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Evolution pattern of wood-related volatiles during traditional and artificial ageing of commercial red and white wines: association with sensory analysis

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Abstract

White and red wines were treated with different ageing techniques, including barrel ageing and the use of wooden chips, to study the evolution pattern of some selected wood-related volatiles and their impact on the aromatic profile of the wines. Furfural was by far the predominant substance and its concentration peaked after six months of ageing, irrespective of the technique used. *cis*-β-Methyloctalactone was found to have a different motive of evolution, as it tended to accumulate towards the end of the ageing period (nine months), while its concentration was higher in the samples aged in the barrel made of American oak. Data regarding guaiacol and vanillin were inconclusive, as their concentrations were low and they were detected only in a limited number of samples. The sensory evaluation indicated that samples that received ageing in barrels made of Americak oak had the higher average scores, exhibiting more intense aromatic profile. On the other hand, samples treated with oak chips were rather more balanced in this regard.

Introduction

Ageing is a process that has a great impact on wine quality, affecting the organoleptic characteristics pertaining to aroma, flavour, taste and colour. Although ageing is traditionally carried out in wooden barrels, the use of wood chips is a technique that is largely employed, as it is more controllable, requiring reduced treatment period and lower cost. The beneficial quality attributes brought about as a result of ageing are largely ascribed to phenomena involving diffusion of both volatiles and non-volatiles from the wood. Extraction of volatile compounds from oak barrels depends mainly on the quantity of compounds that are potentially extractable, on the contact time between wine and wood and on the wine composition (Garde-Cerdán and Carmen Ancín-Azpilicueta, 2006).

The wood used for barrel but also chip making is primarily oak, but alternative sources of wood have been used, including acacia, chestnut, and cherry, in an effort to produce wines with distinct character (Garcia *et al*., 2012). The use of chips allows for an easy handling of the ageing process, specifically with regard to the degree of toasting, which greatly affects the composition of wood, with respect to the volatile fraction. Toasting is of high significance to the formation of volatile substances that enrich the aromatic profile of wines (Chira and Teissedre, 2013; Michel *et al*., 2013), by causing thermal degradation of lignin and cellulose/hemicellulose, and generation of compounds with peculiar flavour tones, such as honey/caramel (furfural), vanilla (vanillin), smoky/spicy (guaiacol), etc. However, native wood constituents, such as β-methyloctalactone (whiskey lactone) may also have an important contribution in this direction, lending the wines tones of coconut.

The Greek vineyard is composed mainly of native *Vitis vinifera* varieties and the impact of ageing processes on the wines produced has never been examined in details. In such a framework, this study represents a first investigation regarding the evolution of selected volatiles, during ageing of white and red wines, using barrels and chips. The wine samples chosen were made from native varieties of Crete (southern Greece) and the target compounds were selected on the basis of their origin. In particular, furfural, vanillin and guaicol derive from the thermal

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Table 1. Enological characteristics of the wines treated

Characteristic	White wines		Red wines	
	Vilana	Dafni	Kotsifali	Mantilari
pH	3.37	3.70	3.60	3.45
Titratable acidity (g L^{-1})[1]	5.6	4.3	4.7	6.0
Volatile acidity (g L^{-1})[2]	0.45	0.38	0.49	0.47
Alcohol (%, v/v)	12.4	13.1	12.2	13.3
Reducing sugars (g L^{-1})	1.56	2.25	2.02	1.96
Free SO_2 (mg L^{-1})	21.0	25.5	18.0	24.0
Total SO_2 (mg L^{-1})	104.3	104.5	92.0	95.5

[1] Expressed as tartaric acid equivalents
[2] Expressed as acetic acid equivalents

degradation of hemicellulose and lignin, whereas *cis*-β-methyloctalactone is predominant intrinsic wood constituent. The evolution pattern of these volatiles was recorded using gas chromatography-mass spectrometry and the data obtained were assessed in relation with the outcome of sensory analysis.

