IT/MS) approach was used with a double aim: firstly, to develop an in-situ preparation step since homogeneous heating of wood powder can be carried out under controlled temperature and atmosphere in the sealed vial; and secondly, to propose global "fingerprinting" of the volatile profile formed by heating each sample, based on mass spectrometry since the headspace content is injected into the gas chromatograph where it is separated and transferred to the ionization chamber of the MS where the volatile compounds are fragmented.[20,21] Chemometric data treatment of the MS complex data matrix allows comparison and classification of the samples as a function of their composition in volatile compounds.[20]

## 2. Experimental

### 2.1 Samples

Vine-shoots from different red and white *Vitis vinifera* cultivars were sampled from the same plantation located at “Bodega y Viñedos Vallebravo” (Sierra de Segura, Jaén, Spain) in autumn 2011, after leaf-fall, by randomized selection of ten similar stocks of each cultivar. Vine shots were selected from the following cultivars: Airen, Baladí, Bobal, Cabernet Franc,

**Table 1. Headspace parameters for analysis of powder vine-shoots and oak chips.**

| | | | | |
|---|---|---|---|---|
| **Heating temperature, ºC** | 120 | 150 | 180 | 200 |
| **Vial temperature, ºC** | 120 | 150 | 180 | 200 |
| **Loop temperature, ºC** | 130 | 160 | 190 | 200 |
| **Transfer line temperature, ºC** | 145 | 175 | 200 | 200 |
| **Sample equilibration time, min** | 20 | | | |
| **Vial pressurization time, min** | 0.2 | | | |
| **Loop fill time, min** | 0.02 | | | |
| **Loop equilibration time, min** | 0.05 | | | |
| **Injection time, min** | 0.3 | | | |
| **GC cycle time, min** | 45 | | | |
| **Loop size, mL** | 1 | | | |
| **Vial pressure, psi** | 10 | | | |
| **Shaking** | Intense shaking for 5 min | | | |

Cabernet Sauvignon, Chardonnay, Garnacha Tinta, Garnacha Tintorera, Malbec, Mazuelo, Merlot, Montepila, Moscatel, Pedro-Ximénez, Petit Verdot, Sauvignon Blanc, Syrah and Tempranillo. All of them were from the same plot, cultivated under the same agronomic conditions in terms of soil properties, climate, hydric regime, etc. A piece of 10 cm of vine shoot at the height of the first leaf bud was taken in all cases.

Samples of five untoasted commercial oak chips representing different types of oak barrels used for wine ageing (American Blend, American Fresh, French Sweet, French Spice and French Intense) were kindly supplied by Laffort España S.A. (Guipúzcoa, Spain).

Each vine-shoot sample was dried for 72 h at 30 ºC and milled to produce a homogeneous particle size (less than 0.42 mm diameter), then, stored at –20 ºC until use. As oak chips are commercialized as a dried product, they were milled and stored following the same protocol.

### 2.2 Standards

Vanillin, acetovanillone, 4-ethylguaiacol, syringol, 4-vinylguaiacol, coniferaldehyde, guaiacol, *trans* and *cis* oak lactone, 5-hydroxymethylfurfural, eugenol, acetosyringone and furfural from Sigma–Aldrich (St. Louis, USA) were used as chromatographic standards to confirm identification. The standards mixture of *n*-alkanes ($C_{10}$-$C_{40}$) for performance test of GC systems was from Sigma–Aldrich (St. Louis, USA)

### 2.3 Apparatus

Vine-shoots and oak chips were milled by a ball grinder (Restch MM301, Haan, Germany) and homogenized by a 40-mesh sieve (particle size less than 0.42 mm diameter).

For chromatographic separation, 1.5 g of the given sample was placed in a 10 mL headspace vial, then sealed using a 20 mm aluminium vial cap (Análisis Vínicos, Tomelloso, Spain) with a 20 mm silicone/PTFE septum (Análisis Vínicos). The vials were placed in the headspace rack, where sample heating was carried out at four different temperatures (120, 150, 180 and 200 ºC) to obtain detailed information on the changes produced in the volatile fraction as a function of temperature. Parameters of the headspace device are listed in **Table 1.**

Individual separation of volatile compounds was carried out by a Varian CP 3800 gas chromatograph (Walnut Creek, CA, USA) equipped with a programmable-temperature injector and coupled to a Saturn 2200 ion-trap mass spectrometer (Sunny Valley, TX, USA). A 7694E headspace autosampler from Agilent (Palo Alto, CA, USA) and a Factor Four VF-5ms fused silica capillary column (30 m × 0.25 mm I.D., 0.25µm film thickness, Varian) completed the experimental approach.

### 2.4 GC/MS analysis

One mL of the headspace content was injected into the chromatograph. The injector temperature was fixed at 180 ºC, and injection was in the splitless mode. The oven temperature program was as follows: initial temperature 50 ºC (held for 5 min) and increased at 6 ºC/min to 200 ºC (held for 31.67 min). The total analysis time took 36.67 min, and 2 min extra time was necessary for re-establishing and equilibrating the initial conditions. The ion-trap mass spectrometer was operated in the electron impact ionization (EI) fixed mode, for which the instrumental parameters were set as follows: filament emission current 70 µA; transfer-line, ion-trap and manifold temperatures were kept at 170, 150 and 40 ºC, respectively. Data acquisition was set between 50 *m/z* and 450 *m/z* using total ion current (TIC) scan mode. Digital selected ion monitoring (SIM) was applied as data treatment to remove the chromatographic background. Additionally, chromatograms were smoothed by application of a Savitzky-Golay filter (5 points). Automated Mass Spectral Deconvolution and Identification System (AMDIS) v2.66 software was used to transform raw data files into generic files.

### 2.5 Data processing and statistical analysis

Mass Profiler Professional (MPP) software package (Version 12.0, Agilent Technologies, Santa Clara, CA, USA) was used for processing all data obtained once they were transformed into AMDIS generic files. The feature extraction algorithm took into account all single charged ions exceeding 5000 counts with a signal-to-noise ratio (*S/N*) higher than 10. Unique mass was used for peak area calculations, while the peak width was set at 0.7 s. The NIST Mass Spectral Search Program v.1.6d (NIST, Washington, DC, USA) was used for the spectral search (Mainlib and Replib libraries). Tentative identification was supported on correlation between experimental mass and database spectra above 700 in normal search mode. The retention index (*I*) for each compound was calculated using as reference linear hydrocarbons from C10 to C40, which were analyzed by the same chromatographic method. *I* values were calculated on the basis of retention times. The experimental *I* for each compound was compared

