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Influence of supplementing red wine with oak staves of various ellagitannin release potentials and different micro-oxygenation doses on wine colour and phenolic and volatile composition

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ABSTRACT

Aim: The aim of the study was to evaluate the effect on wine colour and phenolic and volatile composition of supplementing a red wine with different oak staves - selected using a non-invasive measurement method based on infrared spectrometry (Oakscan system) - during a micro-oxygenation treatment. **Methods and results:** Aliquots of 165 liters of a Merlot wine were micro-oxygenated at two doses of oxygen (2.5 and 5.0 mg of O2/L.month) in the presence or not of oak staves of different potential ellagitannin release (PER) for three months. Micro-oxygenation generally increased colour intensity and stability, probably because it favours the formation of new pigments. The presence of staves increased the total phenolic index and the ellagitannin concentration and encouraged the combination of anthocyanins with flavanols. The greater the PER of the staves, the greater this effect was. Finally, the micro-oxygenation dose only affected the concentration of total furanic compounds, whereas the PER of the staves seemed to determine the concentrations of furanic compounds, volatile phenols and β-methyl-γ-octalactones. To be specific, the lower the PER of the staves, the higher the concentration of β-methyl-γ-octalactones (coconut notes) and the lower the concentration of furanic compounds (toasted nut notes) and volatile phenols (smoked notes). A sensory analysis of the wines confirmed this trend. **Conclusions:** The main conclusion is that it is possible to use a non-invasive measurement method based on infrared spectrometry oak staves for their potential release of ellagitannins, as well as different volatile substances. **Significance and impact of the study:** These results indicate that by choosing the staves winemakers can modulate both the structure and the aromatic profile of their wines.

KEYWORDS

Micro-oxygenation, Oak staves, Ellagitannins, Wine colour, Phenolic compounds, Wine aroma

INTRODUCTION

Wine aging in oak barrels is a highly complex process, during which the wine undergoes a number of changes and gains in complexity and stability (Garde-Cerdán and Ancín-Azpilicueta, 2006). The oak wood contributes to the wine by adding volatile substances that improve its quality in terms of aroma and flavour (Navarro *et al.*, 2018), as well as phenolic compounds that contribute to its textural sensations (Navarro *et al.*, 2016a).

These volatile compounds - which are released by the oak into the wine during barrel aging – are either naturally present in the original oak wood or are derived from other substances in the wood during the toasting process (Chira and Teissedre, 2013). Several volatile compounds belonging to very different chemical families have been described (Cadah Cadahía *et al.*, 2003), but only a few of them have a significant impact on wine aroma. It is generally accepted that the main volatile substances released by oak wood to wine are furans, phenolic aldehydes and ketones, volatile phenols and β-methyl-γ-octalactones (Garde-Cerdán *et al.*, 2004; Prida and Chatonnet, 2010). The furanic compound family - which mainly includes furfural, methyfurfural, hydroxymethylfurfural and furfurilic alcohol - contributes to the smoked and toasted nut notes found in wine (Spillman *et al.*, 2004). The family of phenolic aldehydes and ketones contributes to the characteristic vanilla aroma of aged wines, with vanillin being the major contributor (Prida and Chatonnet, 2010). The volatile phenol family mainly includes ethylphenol, guaiacol, methylguaiacol, ethylguaiacol, vinylguaiacol, eugenol and *trans*-isoeugenol. Eugenol provides an interestingly spicy note of cloves (Boidron *et al.*, 1988), while all the others contribute smoked/toasted notes (Chatonnet *et al.*, 1999). Depending on their concentrations, these volatile phenols can have a negligible effect if they are below their sensory threshold, a pleasant effect when their presence provides slight notes of toasted bread, or an unpleasant effect when their concentrations are so high that their burnt bread notes overpower the rest of the olfactory matrix (Navarro *et al.*, 2018). Finally, β-methyl-γ-octalactones (also known as whiskey lactones), which are present in the form of two isomers (*cis* and *trans*), are responsible for the coconut flavour. The *cis* isomer has a much lower perception threshold than the *trans* isomer, therefore it contributes much more to a perception of coconut (Abbott *et al.*, 1995).