Materials and Methods

Chemicals

Furfural, guaiacol, vanillin and *cis*-β-methyloctalactone were purchased from Sigma-Aldrich (Steinheim, Germany). The SPME fiber (50/30-µm DVB/Carboxen/PDMS) was from Supelco (Bellefonte, PA, USA).

Wines

The wines treated were monovarietal experimental samples made from the Cretan native *Vitis vinifera* cultivars Villana (white), Dafni (white), Kotsifali (red) and Mandilari (red). All samples were provided by Lyrarakis Winery Ltd (Arkalochori, Heraklion, Crete) and were vinified according to the specifications of the company. The œnological characteristics of the samples are shown in Table 1.

Ageing treatments

Classic ageing procedure was carried out by placing the wines in wooden barrels (225 L), while accelerated ageing was performed by adding wooden chips (7 g L^{-1}) in wines placed in inox tanks (InCh). Wine samples without addition of chips were also maintained in inox tanks to serve as control (Inox). Barrels used were made of American oak *(Quercus alba)* (AmOak), French oak *(Quercus petraea)* (FrOak) and acacia *(Robinia pseudoacacia)* (Acac). The chips used were made of French oak. The samples remained throughout the whole ageing period (nine months) at the same vault within the premises of Lyrarakis Winery Ltd, under identical conditions of temperature and aeration and sampling was accomplished at regular intervals for volatile analysis and sensory assessment.

Enological analyses

Titratable acidity, volatile acidity, alcohol content, pH, and sulphur dioxide were determined using well-established, standard methods (OIV).

Headspace solid-phase microextraction (HS-SPME)

A modified protocol of that described previously was used (Jiang and Zhang, 2010). Briefly, 6.6 mL of wine sample and 1.5 g NaCl were placed in a 20-mL sample vial. The vial was tightly capped with a PTFE-silicon septum and heated at 70°C on a heating platform (YellowLine MST Basic C, Richmond, VA, U.S.A.), under continuous stirring at 400 rpm. Temperature was controlled by a YellowLine TC1 thermostat. The SPME fiber (50/30-µm DVB/Carboxen/PDMS), preconditioned according to manufacturer's instructions, was then inserted into the headspace, where extraction was allowed to occur for 40 min with continued heating and agitation. The fiber was subsequently desorbed in the GC injector for 3 min.

Gas chromatography-mass spectrometry (GC-MS)

The GC-MS system used was a Shimadzu QP 2010. The column used was a ZB-5 MS, Zebron, Phenomenex capillary column (0.25 µm film