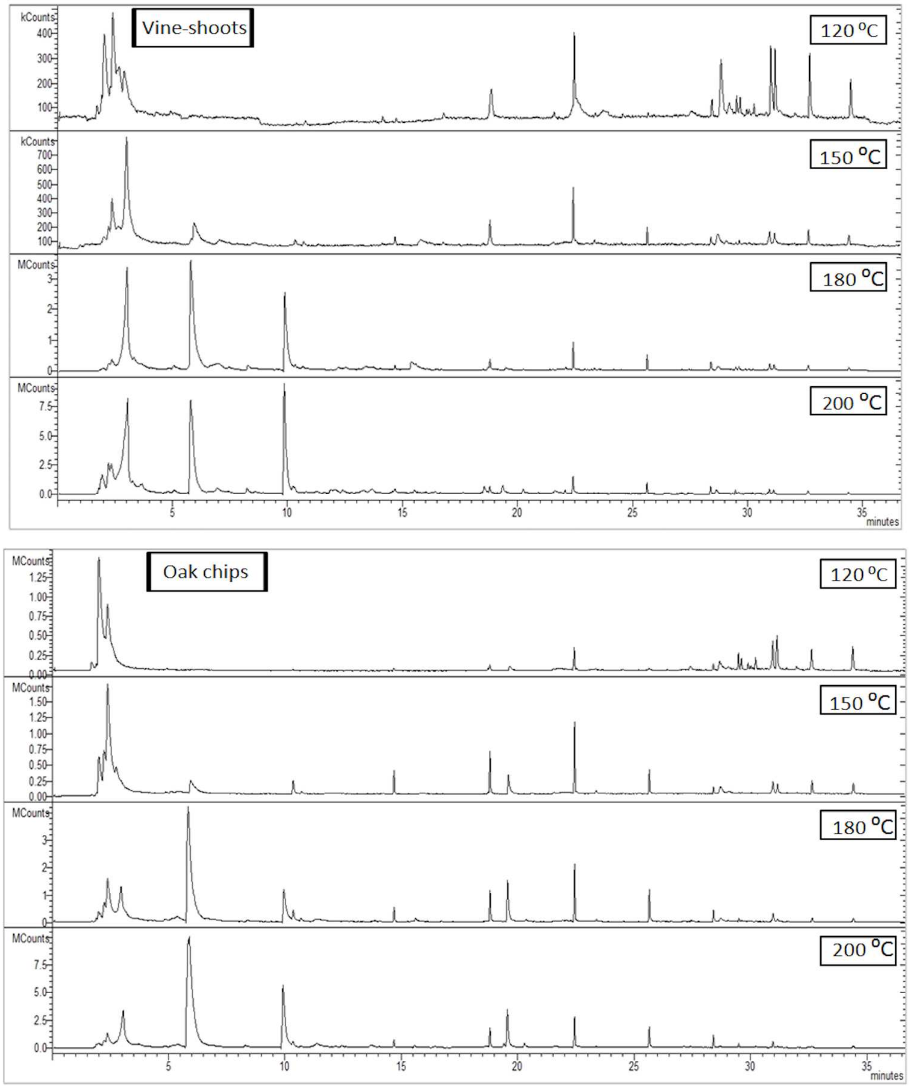

**Figure 1. Chromatograms from Cabernet Franc powder vine-shoot (A) and American Fresh powder oak chips (B) at different heating temperatures. The y-axis scale for each chromatogram has been adjusted to the highest peak for a better comparison among chromatographic profiles.**

with experimental or theoretical values reported in the literature included in the NIST database. The cut-off limit for *I* difference was set to 100 units for theoretical references, while 30 units was the value used for experimental references.

The *.elu* and *.fin* files created for each sample by the AMDIS software were exported to the MPP software for further processing. Within this algorithm, ions with related *m/z* values were extracted as molecular features (MFs) or entities characterized by retention time (RT) and intensity in the apex of chromatographic peak. In the next step, alignment of RT and *m/z* values was carried out across the sample set using a tolerance window of 0.2 min retention time and 10 ppm mass accuracy. Baseline correction and data mean-centering were used as data pretreatment.

## 3. Results and discussion

### 3.1 Evaluation of the heating conditions

One of the main aims of the present study was the characterization of the volatile fraction detected in the two types of samples, vine-shoots and oak chips. For this purpose, both types of materials were prepared as described above. Before optimization of the main variables involved in the heating process, a variability study was programmed by analyzing consecutively five replicates of one of the samples of each group (oak chips and vine-shoots). This study allowed detecting an experimental variability in the peak areas of 10%, which is clearly below the variability expected among the different samples included in this study.

The first variable studied was the heating time, tested at 6, 20 and 40 min, (**Supplementary Figure 1.A, B and C**) to compare the relative concentration of interesting compounds. At this step, the heating temperature was set at 180 ºC. As can be seen, heating for 6 min was not enough to promote the formation of volatile compounds. On the other hand, the most intense chromatographic peaks were obtained for 20 min heating time, since the experiment carried out for 40 min reported a slight decrease in the intensity of the peaks, which could be ascribed to degradation. Longer heating times were also processed but overpressure problems were found; therefore, they were discarded. Consequently, 20 min was selected as heating time.

The influence of temperature was studied by control of the heating unit of the headspace autosampler to check the effect temperature exerts on the volatile profile of the samples. The temperatures selected in this study were 120, 150, 180 and 200 ºC to check the influence of this parameter on the volatile profile. The temperature used for heating oak wood with oenological purposes is around 200 ºC.[2,22] **Figure 1.A** illustrates the chromatographic profiles of volatiles obtained by analysis of Cabernet Franc powder vine-shoot at the selected heating temperatures. As can be seen, there is an evolution in the chromatographic profile with the heating temperature. The best temperatures were 120 and 200 °C as they provided the highest number of volatile compounds. An increased temperature exerted a contradictory effect on the chromatographic peaks depending on their retention time: in the first part of the chromatogram the peaks increased significantly, while peaks eluting within the second part of the chromatogram (15–38 min) decreased. **Table 2** shows the volatile profile from heating powder vine-shoots at 200 ºC, which is rich in compounds belonging to very different chemical families such as volatile phenols, furans, phenolic aldehydes and phenolic ketones.

**Table 2. Identification of compounds detected in the volatile fraction sampled at 200 ºC in the different varieties of powder vine-shoots.**