Oak wood also releases ellagitannins that contribute to some of the textural sensations of wine, such as body and astringency (Glabasnia and Hofmann, 2006; Michel *et al.*, 2011). The main ellagitannins released from oak wood to wine are the well-known castalagin and vescalagin, the C-lyxoside and C-xyloside conjugates of vescalagin (grandinin and roburin E respectively), together with C-glycosidic derivatives, such as the quasi-dimers of all the latter compounds (roburins A, D, B and C respectively) (Jourdes *et al.*, 2009).

All these volatile and non-volatile substances are released from oak wood into the wine during barrel aging and their amount and proportion will depend on various factors, such as the botanical and geographical origin of the oak, seasoning technique, degree of toasting, and number of times the barrel has been used before (Navarro *et al.*, 2016a; Navarro *et al.*, 2018).

Aging in oak barrels also allows a moderate amount of oxygenation to take place via the porosity of the wood itself, the bunghole and the interstices between the staves (Del Alamo *et al.*, 2017). This natural micro-oxygenation leads to the formation of ethanal from ethanol. This ethanal can then react with flavanols to form a very reactive carbocation, which in turn quickly reacts with either another flavanol molecule or an anthocyanin to produce ethyl-bridged flavanol-flavanol and/or flavanol-anthocyanin oligomers (Escribano-Bailón *et al.*, 2001). Ethanal can also participate in the formation of vitisin B and other pyranoanthocyanins (Mateus *et al.*, 2002; Morata *et al.*, 2007). It is generally accepted that these reactions generated by the oxygen supply involve colour stabilization and astringency reduction in red wines (Ribéreau-Gayon *et al.*, 2006a; Gambuti *et al.*, 2013). In addition, a certain precipitation of part of the colouring substance of the wine will take place, which means that this unstable part of the colour will not precipitate later in the bottle (Zamora, 2003; Garde-Cerdán and Ancín-Azpilicueta, 2006).

However, oak aging is an expensive and laborious process that can only be applied to wines with a certain added value. For this reason, the use of oak alternatives coupled with micro-oxygenation (MOX) has progressively increased over recent years, because it can reproduce the processes taking place in the barrels more economically and quickly (Del Alamo *et al.*, 2010; Cano-López *et al.*, 2010).

The MOX technique consists of supplying a small controlled flow of oxygen to the wine in the form of microbubbles injected through a microdiffuser (Parish *et al.*, 2000; Moutounet *et al.*, 2001; De Llaudy *et al.*, 2006). It is commonly applied in wineries all over the world today. It is generally accepted that MOX stabilizes the colour and decreases the bitterness, astringency and herbaceous characters of wine (Atanasova *et al.*, 2002; Cano-López *et al.*, 2008). Its influence on wine quality depends on various parameters, the most important being the dose of oxygen, the point at which it is applied, and the composition of the initial wine (Kontoudakis *et al.*, 2011; Gómez-Plaza and Cano-López, 2011).

Oak alternatives (chips, beans, blocks and staves, etc) have also been widely used to flavour wine for many years (Bertrand *et al.*, 1997; Chassin, 1999; Bautista-Ortín *et al.*, 2008; Granes *et al.*, 2009). They enrich the wine with the same volatile substances that are released during oak barrel aging, although some differences between wines aged in oak barrels and wines macerated with oak fragments have been described (Hernández-Orte *et al.*, 2014). Oak alternatives also release ellagitannins into the wine (Chira and Teissedre, 2013) and our research group has recently shown that these very efficiently consume the dissolved oxygen in a model wine solution (Navarro *et al.*, 2016b; Pascual *et al.*, 2017; Vignault *et al.*, 2018). Consequently, the simultaneous application of micro-oxygenation (MOX) with oak alternatives - currently a common practice in wineries - means that part of the oxygen will be consumed by the ellagitannins and part by the natural components of the wine.