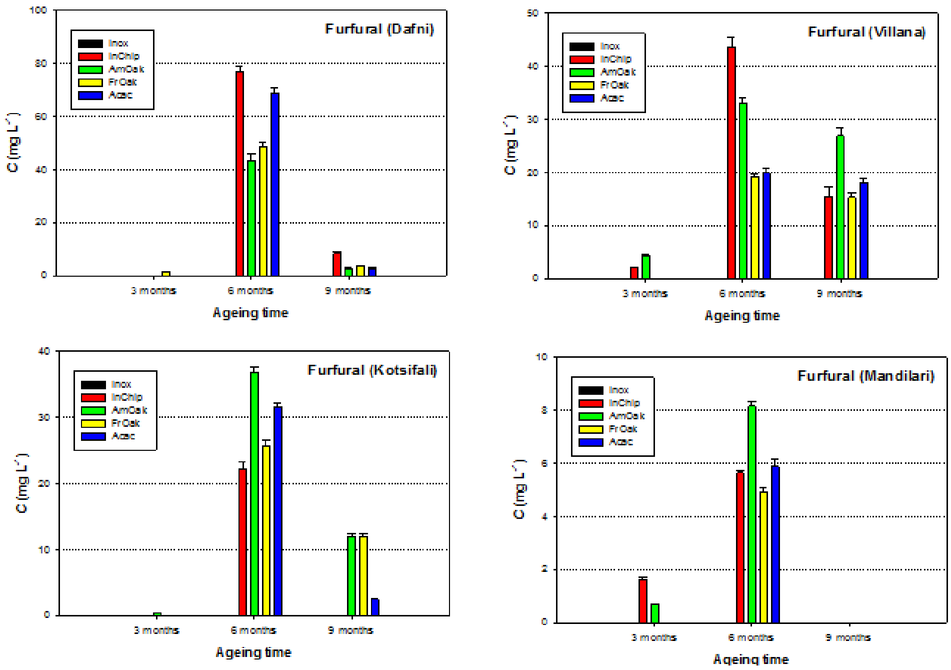

Figure 1. Comparative diagram showing the evolution of furfural during the ageing of the two white (Dafni, Villana) and the two red (Kotsifali, Mandilari) wine samples

thickness × 30 m × 0.25 mm). The carrier gas was helium at a flow rate of 1 mL min^{-1}. Samples were injected by placing the SPME fiber at the GC with the splitless mode. The oven's starting temperature was 40°C, which was held for 5 min, then raised to 230°C at a rate of 3°C min^{-1} and held at 230°C for 10 min. The mass spectrometry in the electron impact mode (MS/EI) at 70 eV was recorded in the range *m/z* from 20 to 450 U. Transfer line temperature was 220°C, injection temperature was 230°C and mass ion source temperature was 230°C. The mass spectrometer was operated in the selective ion mode under autotune conditions and the area of each peak was determined by GCMSsolution software (Shimadzu). Quantitative analyses were carried out by using calibration curves, constructed for each compound analysed, using commercial standards.

Sensory analysis

A panel of nine expert trained œnologists evaluated the wine samples with regard to their aromatic profile. Samples were presented in random order and no information was provided to the panel prior to the assessment. Wine tasting was carried out in an air-conditioned chamber with individual booths and panel members assessed the samples using an evaluation sheet with thirteen aroma descriptors for the white wines, scaled from 1 (null) to 10 (very strong), including green, earthy, flowers, balsamic, exotic fruit, dried fruit, spices, nuts, oak, honey, vanilla, coconut and smoky. For the red wines the descriptors included green, botanic, red fruits, jam, dried fruits, spices, oak, coffee, vanilla, coconut and smoky.

Statistical analysis

All GC/MS analyses were carried out at least in duplicate and values were averaged and given along with the standard deviation. Scores of the sensory analysis for each descriptor were averaged and results for each sample were given in the form of spider web plots. Student's t-test was performed to distinguish statistically different score values. For all statistical analyses, SigmaPlot™ 12.0 and Microsoft Excel™ 2010 were used.

Results and Discussion

Evolution of target compounds during ageing

The evolution of furfural over the ageing period can be seen in Figure 1. For all samples the pattern was very similar and after three months only trivial amounts were detected, reaching the highest concentration of 4.33 mg L^{-1}, in Villana (AmOak). The concentration of furfural peaked at the sixth month, where the richest sample was Dafni (InChip) with 77.11 mg L^{-1}, followed by Dafni (Acac) with 68.85 mg L^{-1}. To the contrary, Mandilari (FrOak) had the lowest concentration of furfural (4.93 mg L^{-1}). At the ninth month a decline was observed for all samples, but in Villana (AmOak) the levels were maintained over than 25 mg L^{-1}, as opposed to Mandilari, where no furfural was detected. Similar pattern for furfural evolution has been previously