| Vine-shoots 200 ºC | | | | | | |
|---|---|---|---|---|---|---|
| **Compound** | **Mass** | **RI (Ri)** | **Formula** | **Characteristic fragments** | **Red wine varieties** | **White wine varieties** |
| **Propylenesulfide** | 74 | 538 (562) | $C_3H_6S$ | 41, 59, 74 | ✓ | |
| **2-Methylfuran** | 82 | 519 (602) | $C_5H_6O$ | 82, 53, 39 | ✓ | ✓ |
| **1,5-Heptadiene** | 96 | 766 (715) | $C_7H_{12}$ | 55, 81, 67 | | ✓ |
| **Furfural** | 96 | 723 (831) | $C_5H_4O_2$ | 96, 95, 39 | ✓ | ✓ |
| **Isopropylbutylamine** | 115 | 801 (859) | $C_7H_{17}N$ | 58, 72, 100 | ✓ | |
| **Methyl 5-hexenoate** | 128 | 890 (874) | $C_7H_{12}O_2$ | 74, 43, 68 | | ✓ |
| **1-(2-Furanyl)ethanone** | 110 | 899 (878) | $C_6H_6O_2$ | 95, 110, 67 | ✓ | ✓ |
| **2-Furanmethanol** | 98 | 860 (885) | $C_5H_6O_2$ | 98, 69, 81 | ✓ | ✓ |
| **Methyl (2E,4E)-hexadienoate** | 126 | 936 (900) | $C_7H_{10}O_2$ | 67, 111, 95 | | ✓ |
| **2H-Pyran-2-one** | 96 | 873 (909) | $C_5H_4O_2$ | 96, 38, 69 | ✓ | |
| **Methyl-2-furoate** | 126 | 961 (909) | $C_6H_6O_3$ | 95, 126, 67 | ✓ | ✓ |
| **4-Methylpentanoic acid** | 116 | 956 (910) | $C_6H_{12}O_2$ | 57, 73, 83 | | ✓ |
| **2,3-Dihydroxypropanal** | 90 | 827 (913) | $C_3H_6O_3$ | 43, 61, 73 | ✓ | ✓ |
| **5-Methyl-2-furancarboxaldehyde** | 110 | 948 (920) | $C_6H_6O_2$ | 110, 53, 81 | ✓ | ✓ |
| **2-Cyclopentene-1,4-dione** | 96 | 903 (924) | $C_5H_4O_2$ | 96, 68, 54 | | ✓ |
| **Cyclohexane-2-propenyl** | 124 | 865 (926) | $C_9H_{16}$ | 83, 55, 53 | ✓ | ✓ |
| **N-Butyl-tert-butylamine** | 129 | 944 (930) | $C_8H_{19}N$ | 86, 58, 114 | | ✓ |
| **2-Hydroxy-2-methylbutanoic acid** | 118 | 960 (966) | $C_5H_{10}O_3$ | 55, 73, 89 | ✓ | |
| **Glycerin** | 92 | 903 (967) | $C_3H_8O_3$ | 61, 43, 31 | ✓ | ✓ |
| **Methoxymethylbenzene** | 122 | 927 (969) | $C_8H_{10}O$ | 91, 122, 65 | ✓ | ✓ |
| **(5-Methyl-2-furyl)methanol** | 112 | 918 (975) | $C_6H_8O_2$ | 95, 112, 69 | ✓ | ✓ |
| **Pyrrole-2-carboxaldehyde** | 95 | 912 (988) | $C_5H_5NO$ | 95, 66, 50 | ✓ | |
| **2-Furanmethanol acetate** | 140 | 978 (1009) | $C_7H_8O_3$ | 81, 98, 140 | ✓ | ✓ |
| **2-Acetylpyrrole** | 109 | 1066 (1035) | $C_6H_7NO$ | 94, 66, 109 | | ✓ |
| **2-Pentylfuran** | 138 | 997 (1040) | $C_9H_{14}O$ | 81, 53, 138 | ✓ | |
| **1-Methyl-4-(1-methylethylidene)cyclohexane** | 138 | 1058 (1041) | $C_{10}H_{18}$ | 95, 81, 67 | | ✓ |
| **5-Methyl-2-propionylfuran** | 138 | 1098 (1067) | $C_8H_{10}O_2$ | 109, 138, 53 | ✓ | ✓ |
| **3-Ethyl-2-hydroxy-2-cyclopenten-1-one** | 126 | 1103 (1072) | $C_7H_{10}O_2$ | 126, 83, 55 | | ✓ |
| **Guaiacol** | 124 | 1088 (1090) | $C_7H_8O_2$ | 109, 81, 124 | ✓ | ✓ |
| **6-Nonenal** | 140 | 1136 (1112) | $C_9H_{16}O$ | 55, 67, 81 | ✓ | ✓ |
| **Phenylethyl Alcohol** | 122 | 1158 (1136) | $C_8H_{10}O$ | 91, 122, 65 | | ✓ |
| **1-Cyclohexene-1-carboxylic acid** | 126 | 1179 (1148) | $C_7H_{10}O_2$ | 81, 108, 126 | ✓ | ✓ |
| **2,2'-Difurylmethane** | 148 | 1186 (1164) | $C_9H_8O_2$ | 148, 91, 120 | ✓ | |
| **2,4-Dimethylundecane** | 184 | 1106 (1185) | $C_{13}H_{28}$ | 57, 75, 81 | ✓ | |
| **Pentylbenzene** | 148 | 1126 (1191) | $C_{11}H_{16}$ | 65, 91, 148 | ✓ | |
| **1-Methyl-4-(1-methylethylidene)cyclohexanol** | 154 | 1256 (1191) | $C_{10}H_{18}O$ | 93, 121, 136 | ✓ | |
| **1,3-Octanediol** | 146 | 1196 (1221) | $C_8H_{18}O_2$ | 75, 57, 99 | | ✓ |
| **2,2-Dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylic acid** | 168 | 1284 (1256) | $C_{10}H_{16}O_2$ | 123, 81, 168 | | ✓ |