Another recent proposal is a device based on near-infrared spectroscopy (NIRS), the Oakscan system (Giordanengo *et al.*, 2009; Giordanengo *et al.*, 2012; Chaix *et al.*, 2018), which can be used to non-invasively determine the potential wood polyphenol index in wood. This procedure enables the wood staves to be classified according to their levels of potential ellagitannin release (PER), making it possible to select barrels or other wood alternatives following a new criterion (Michel *et al.*, 2013).

Several studies have explored how MOX (Atanasova *et al.*, 2002; De Llaudy *et al.*, 2006; Kontoudakis *et al.*, 2011; Gómez-Plaza and Cano-López, 2011) and oak alternatives (Bautista-Ortín *et al.*, 2008; Chira and Teissedre, 2013; Hernández-Orte *et al.*, 2014; Gómez-García-Carpintero *et al.*, 2012¸) can contribute to wine composition and quality, but little is known about the simultaneous application of these techniques (Del Alamo *et al.*, 2010; Oberholster *et al.*, 2015, and almost nothing about the influence of using oak staves of different PERs. Furthermore, to our knowledge, this is the first time that the influence of the PER of the staves on the aromas released by the oak into the wine has been studied.

The aim of this research was therefore to study how different doses of oxygen and supplementation with different doses of oak staves of different PERs during a three-month period of micro-oxygenation would influence the colour and phenolic and volatile composition of a Merlot red wine, especially with regard to the substances released by oak wood.

MATERIALS AND METHODS

1. Chemicals

Methanol, acetonitrile, formic acid, acetic acid, ethyl acetate and absolute ethanol were of HPLC grade and purchased from Panreac (Barcelona, Spain). Acetaldehyde, phloroglucinol, ascorbic acid and sodium acetate were purchased from Sigma-Aldrich (Madrid, Spain). Dichloromethane (LiChrosolv quality) was purchased from Merck (Darmstadt, Germany) and pentane from Fluka (Buchs, Switzerland). Standards for proanthocyanidin analysis, (+)-Catechin (≥ 99 % %), (−)-epicatechin (≥ 99 %), (−)-epigallocatechin (≥ 98 %), and (−)-epicatechin- 3-O-gallate (≥ 97.5 %), were purchased from Extrasynthese (Genay, France). Standards for ellagitannin analysis, castalagin (99 %), vescalagin (98 %), roburin A (98 %), roburin B (93 %), roburin C (93 %), roburin D (98.5 %), grandinin (98.5 %) and roburin E (97 %), were purchased from Adera (Pessac, France). The chemical standards for gas chromatography were purchased from Aldrich and PolyScience (Niles, USA). The rest of the chemicals were of high purity and purchased from Panreac (Barcelona, Spain). Pure water was obtained from a Milli-Q purification system (Millipore, USA).

2. Oak staves

Medium toasted staves of French oak (*Quercus petraea*) were provided by Tonnellerie Radoux-Pronektar (Jonzac, France). These staves were selected with three levels of potential ellagitannin release (PER). The PER was determined by the supplier company itself (Tonnellerie Radoux-Pronektar) using its non-invasive measurement method based on infrared spectrometry

(Radoux OakScan®) (Giordanengo *et al.*, 2009; Giordanengo *et al.*, 2012; Chaix *et al.*, 2018).

To develop this method, an important collection of oak samples was built, covering a large variability of wood composition. The extracts of the samples were characterized by chemical analysis (optical density at 280 nm, total phenols by Folin-Ciocalteu and ellagitannins content by liquid chromatography) and then measured by near infrared spectrometry. Near infrared calibrations were computed with this dataset (Giordanengo *et al.*, 2009). A specific optical sensor was designed to function in a wood workshop, which was developed to realize reliable and robust near infrared analyses, by optimizing the physical conditions of the measurement, and processing the spectral data with chemometric methods (Chaix *et al.*, 2018). For each scanned oak stave, a near infrared spectrum can be quickly collected. The sensor gives an estimation of the oak polyphenol content using the calibrations. PER is thus estimated by a normalized index ranging from 0 to 100.