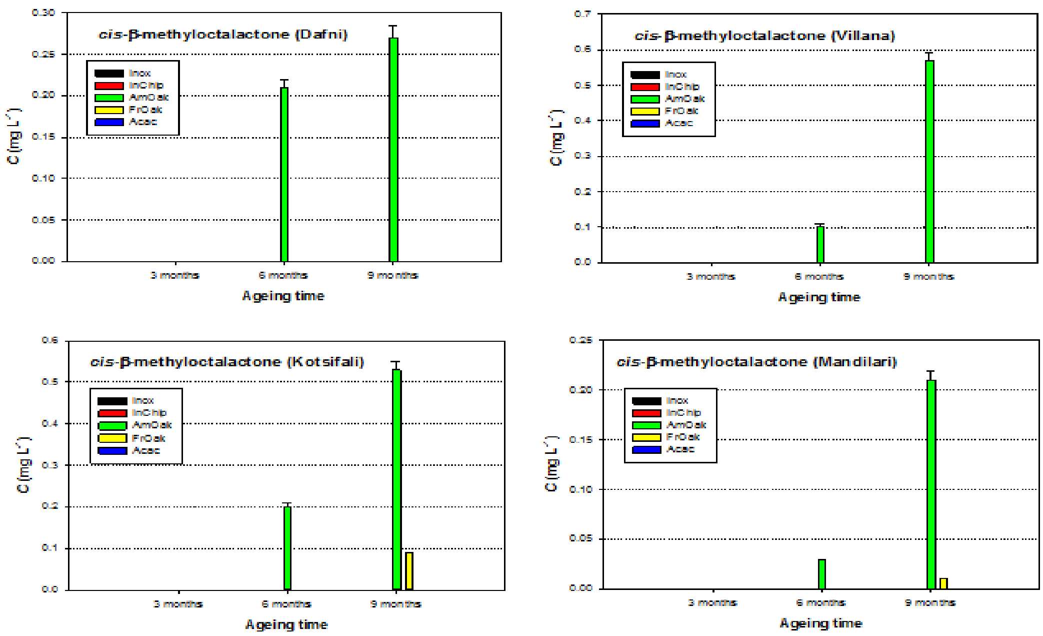

Figure 2. Comparative diagram showing the evolution of *cis*-β-methyloctalactone during the ageing of the two white (Dafni, Villana) and the two red (Kotsifali, Mandilari) wine samples

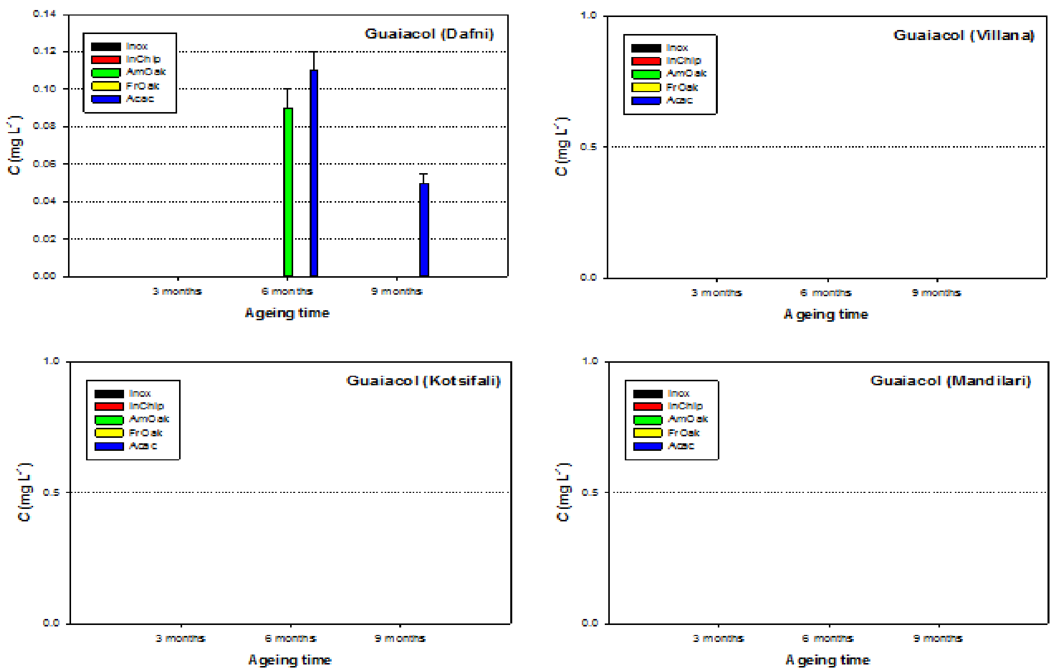

Figure 3. Comparative diagram showing the evolution of guaiacol during the ageing of the two white (Dafni, Villana) and the two red (Kotsifali, Mandilari) wine samples