| | | | | | | |
|---|---|---|---|---|---|---|
| **3,5-Dihydroxy-6-methyl-2,3-dihydro-4H-pyran-4-one** | 144 | 1266 (1269) | $C_6H_8O_4$ | 144, 101, 55 | | ✓ |
| **2,6-Dimethoxyphenol (Syringol)** | 154 | 1245 (1279) | $C_8H_{10}O_3$ | 154, 139, 111 | ✓ | ✓ |
| **Methylsalicylate** | 152 | 1223 (1281) | $C_8H_8O_3$ | 120, 92, 152 | ✓ | ✓ |
| **5-Acetoxymethyl-2-furaldehyde** | 168 | 1269 (1286) | $C_8H_8O_4$ | 126, 79, 109 | ✓ | ✓ |
| **4-Vinylguaiacol** | 150 | 1291 (1293) | $C_9H_{10}O_2$ | 135, 150, 77 | ✓ | ✓ |
| **Eugenol** | 164 | 1352 (1392) | $C_{10}H_{12}O_2$ | 164, 149, 77 | ✓ | ✓ |
| **Vanillin** | 152 | 1374 (1392) | $C_8H_8O_3$ | 151, 123, 81 | ✓ | ✓ |
| **1,9-Nonanediol** | 160 | 1388 (1401) | $C_9H_{20}O_2$ | 55, 68, 82 | ✓ | |
| **3-tert-Butyl-4-hydroxyanisole** | 180 | 1390 (1417) | $C_{11}H_{16}O_2$ | 165, 180, 137 | ✓ | |
| **Acetovanillone** | 166 | 1455 (1439) | $C_9H_{10}O_3$ | 151, 166, 123 | ✓ | ✓ |
| **2',6'-Dihydroxyacetophenone** | 152 | 1442 (1470) | $C_8H_8O_3$ | 137, 152, 81 | ✓ | ✓ |
| **EthylVanillin (Bourbonal)** | 166 | 1463 (1491) | $C_9H_{10}O_3$ | 137, 166, 109 | ✓ | ✓ |
| **3,4-Dimethoxyphenylacetone** | 194 | 1542 (1507) | $C_{11}H_{14}O_3$ | 151, 194, 107 | | ✓ |
| **Vanillylmethylketone (Guaiacylacetone)** | 180 | 1496 (1538) | $C_{10}H_{12}O_3$ | 137, 180, 122 | ✓ | ✓ |
| **2-Cyclohexylidenecyclohexanone** | 178 | 1586 (1551) | $C_{12}H_{18}O$ | 149, 178, 81 | | ✓ |
| **Syringaldehyde** | 182 | 1597 (1581) | $C_9H_{10}O_4$ | 182, 167, 139 | ✓ | ✓ |
| **Methoxyeugenol** | 194 | 1611 (1581) | $C_{11}H_{14}O_3$ | 194, 91, 119 | ✓ | ✓ |
| **13-Tetradecenal** | 210 | 1612 (1591) | $C_{14}H_{26}O$ | 55, 67, 98 | ✓ | |
| **3-(4-Hydroxy-3-methoxyphenyl)-2-propenal (Coniferaldehyde)** | 178 | 1623 (1599) | $C_{10}H_{10}O_3$ | 178, 135, 107 | ✓ | ✓ |
| **1-Hexadecyne** | 222 | 1644 (1609) | $C_{16}H_{30}$ | 81, 67, 55 | | ✓ |
| **Tributyl phosphate** | 235 | 1629 (1613) | $C_{12}H_{27}O_4P$ | 99, 155, 125 | | ✓ |
| **Acetosyringone** | 196 | 1622 (1628) | $C_{10}H_{12}O_4$ | 181, 196, 153 | ✓ | |
| **2,6-bis(1,1-Dimethylethyl)-2,5-cyclohexadiene-1,4-dione** | 220 | 1598 (1633) | $C_{14}H_{20}O_2$ | 177, 220, 135 | | ✓ |
| **2,5-di-tert-Butyl-1,4-benzoquinone** | 220 | 1602 (1633) | $C_{14}H_{20}O_2$ | 205, 220, 177 | | ✓ |
| **4-(3-Hydroxy-1-propenyl)-2-methoxyphenol (Coniferyl alcohol)** | 180 | 1608 (1653) | $C_{10}H_{12}O_3$ | 137, 124, 180 | ✓ | |
| **9,12-Tetradecadien-1-ol** | 210 | 1677 (1672) | $C_{14}H_{26}O$ | 68, 81, 55 | ✓ | |
| **HomoprotocatechuicAcid** | 168 | 1668 (1691) | $C_8H_8O_4$ | 123, 77, 51 | ✓ | |
| **6,10,14-Trimethyl-2-pentadecanone** | 268 | 1755 (1754) | $C_{18}H_{36}O$ | 58, 71, 250 | ✓ | ✓ |
| **2-Hexyl-1-decanol** | 242 | 1803 (1790) | $C_{16}H_{34}O$ | 57, 71, 85 | ✓ | ✓ |
| **2-Methyl-7-octadecyne** | 264 | 1866 (1863) | $C_{19}H_{36}$ | 81, 67, 95 | ✓ | ✓ |
| **Hexadecanoicacidmethylester (Methylpalmitate)** | 270 | 1892 (1878) | $C_{17}H_{34}O_2$ | 74, 57, 85 | ✓ | ✓ |
| **3,7,11,15-Tetramethyl-1-hexadecen-3-ol (Isophytol)** | 296 | 1893 (1899) | $C_{20}H_{40}O$ | 71, 57, 82 | ✓ | ✓ |
| **Hexadecanoicacidethenylester** | 282 | 2021 (1968) | $C_{18}H_{34}O_2$ | 239, 57, 71 | ✓ | |
| **1,2-Benzenedicarboxylic acid butyl 2-methylpropyl ester** | 278 | 1988 (1972) | $C_{16}H_{22}O_4$ | 149, 223, 57 | ✓ | ✓ |
| **Hexadecanoicacidethylester (Ethylpalmitate)** | 284 | 1978 (1978) | $C_{18}H_{36}O_2$ | 88, 101, 43 | ✓ | ✓ |
| **3,7,11,15-Tetramethyl-2-hexadecen-1-ol (Phytol)** | 296 | 2012 (2045) | $C_{20}H_{40}O$ | 67, 95, 123 | ✓ | ✓ |
| **9-Octadecen-1-ol** | 268 | 2014 (2061) | $C_{15}H_{30}O$ | 82, 67, 55 | ✓ | |
| **9,12-Octadecadien-1-ol** | 266 | 2033 (2069) | $C_{18}H_{34}$ | 81, 67, 95 | ✓ | ✓ |
| **Dodecenylsuccinicanhydride** | 266 | 2109 (2159) | $C_{16}H_{26}O_3$ | 55, 69, 83 | ✓ | |

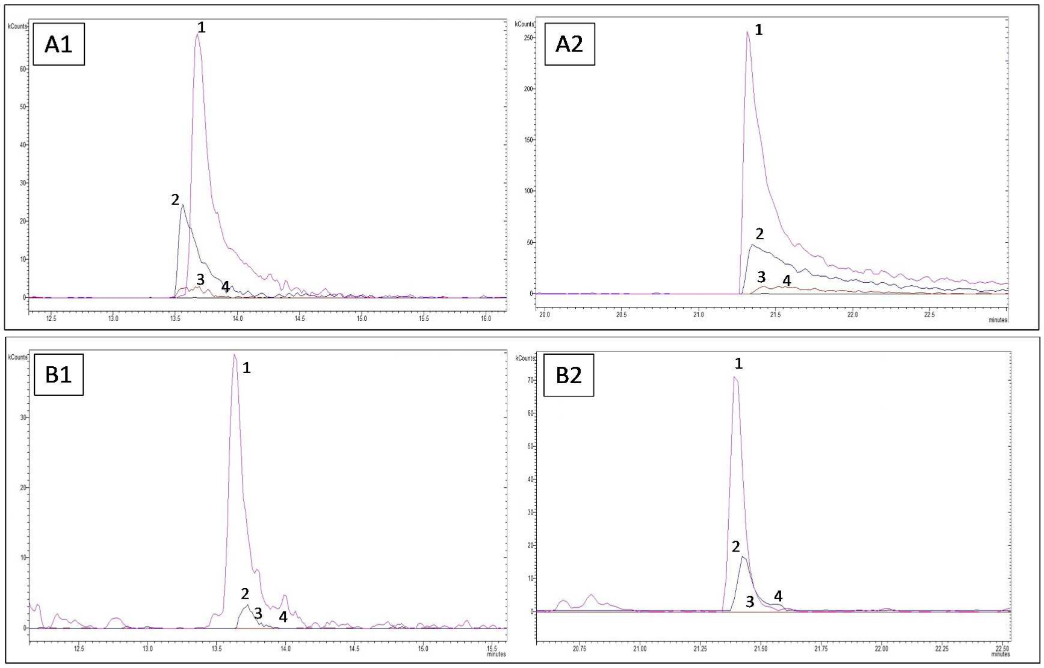

**Figure 2. Extracted ion chromatograms from French Intense powder oak chips and Chardonnay powder vine-shoots for guaiacol and vanillin at 200, 180, 150 and 120 ºC (1, 2, 3 and 4, respectively).**