For this study, oak material was harvested from the French National Forest of Traconne (Marne). The logs were sawn and the oak was dried naturally for 24 months. The Oakscan sensor was employed to measure the PER of 1000 staves from this production (mean value ± standard deviation: 36 ± 10). Three groups of 30 staves were selected: Low PER (22 ± 3), Medium PER (36 ± 3) and High PER (50 ± 4). The grain size of the oak samples was homogeneous for the three groups. All the staves were then heat treated in an industrial oven in the same production batch (Medium toast), in order to avoid variations due to oak toasting. The staves were finally sawn to a size of 7 x 47 x 135 mm, in order to fit the dose needed for the wine trial. Hence, high, medium and low PER staves were employed in this experiment.

3. Micro-oxygenation equipment

Micro-oxygenation was performed using a multiple diffuser micro-oxygenator (DosiOx pupitre, Agrovin, Alcazar de San Juan, Spain), which was connected to each of 24 stainless steel tanks. These tanks, with a volume capacity of 165 liters, were 2.5 m in height and 0.30 m in diameter, and were equipped with a ceramic diffuser placed 10 cm above the bottom of the tank. These dimensions were necessary in order for the oxygen bubbles produced during micro-oxygenation to have sufficient displacement height to guarantee their complete dissolution.

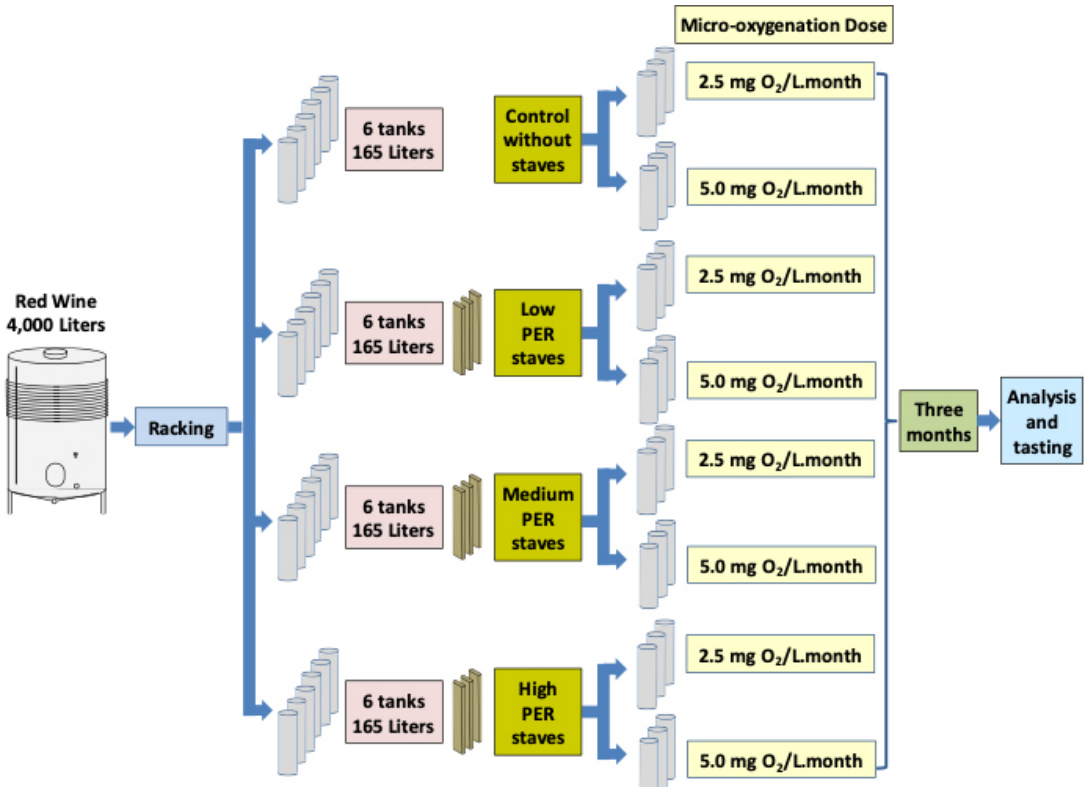

FIGURE 1. Experimental Design.