observed (Jarauta *et a*l., 2005; Rodríguez-Rodríguez and Gómez-Plaza, 2012).

On the other hand, *cis*-β-methyloctalactone was detected essentially only in the samples aged in AmOak (Figure 2). In Kotsifali and Mandilari, amounts lower than 0.20 mg L^{-1} were also found in samples aged in FrOak. These findings are in accordance with previous investigations, which demonstrated that American oak *(Quercus alba*) contains significantly higher amounts of this particular substance, compared with French oak species (Cerdán *et al.*, 2002; Díaz-Plaza *et al.*, 2002; Hernández-Orte *et al.*, 2014). Furthermore, the fact that no *cis*-β-methyloctalactone was detected in samples aged in acacia barrels is reasonable, since there have never been reports for its occurrence in *Robinia pseudoacacia* species. *cis*-β-Methyloctalactone evolution displayed a different pattern from that recorded for furfural and, with the exception of Dafni, its concentration increased from the sixth to the ninth month 2.65 to 7 times. Such behaviour has been previously seen in wines aged in oak barrels (Jarauta *et al.*, 2005; Pérez-Prieto *et*

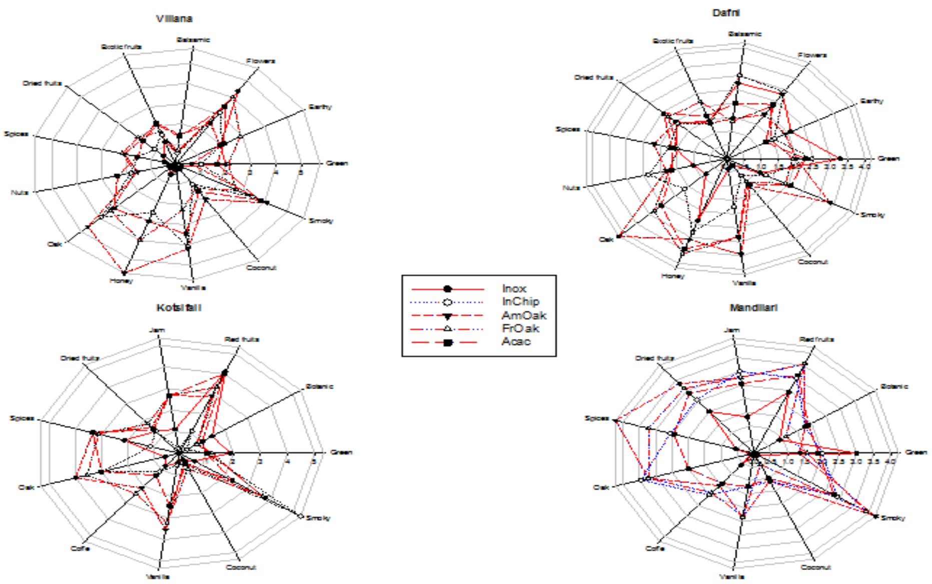

Figure 4. Spider web plots illustrating the aromatic impact of the white wines treated with the various ageing techniques, as revealed by the sensory analysis. Villana, upper left; Dafni, upper right; Kotsifali, lower left; Mantilari, lower right

al., 2003; Rodríguez-Rodríguez and Gómez-Plaza, 2012). After 9 months of ageing, Villana had the highest concentration in *cis*-β-methyloctalactone, reaching 0.57 mg L^{-1}. This value is close to 0.40 mg L^{-1} reported for red wine aged in American oak barrels after six months (Pérez-Prieto *et al*., 2002) and 0.71 mg L^{-1} after twelve months (Fernández de Simón *et al*., 2003).