The results provided by vine-shoots were compared to those from powder oak chips (American Fresh, in this case) subjected to the same heating temperatures, and a similar behavior was observed, as shows **Figure 1.B**. The increase in temperature also provided an increase in the number and intensity of the chromatographic peaks generated by pyrolysis of polysaccharides (furanic aldehydes) or Maillard reaction (furanones and pyranones), and those formed by degradation of lignin (phenolic aldehydes and volatile phenols). **Table 3** shows the volatile profile obtained from powder oak chips toasted at 200 ºC. These results are in agreement with the study reported by Chatonnet *et al.*,[22] who proved that high toasting temperatures (heavy toasting, between 220 and 230 ºC) decreased the levels of furans and volatile phenols. The highest detected peaks corresponded to furfural, eluting at 5.8 min, and 5-methyl-2-furancarboxaldehyde, at 9.8 min, which are known to be responsible for the almond, toasty and toasted almond flavor and contribute to stabilize wines.[15-17] Glycerin, which is known for its contribution to round organoleptic properties of wines,[23] appears in the first part of the chromatogram, at 2.97 min. In oak wood, the concentration of glycerin decreases when the temperature increases; appearing the opposite effect on vine-shoots. Additionally, vanillin and guaiacol, known for their vanilla and smoky taste, respectively, also increased the intensity of their chromatographic peaks in vine-shoots and oak chips when the heating temperature was increased, as can be seen in **Figure 2**. On the other hand, two chromatographic peaks were identified as oak lactone in all varieties of oak wood (at 18.9 and 19.6 min). According to the literature, the *cis* isomer is the predominant form present in oak wood, eluting after the *trans* isomer, which is consistent with our results, as the second peak showed a higher intensity in all cases. The relative concentration of the *cis* isomer of whisky lactone increased by increasing the heating temperature, as shows **Figure 3.A**. Additionally, the content of this compound was considerably higher in American oak chips than in French varieties, as shown in **Figure 3.B**, which is also in agreement with previous results.[22,24]

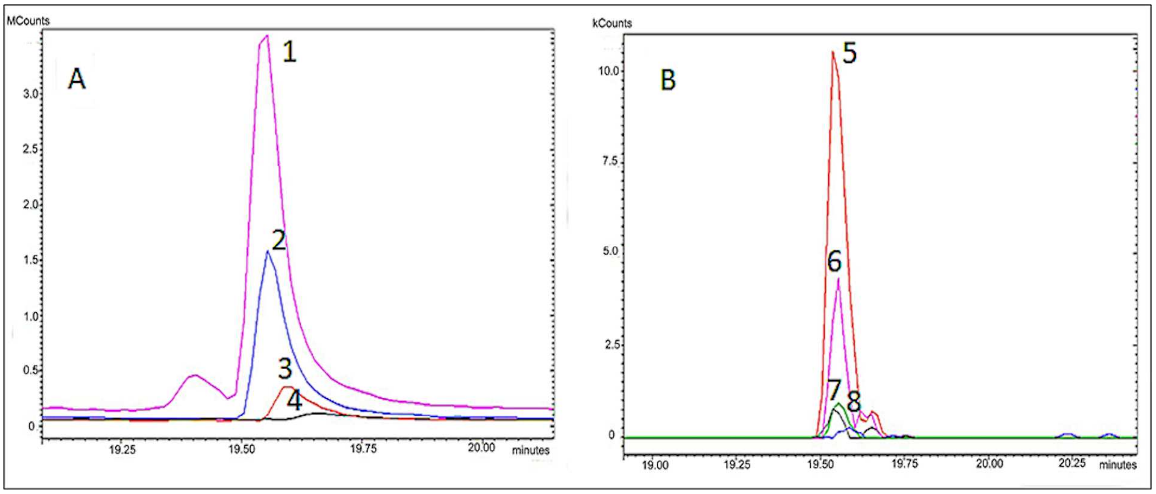

**Figure 3. Extracted ion chromatograms from: (A) American Fresh oak powder monitoring characteristic ions for *cis* oak lactone at 200, 180, 150 and 120 ºC (1, 2, 3 and 4, respectively). (B) American Blend, American Fresh, French Intense, French Sweet and French Spice oak wood powder heated at 200 ºC (5, 6, 7 and 8, respectively).**

**Table 3. Identification of compounds detected in the volatile fraction sampled at 200 ºC in the different varieties of oak chips.**