4. Experimental design

Figure 1 shows a schematic diagram of the experimental design. This study was carried out with a Merlot wine from the 2014 vintage of AOC Tarragona once malolactic fermentation was completely finished.

The standard parameters of the wine at the start of the experiment were as follows: ethanol content, 13.8 %; titratable acidity, 6.6 g of tartaric acid/L; volatile acidity, 0.49 g of acetic acid/L; pH, 3.4 and free sulfur dioxide, 23 mg/L. Around 4000 liters of this wine were distributed among 24 stainless steel tanks of 165 L capacity. Argon was used during the wine-racking process to ensure that the wine only received oxygen through micro-oxygenation. Six tanks were then supplemented with 5.0 g/L of low-PER staves, 6 with 5.0 g/L of medium-PER staves and 6 with 5.0 g/L of high-PER staves, while the six remaining tanks were used as controls without staves. Micro-oxygenation was carried out in triplicate for 3 months using two different oxygen doses: 2.5 or 5 mg O_2/L per month. More specifically, for each PER-level staves or for the control, three tanks were micro-oxygenated with the low dose of oxygen and the other three with the high dose. All the wines were kept at a temperature of 16 ± 2 ºC throughout the experiment. After that, 24 glass bottles (750 mL), previously purged with argon, were filled with wine from each tank and sealed with 49 mm natural corks. Analyses were done immediately after bottling. Sensory analysis was carried out two months after bottling.

5. Spectrophotometric analysis

Absorbance measurements were performed using a Helios Alpha UV−vis spectrophotometer (Thermo Fisher Scientific Inc., Waltman, MA, USA).

Colour intensity (CI), total anthocyanins (TA) and PVPP Index were estimated following the methods described by Glories (1984). The CIELab coordinates (lightness (L*), chroma (C*), hue (h*), red-greenness (a*), and yellow-blueness (b*)) were determined according to Ayala *et al.* (1997) and data processing was performed with MSCV software (Ayala *et al.*, 2001). The total phenolic index (TPI) was determined in accordance with Ribéreau-Gayon *et al.* (2006b).

6. Analysis of proanthocyanidins following acid catalysis with phloroglucinol

Acid-catalyzed depolymerisation of proantho cyanidins in the presence of an excess of phloroglucinol (phloroglucinolisis method) was used to analyse the proanthocyanidin content, monomeric composition and mean degree of polymerization (mDP) of all the wines. The proanthocyanidins were extracted and analysed by acid depolymerisation in the presence of an excess of phloroglucinol (Kennedy and Jones, 2001). The proanthocyanidins were analysed using an Agilent 1200 Series HPLC equipped with a G1362A refractive index detector (RID), a G1315D DAD, a G1311A quaternary pump, a G1316A column oven and a G1329A autosampler (Agilent Technologies, Santa Clara, CA, USA). The chromatographic system was managed by an Agilent ChemStation (version B.01.03) for data processing.

The number of terminal subunits was considered to be the difference between the total monomers measured in normal conditions (with phoroglucinol) and those obtained when the analysis was performed without the addition of phloroglucinol. The number of extension subunits was considered to be the sum of all the phloroglucinol adducts. The total proanthocyanidin concentration (PA) was considered to be the sum of all terminal and extension subunits. The mean degree of polymerisation (mDP) was calculated by adding the terminal and extension subunits (in moles) and dividing by the terminal subunits. The proportion of prodelphinidins (% PD) was calculated as the quotient between total (−)-epigallocatechin units and total monomeric units expressed as a percentage. The proportion of galloylation (% GAL) was calculated as the quotient between total (−)-epicatechin-3-gallate units and total monomeric units expressed as a percentage.