Guaiacol was detected only in Dafni and in a similar fashion to that of furfural, a decline was observed at the ninth month of ageing (Figure 3). The highest concentrations were 0.09 mg L^{-1} (AmOak) and 0.11 mg L^{-1} (Acac), determined after six months. Likewise, vanillin was detected only in Villana (FrOak) and after six months its concentration was 0.30 mg L^{-1}, while after nine months it was undetectable. This finding is consistent with previous outcome, which demonstrated a decline in vanillin concentration from the sixth to the twelfth month of ageing (Jarauta *et al*., 2005). The concentration found is of comparable magnitude to that previously reported for barrel and chip ageing, which varied from 0.15 to 0.64 mg L^{-1} (Hernández-Orte *et al*., 2014) and oak barrel ageing, giving a concentration of 0.41 mg L^{-1} after 12 months (Fernández de Simón *et al*., 2014).

The nature and the relative amounts of the volatile compounds originating from wood used for wine ageing may vary largely, since it may depend on a few factors that profoundly affect their occurrence, including seasoning period (Martínez *et al*., 2008), surface contact (barrels vs chips) (Hernández-Orte *et al*., 2014), wood species (De Rosso *et al*., 2009a, b) and ageing period (Pérez-Prieto *et al*., 2003). Therefore the analytical profile of the wood-related volatiles would be expected to exhibit large variations, precluding the detection of a generalised pattern. In addition, the importance of wine composition should also be stressed. It has been demonstrated that some major wood-related compounds, such as furfural and vanillin could react with catechin, which is an abundant wine polyphenol, giving rise to several adducts (Nonier Bourden *et al*., 2008). Thus ageing of red and white wines would certainly follow quite different evolution routes, in terms of the enrichment in wood-related volatiles.

Sensory assessment

The position of the wines on the spider web plots provided a graphic representation of the wines' sensory character, which was consistent with the analytical profile of the target substances, as revealed by GC/MS. In the case of Villana it was clear that, for AmOak treatment, its aromatic profile was characterised by notes pertaining to barrel ageing ("oak"). The profile of Acac was rather more balanced in this regard (Figure 4, upper left plot). The same was also observed for Dafni (AmOak), where notes associated with "oak" were prevalent (Figure 4, upper right plot). Similar results for barrel-aged wines have been previously reported (Gallego *et al*., 2012). For Kotsifali, the predominance of "red fruits" was apparent in the cases of Inox and InChip (Figure 4, lower left plot); for Mantilari the most pronounced notes were those originating from AmOak (Figure 4, lower right plot), but in the case of InChip the aromatic impact was rather shared amongst "oak", "red fruits" and "jam". Overall, samples treated with AmOak had on average higher score ($p < 0.05$), but samples received the InChip treatment appeared to be more balanced.

It should be emphasised that knowledge of volatile composition and concentration alone is not enough to completely understand the flavour of a sample. Interactions among odorants, interactions between sense modalities and matrix effects can all impact the odorant volatility, aroma release, and overall perceived aroma intensity and quality (Polášková *et al*., 2008).

Conclusions

The study presented herein is the first examination regarding the behaviour of certain native Cretan wines with regard to various modes of ageing. The GC/MS analyses illustrated that the evolution pattern is not the same for all target compounds examined, but in general the higher concentrations appeared to peak following a six-month ageing, whereas in most cases the concentration of volatiles tended to decline after nine months. The highest concentration was found for furfural, followed by *cis*-β-methyloctalactone. The sensory evaluation indicated that samples that received ageing in barrels made of Americak oak had the higher average scores, exhibiting more intense aromatic profile. On the other hand, samples treated with oak chips were rather more balanced in this regard.

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