| Oak wood 200 ºC | | | | | | |
|---|---|---|---|---|---|---|
| **Compound** | **Mass** | **RI (Ri)** | **Formula** | **Characteristic fragments** | **French oak** | **American oak** |
| **1,1-Dimethyl-2-propynylamine** | 83 | 701 (675) | $C_5H_9N$ | 51, 68, 82 | ✓ | |
| **Propanoicacid** | 74 | 688 (676) | $C_3H_6O_2$ | 74, 56, 57 | ✓ | ✓ |
| **3-Penten-1-ol** | 86 | 711 (769) | $C_5H_{10}O$ | 55, 68, 85 | ✓ | ✓ |
| **Hexanal** | 100 | 811 (806) | $C_6H_{12}O$ | 56, 72, 82 | ✓ | |
| **Furfural** | 96 | 812 (831) | $C_5H_4O_2$ | 96, 95, 67 | ✓ | ✓ |
| **Pentanoicacid** | 102 | 872 (875) | $C_5H_{10}O_2$ | 60, 73, 87 | | ✓ |
| **1-(2-Furanyl)ethanone** | 110 | 885 (878) | $C_6H_6O_2$ | 95, 110, 67 | | ✓ |
| **5-Methyl-2-furancarboxaldehyde** | 110 | 896 (920) | $C_6H_6O_2$ | 110, 53, 81 | ✓ | ✓ |
| **N-Butyl-tert-butylamine** | 129 | 952 (930) | $C_8H_{19}N$ | 114, 58, 34 | ✓ | |
| **Glycerin** | 92 | 955 (967) | $C_3H_8O_3$ | 61, 60, 47 | ✓ | ✓ |
| **2-Hexenoic acid** | 114 | 1016 (982) | $C_6H_{10}O_2$ | 73, 99, 68 | | ✓ |
| **1,5-Pentanediol** | 104 | 998 (1004) | $C_5H_{12}O_2$ | 56, 68, 74 | | ✓ |
| **Guaiacol** | 124 | 1102 (1090) | $C_7H_8O_2$ | 109, 81, 124 | ✓ | ✓ |
| **6-Nonenal** | 140 | 1132 (1112) | $C_9H_{16}O$ | 55, 70, 86 | ✓ | ✓ |
| **5-Hydroxymethylfurfural** | 126 | 1151 (1163) | $C_6H_6O_3$ | 97, 126, 69 | ✓ | |
| **2-Hydroxybenzaldehyde** | 122 | 1186 (1203) | $C_7H_6O_2$ | 122, 65, 76 | ✓ | ✓ |
| **4-Methylguaiacol** | 138 | 1198 (1203) | $C_8H_{10}O_2$ | 138, 123, 95 | ✓ | ✓ |
| **Pentanedioicacid** | 132 | 1216 (1231) | $C_5H_8O_4$ | 86, 55, 114 | | ✓ |
| **5-Butyldihydro-4-methyl-2(3H)-furanone**<br>**(*trans*-Oak lactone)** | 156 | 1243 (1245) | $C_9H_{16}O_2$ | 99, 71, 87 | ✓ | ✓ |
| **5-Butyldihydro-4-methyl-2(3H)-furanone**<br>**(*cis*-Oak lactone)** | 156 | 1259 (1245) | $C_9H_{16}O_2$ | 99, 71, 87 | ✓ | ✓ |
| **1,2,4-Trimethoxybenzene** | 168 | 1257 (1248) | $C_9H_{12}O_3$ | 168, 153, 125 | ✓ | |
| **2,6-Dimethoxyphenol (Syringol)** | 154 | 1262 (1279) | $C_8H_{10}O_3$ | 154, 139, 111 | ✓ | |
| **4-Vinylguaiacol** | 150 | 1292 (1293) | $C_9H_{10}O_2$ | 150, 135, 107 | ✓ | ✓ |
| **6-Octen-1-ol, 3,7-dimethylacetate** | 198 | 1321 (1302) | $C_{12}H_{22}O_2$ | 81, 69, 95 | ✓ | |
| **4-Ethylguaiacol** | 152 | 1332 (1303) | $C_9H_{12}O_2$ | 137, 152, 122 | ✓ | |
| **δ Nonalactone** | 156 | 1332 (1304) | $C_9H_{16}O_2$ | 99, 71, 55 | ✓ | |
| **p-Methoxybenzoicacid** | 152 | 1366 (1339) | $C_8H_8O_3$ | 135, 150, 77 | ✓ | |
| **Eugenol** | 164 | 1388 (1392) | $C_{10}H_{12}O_2$ | 164, 149, 77 | ✓ | ✓ |
| **Vanillin** | 152 | 1397 (1392) | $C_8H_8O_3$ | 151, 109, 81 | ✓ | ✓ |
| **6-Octen-1-ol-3,7-dimethylpropanoate** | 212 | 1376 (1402) | $C_{13}H_{24}O_2$ | 81, 69, 57 | | ✓ |
| **Dihydroeugenol** | 166 | 1416 (1402) | $C_{10}H_{14}O_2$ | 137, 166, 122 | ✓ | |
| **Acetovanillone** | 166 | 1428 (1439) | $C_9H_{10}O_3$ | 151, 166, 123 | ✓ | ✓ |
| **2-tert-Butyl-4-methoxyphenol** | 180 | 1442 (1417) | $C_{11}H_{16}O_2$ | 165, 137, 180 | ✓ | |
| **2’,6’-Dihydroxyacetophenone** | 152 | 1455 (1470) | $C_8H_8O_3$ | 137, 152, 109 | | ✓ |
| **Homovanillyl alcohol** | 168 | 1588 (1545) | $C_9H_{12}O_3$ | 137, 168, 122 | ✓ | |
| **Tributylphosphate** | 266 | 1587 (1613) | $C_{12}H_{27}O_4P$ | 99, 155, 57 | | ✓ |
| **4-Methyl-2,6-di-tert-butyl-phenol** | 220 | 1654 (1668) | $C_{15}H_{24}O$ | 205, 220, 57 | | ✓ |
| **1,2-Cyclododecanediol** | 200 | 1844 (1815) | $C_{12}H_{24}O_2$ | 55, 82, 96 | ✓ | |
| **1-Octadecyne** | 250 | 1846 (1808) | $C_{18}H_{34}$ | 81, 55, 67 | | ✓ |
| **9-Octadecyne** | 250 | 1844 (1828) | $C_{18}H_{34}$ | 81, 67, 95 | | ✓ |
| **2-Methyl-7-octadecyne** | 264 | 1892 (1863) | $C_{19}H_{36}$ | 81, 67, 95 | ✓ | |
| **Hexadecanoicacidethylester**<br>**(Ethylpalmitate)** | 284 | 1884 (1878) | $C_{18}H_{36}O_2$ | 74, 87, 55 | ✓ | ✓ |
| **3,7,11,15-Tetramethyl-2-hexadecen-1-ol**<br>**(Phytol)** | 296 | 2077 (2045) | $C_{20}H_{40}O$ | 81, 95, 123 | ✓ | ✓ |
| **9,12-Octadecadienoic acid**<br>**(Linoleicacid)** | 280 | 2179 (2183) | $C_{18}H_{32}O_2$ | 67, 81, 55 | ✓ | ✓ |
| **1,2-Benzenedicarboxylic acid butyl cyclohexyl ester** | 304 | 2315 (2299) | $C_{18}H_{24}O_4$ | 149, 55, 76 | | ✓ |

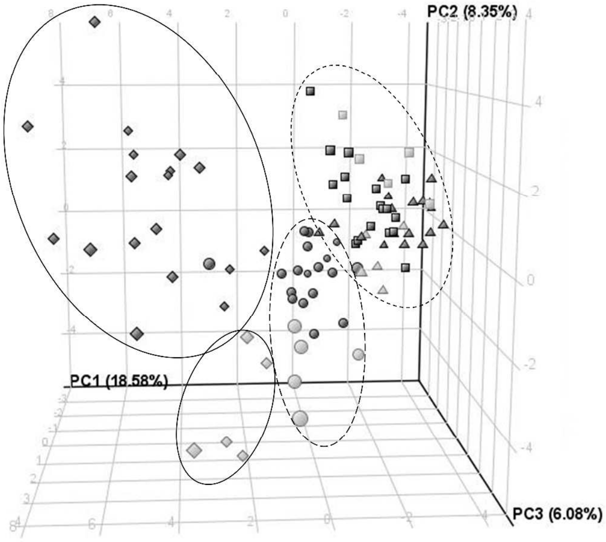

**Figure 4. PCA scores plot to evaluate the influence of the heating temperature (squares: 120 ºC, triangles: 150 ºC, circles: 180 ºC, diamonds: 200 ºC) on the volatile fraction isolated from oak chips (grey) and vine-shoots (black).**

The influence of the heating temperature was also globally evaluated by comparison of volatile profiles using multivariate statistical analysis. For this purpose, AMDIS generic files were aligned according to the protocol described in the experimental section. This step allowed obtaining a data set composed by the molecular features detected in the volatile fraction of the different varieties of vine-shoots and oak chips. Filters by frequency algorithms were applied to ensure representativeness of the data set by keeping the detected molecular features at least in a preset percentage of samples.

Due to variability between oak chips and vine-shoots, and also among samples within each class, a 50% frequency filter of all samples was selected, which led to a final data set formed by 65 molecular features. Comparison of volatile profiles was carried out by Principal Component Analysis (PCA). **Figure 4** shows the PCA scores plot, which allows identifying the heating temperature as the main factor explaining the observed variability. The lowest tested temperatures, 120 and 150 ºC, led to volatile profiles with a similar composition, while profiles for 180 and 200 ºC formed separated clusters. However, low temperatures in the autosampler did not lead to volatile profiles involving a high number of compounds. Complete discrimination between vine-shoots and oak chips samples was only found at the two highest temperatures. In fact, the number of molecular features detected in the samples decreased considerably with the heating temperature. Thus, the number of molecular features in the set of samples heated at 200 ºC was 286 (after application of a 50% frequency filter algorithm), while this number decreased up to 95 at 180 ºC and to 33 at the two lowest temperatures. Taking into account the profile of compounds formed at 200 ºC for oak chips and vine-shoots, this temperature was selected for further studies.

## 3.2 Qualitative comparison of the volatile fraction of vine-shoots and oak chips

Once the influence of the main variables involved in the heating process was assessed, the next step was the comparative analysis of samples pertaining to both materials, vine-shoots and oak chips. Qualitative comparison was carried out by Venn diagrams that allowed establishing the overlapping in composition between both types of samples.