7. Ellagitannin analysis

The wine samples were first fractionated to obtain ellagitannin-rich fractions using a previously described method ([51]. A mother solution containing all the individual ellagitannin standards was suitably diluted to obtain the calibration curves necessary for quantification, covering concentration ranges up to 40 mg/L of each ellagitannin.

The ellagitannins were analysed by HPLC using a modification of a previously described method (García-Estevez *et al.*, 2010). This modified method was adapted for the use of fused core C18 chromatographic columns (Ascentis Express, 150 × 4.6 mm, 2.7 µm particle size), thermostatted at 40 °C (Navarro *et al.*, 2017). The ellagitannins were identified by matching the retention time and spectral data (DAD-UV–vis and MS/MS) against

those of authentic standards. The quantification was performed using the DAD-chromatograms extracted at 250 nm.

8. Volatile compound analysis

The volatile compounds released from the oak wood were analysed by GC/MS using a Focus-GC system gas chromatograph coupled to an ISQ mass spectrometer with electron impact ionisation source and quadrupole analyser equipped with a TriPlus autosampler, all from ThermoQuest. The conditions of the detector were as follows: electron multiplier voltage, 1250 V; impact energy, 70 eV; ion source temperature 250 °C; and mass scanning range, 40–250 amu. A BP21 column (SGE) of 60 m–0.32 mm internal diameter and 0.25 µm thick of free fatty acid phase (FFAP) (polyethylene glycol treated with nitroterephthalic acid) was used.

Volatile compounds were extracted and analysed using the method developed by Ibarz *et al.* (2006). 25 mL of wine was passed through columns filled with 0.2 g of LiChrolut EN (40–120 µm, Merck) using 4-nonanol as the internal standard. The columns were then washed with 25 mL of water to remove sugars, acids and other polar substances. The fraction of volatile compounds was eluted with 15 mL of pentane: dichloromethane (2:1 v/v). Extracts were concentrated by distillation in a Vigreux column and then under nitrogen stream to 100 µL and then kept at −20 °C until analysis.

Separated compounds were identified by their mass spectra and chromatographic retention times, using commercial products as a standard. Quantification was performed by analysing the characteristic m/z fragment for each compound using the internal standard method. Results for non-available compounds were expressed in concentration units (µg/L or mg/L) as internal standard equivalents obtained by normalizing the compound peak to that of the internal standard and multiplying by the concentration of the internal standard. Only the main volatile compounds released by oak wood (furanic compounds, vanillin, β-methyl-γ-octalactones and volatile phenols) are shown as this study focused on the aromas that wood releases.

9. Sensory analysis

All sensory analyses were performed in the tasting room of the Faculty of Enology of Tarragona (University Rovira i Virgili), which was designed in accordance with UNE 87004.197 (aenor, 2010). Tasting was carried out using ISO official tasting glasses (ISO-3591, 1997). Each sample consisted of 30 mL of wine presented at room temperature (20 °C), covered with clear plastic petri dishes to minimize the escape of volatile components and randomly coded with three-digit numbers.

All the samples were tasted by 18 students in their final year of the Bachelor in Enology at the University Rovira i Virgili (four-year degree). This panel comprised 10 males and 8 females aged between 21 and 25, who had trained together for 3 years while studying sensory analysis as part of the enology degree.

Two months after bottling, sensory descriptive analyses of the various wines were carried out over two sessions so as not to fatigue the panelists. In the first session, the wines treated with an oxygen dose of 2.5 mg of O_2/L.month were compared, while in the second those treated with an oxygen dose of 5.0 mg of O_2/L.month were compared. There was a 30-minute break between the two sessions. To simplify the tasting, the wines from three similar (triplicate) samples of each experimental group were mixed.

For each sample, the tasters were required to evaluate the intensity of four olfactory sensory attributes (red fruits, coconut, vanilla and smoked notes) and two mouthfeel sensory attributes (structure and astringency) on a scale of 1 to 10 (1='slight intensity', 10='maximum intensity'). The intensity level of each descriptor was then expressed as the mean value of the scores given by all the judges. A sensory training session had been held beforehand in order for the panelists to agree on the criteria for each of the different sensory attributes. Samples were served randomly to avoid any influence from the tasting order.