The results are illustrated in **Figure 5** that shows the similarity between the volatile fractions from vine-shoots and oak chips after heating at high temperatures, since most of the molecular features were detected in both types of samples. As shown, 59 molecular features were detected in both types of wood at 180 ºC, however, only 7 and 29 features belonged exclusively to vine-shoots and oak chips, respectively, which allowed setting characteristic differences between both types of wood. On the other hand, at 200 ºC, all molecular features belonging to oak chips were detected in both types of wood, while only 40 molecular features were detected exclusively in vine-shoots; therefore, despite the high similarity in the composition of both samples, differences allowing complete discrimination of both types of wood must be ascribed to differences in the intensity of the molecular features

These results could open a door to the use of vine-shoots for wine ageing to obtain a wine flavor similar to that of oak, but with bouquet differences, the prevalence of which will be a function of the partition coefficient of the target compounds between the given wine and vine-shoots. Quantitation of these compounds in wine after ageing is necessary to know the magnitude of the transfer step, thus allowing handling of the flavor.

## 3.3 Identification of volatile compounds in samples of vine-shoots and oak chips

Among the compounds identified in the different varieties of vine-shoots and oak chips (**Tables 2** and **3**) it is worth emphasizing the presence of several furans at the shortest retention times in the chromatograms from both materials. They encompass aldehydes such as furfural and 5-methy-2-furancarboxaldehyde, which reported predominant signals with high intensity as compared to the rest of signals. These compounds participate in many chemical reactions involved in wine aging (e.g. formation of furfuryl alcohol or wine adducts with (+)catechin), thus lowering their concentration as free species and making them difficult to reach their high detection

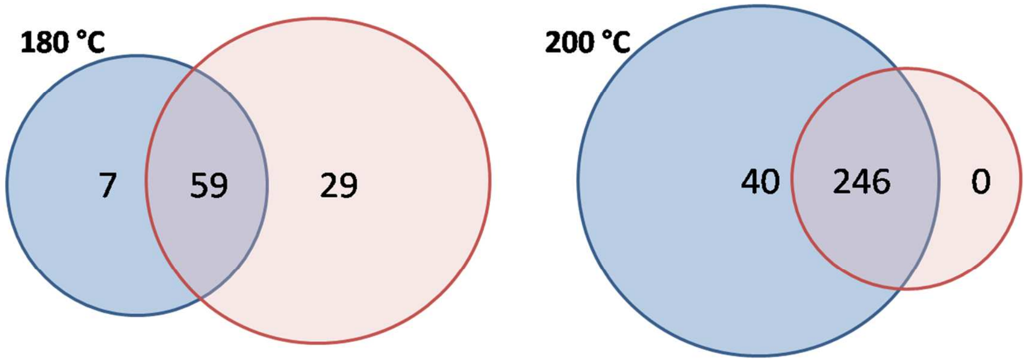

**Figure 5. Venn diagram obtained by qualitative comparison of the volatile fraction isolated from powder vine-shoots (18 varieties, left side) and powder oak chips (5 varieties, right side) for 20 min heating at 180 and 200°C.**

thresholds (20–45 mg/L).

Some authors have described a synergistic effect between furans and the sensory incidence of oak lactone, particularly that of the *cis* isomer,[25] associated to toasted, wood and coconut notes. Oak lactone was detected in all studied oak chip varieties in growing concentrations as the heating temperature increased. The highest concentration of oak lactone in American varieties of oak chips in relative terms as compared to French varieties (**Figure 3.B**) confirms the results described in the literature.[26] The absence of whisky lactones in vine-shoots could be overcome by optimization of wine ageing with mixtures between vine-shoots and oak chips. Other furan derivatives such as alcohols, mainly 2-furanmethanol and 5-methyl-2-furylmethanol, and ester derivatives, mainly 2-furanmethanol acetate and 5-acetoxymethyl-2-furaldehyde, were only detected in the volatile profile associated to vine-shoots. Furan derivatives commonly detected in oak chips and vine-shoots were ketones such as 1-(2-furanyl)ethanone, 5-methyl-2-propionylfuran, 2-acetylfuran and 2-furanmethanol acetate. These compounds, which have been related to coffee-like, toasty caramel, honey and almond odors, were detected in both types of sample regardless of the heating temperature.[24,27] Differences were observed depending on the furan derivatives; thus, only furfural and 2-pentylfuran were present in all samples heated at 120 ºC, while American oak species allowed describing a more varied furan composition. **Supplementary Tables 1** and **2** list the compounds identified in the volatile fraction sampled at 120 ºC in the varieties of vine-shoots and oak chips thus demonstrating similarities and differences between them.

Since phenolic compounds are the final products of lignin thermodegradation, the abundance of guaiacyl- and syringyl-type structures was expected. High heating temperature confers a varied phenolic composition to vine-shoots, mostly common with that in oak chips. These compounds are responsible for smoky and vanilla aroma, especially ethyl vanillin, which is widely used in the aroma industry because it offers a warm vanilla note, three times stronger than vanillin.[28]

Ferulic acid was only detected in oak chips at low temperature (120 ºC) but its absence in the volatile fraction isolated from vine-shoots could be tentatively explained by thermal degradation. This compound was identified in previous studies as a precursor of other phenolic compounds formed by thermal degradation such as 4-vinylguaiacol (carnation odor descriptor), 4-ethylguaiacol (roasted wood), vanillin (vanilla), and guaiacol (smoke), among others, which are main products of pyrolysis.[29] This trend was confirmed by the presence of these compounds in vine-shoots and oak wood. By heating at 200 ºC the chromatographic peak of vanillin is one of the most intense in all samples. Other compounds such as methoxy-eugenol, syringaldehyde and vanillyl methyl ketone were detected in the volatile fraction from all samples, except from oak wood heated at 200 ºC, at which these compounds were degraded to the corresponding alcohol derivatives (viz. eugenol, dihydroeugenol and homovanillyl alcohol).

Some other interesting compounds detected were simple and ramified alcohols such as phenylethyl alcohol, known for its floral aroma and antimicrobial properties,[30] as well as 1,3-octanediol, 1,9-nonanediol, 2-hexyl-1-decanol or 3,4-dimethyl-1-penten-3-ol. Ethyl and methyl esters of aliphatic acids also constitute an important aromatic family in the aroma profile of wines, which were detected in practically all samples. Among them, ethyl and methyl palmitate have previously been detected in different types of wines, being related to fruity odours.[31] Terpenes such as copaene were detected in vine-shoots at low heating temperature, while phytol and isophytol were present in most of the samples regardless of their origin and heating temperature. Terpene derivatives are also important contributors to the aroma of wines because of their low perception threshold and their relationship with floral odor and antimicrobial activity.[32]

On the other hand, some compounds associated to undesirable characters (such as 6-nonenal, which is related with “sawdust” and “sappy” perception in some wines aged in new barrels) were also found.[24] This compound was detected in chromatograms of some vine-shoots corresponding exclusively to experiments carried out at high heating temperatures (180 and 200 ºC).

### 3.4 Confirmatory analysis of compounds with oenological interest

Some representative compounds (viz. vanillin, acetovanillone, syringol, eugenol, 4-vinylguaiacol, coniferaldehyde, guaiacol, 5-hydroxymethylfurfural, acetosyringone, furfural, *cis* and *trans* oak lactone and 4-ethylguaiacol) were selected because of their important sensory properties to confirm their identification. For this purpose, commercial standards were analyzed by using the same chromatographic method, which allowed confirming the presence of these compounds in the volatile fraction of oak chips and vine-shoots by retention times and mass spectra. **Table 4** shows the relative area, expressed as percentage, of these compounds in the volatile fraction sampled at 120, 150, 180 and 200 ˚C in two varieties of vine-shoots and oak wood. The relative areas were calculated in relation to the sum of the total area of the peaks corresponding to the selected compounds in each sample. The effect exerted by the heating temperature on the volatile fraction of oak chips and vine-shoots was especially noticeable for furfural. This compound was found at higher relative concentrations at intermediate heating temperatures (150, 180˚C) in all samples, while its relative concentration decreased at high temperature (200˚C), which agrees with the studies carried out by Chatonnet *et al.* (1999).[22] The same trend was observed for vanillin, whose peak area increased with temperature, as **Figure 1** shows. Nevertheless, its relative abundance decreased due to generation of other compounds under these conditions. It is worth mentioning that threshold data had previously suggested that vanillin has a strong influence on wine aroma, while furfural and 5-methylfurfural possess a minor impact due to their high detection thresholds.[33] The relative concentration of vanillin in the analyzed samples strongly depended on the type of sample, being the highest levels found in the French varieties of oak wood, as previously described in the literature,[34] as well as in Pedro-Ximénez vine-shoot cultivar. On the other hand, oak lactones were always found at higher concentrations in American varieties of oak wood. The absence of oak lactones in vine-shoots is a key qualitative difference as compared to oak chips.

Coniferaldehyde was generally present at low heating temperatures and decreased its concentration when the temperature increased, which could be explained by thermal degradation since coniferaldehyde is the precursor in the synthesis of vanillin, among others. 5-Hydroxymethylfurfural was found at low temperatures in the case of French oak varieties, while its presence was detected at high temperature in the case of American varieties. Some other interesting compounds presented similar evolution patterns in oak chips and vine-shoots, being only found at medium and high heating temperatures. This is the case with syringol, 4-vinylguaiacol, guaiacol and eugenol, highly concentrated, in relative terms, in the volatile fraction of vine-shoots heated at 200 ˚C, as shows **Supplementary Figure 2.** These compounds were specially concentrated in the volatile fraction of Chardonnay and Syrah cultivars, while others, such as Baladí, Bobal, Montepila and Moscatel, reported low or undetectable levels. Vanillin presented higher relative concentrations in the volatile fraction of French varieties of oak wood, being the American varieties more similar to vine-shoots in this aspect. The opposite behavior was found in the case of furfural as vine-shoots exhibited higher concentrations than oak chips, except for the cases of the French Sweet and American Fresh oak varieties that showed levels similar to those in vine-shoots. Finally, 4-ethylguaiacol and coniferaldehyde were randomly present in some of the samples.

**Table 4. Relative concentration of a panel of compounds sampled at 120, 150, 180 and 200 ˚C and expressed as the percentage of the sum of the areas of the selected compounds ("-" means the compound was not detected).**

| | Garnacha Tintorera vine-shoots | | | | Pedro-Ximénez vine-shoots | | | |
|---|---|---|---|---|---|---|---|---|
| | 120˚C | 150˚C | 180˚C | 200˚C | 120˚C | 150˚C | 180˚C | 200˚C |
| Vanillin | - | - | 0.24 | 1.15 | 10.25 | 0.89 | 0.75 | 2.53 |
| Acetovanillone | - | - | - | 0.21 | - | - | - | 0.16 |
| 4-Ethylguaiacol | - | - | - | - | - | - | - | - |
| Syringol | - | - | - | 0.64 | - | - | 0.10 | 0.18 |
| 4-Vinylguaiacol | - | - | 0.62 | 1.03 | - | - | 0.46 | 1.11 |
| Coniferaldehyde | - | - | - | 3.05 | 10.01 | 8.29 | 1.98 | 1.27 |
| Guaiacol | - | - | 0.17 | 1.18 | - | - | - | 0.86 |
| *trans*-Oak lactone | - | - | - | - | - | - | - | - |
| *cis*-Oak lactone | - | - | - | - | - | - | - | - |
| 5-Hydroxymethylfurfural | - | - | - | - | 76.57 | 1.12 | - | - |
| Eugenol | - | - | 0.07 | 1.38 | - | - | - | 1.00 |
| Acetosyringone | - | - | - | 0.03 | - | - | - | - |
| Furfural | - | 100 | 98.90 | 91.33 | 3.17 | 89.70 | 96.71 | 92.90 |
| | French Sweet oak chips | | | | American Fresh oak chips | | | |
| Vanillin | - | 5.45 | 5.83 | 5.24 | - | - | 0.40 | 0.83 |
| Acetovanillone | - | - | - | 0.14 | - | - | - | 0.01 |
| 4-Ethylguaiacol | - | - | 0.04 | 0.11 | - | - | - | - |
| Syringol | - | - | 0.28 | 0.56 | - | - | - | - |
| 4-Vinylguaiacol | - | - | 0.32 | 0.72 | - | - | 0.50 | 0.76 |
| Coniferaldehyde | 5.25 | - | - | - | 92.66 | 3.92 | - | - |
| Guaiacol | - | - | 0.29 | 0.54 | - | - | 0.21 | 0.07 |
| *trans*-Oak lactone | - | - | - | 0.01 | - | - | - | 0.01 |
| *cis*-Oak lactone | - | - | 0.01 | 0.02 | 0.01 | 0.04 | 0.07 | 0.09 |
| 5-Hydroxymethylfurfural | - | - | 0.23 | 0.40 | 2.54 | - | - | - |
| Eugenol | - | - | 0.17 | 0.72 | - | 0.15 | 0.13 | 1.02 |
| Acetosyringone | - | - | - | - | 1.73 | - | - | - |
| Furfural | 94.75 | 94.55 | 92.83 | 91.55 | 3.06 | 95.89 | 98.69 | 97.21 |

**Conclusions.** The volatile profiles from different varieties of vine-shoots have been compared with those from different varieties of commercial oak chips, which are widely used in the oenological field to accelerate the ageing process of wines. A similar composition has been obtained in qualitative terms. The multivariate analysis also enabled identification of varieties of vine-shoots providing volatile profiles with a more similar composition to those obtained from oak chips. These preliminary results could be considered for future tests intended to evaluate the utilization of vine-shoots for wine ageing either combined with oak chips or as single ageing agent to obtain flavors different to those provided by oak chips, a present trend in wines ageing processes.[35]

## Acknowledgments

The Spanish Ministerio de Economía y Competitividad (MINECO) and FEDER Program are thanked for financial support through project CTQ2012-37428. F.P.C. is also grateful to the Ministerio de Ciencia e Innovación (MICINN) for a Ramón y Cajal contract (RYC-2009-03921).

Víctor Puente from Laffort España S.A. (Guipúzcoa, Spain) and Pedro Pérez-Juan (Bodega y ViñedosVallebravo) are thanked for providing commercial oak chips and vine shoot varieties, respectively.

## Notes and References

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