10. Statistics

All analytical data are expressed as the arithmetic average ± standard deviation of the three replicates. All sensory data are expressed as the arithmetic mean ± standard deviation of the scores of the 18 tasters. One-factor analysis of variance (ANOVA) was carried out using SPSS 15.0 software (SPSS Inc., Chicago, IL).

RESULTS AND DISCUSSION

1. Wine colour

Table 1 shows the colour intensity and CIEL*a*b* coordinates of the original wine and the different wines obtained after applying the different micro-

TABLE 1. Influence of the micro-oxygenation dose and supplementation with oak staves of different potential ellagitannin release (PER) on wine colour.

Parameter	Original wine	Oxyge dose (mg O_2/L.month)	Control	Low PER	Medium PER	High PER
CI	15.0 ± 0.1 **B**	2.5	13.6 ± 0.3 **A α**	13.7 ± 0.4 **A α**	14.0 ± 0.2 **A α**	13.9 ± 0.5 **A α**
		5.0	14.4 ± 0.1 **A β**	14.2 ± 0.3 **A α**	14.6 ± 0.4 **AB α**	14.9 ± 0.1 **B β**
L*	42.0 ± 0.2 **A**	2.5	44.5 ± 0.6 **B β**	45.4 ± 0.9 **B α**	44.1 ± 0.6 **B α**	45.0 ± 0.9 **B β**
		5.0	43.1 ± 0.6 **B α**	43.9 ± 0.9 **B α**	43.3 ± 1.5 **AB α**	42.2 ± 0.1 **A α**
C*	60.2 ± 0.3 **C**	2.5	57.7 ± 0.4 **A α**	58.0 ± 0.7 **A α**	58.8 ± 0.5 **B α**	58.5 ± 0.2 **B α**
		5.0	58.9 ± 0.2 **A β**	58.5 ± 0.4 **A α**	58.7 ± 0.3 **A α**	59.2 ± 0.1 **B β**
h*	14.7 ± 0.9 **A**	2.5	15.1 ± 0.7 **A α**	14.4 ± 0.9 **A α**	15.2 ± 1.1 **A α**	15.0 ± 1.6 **A α**
		5.0	20.2 ± 0.7 **B β**	19.3 ± 0.2 **B β**	20.8 ± 1.0 **B β**	19.9 ± 0.4 **B β**
a*	58.2 ± 0.5 **C**	2.5	55.7 ± 0.3 **A β**	56.8 ± 0.4 **B α**	56.5 ± 0.7 **AB α**	59.5 ± 0.6 **AB β**
		5.0	55.4 ± 0.1 **A α**	55.8 ± 0.7 **A α**	55.5 ± 0.5 **A α**	55.7 ± 0.1 **A α**
b*	15.3 ± 0.8 **A**	2.5	15.0 ± 0.5 **A α**	14.5 ± 0.9 **A α**	15.5 ± 1.0 **A α**	15.2 ± 0.2 **A α**
		5.0	19.9 ± 0.3 **B β**	18.3 ± 2.7 **B β**	20.9 ± 0.9 **B β**	20.2 ± 0.2 **B β**

Results are expressed as mean ± standard deviation of three replicates. Different letters in a row indicate the existence of statistical difference ($p < 0.05$). First row (capital letters) indicates the influence of the PER of the staves. Second row (Greek letters) indicates the influence of the oxygen dose. CI: colour intensity; L*: lightness value (CIELab coordinates); C*: chroma value (CIELab coordinates); h*: hue value (CIELab coordinates); a*: green−red component (CIELab coordinates); b*: blue−yellow component (CIELab coordinates).

oxygenation (MOX) conditions. In general, the colour intensity (CI), chroma (C*) and green-red component (a*) of the MOX wines tended to decrease in comparison with the original wine, whereas lightness (L*), hue (h*) and the blue-yellow component (b*) did the opposite. These data show that wine colour followed its natural evolution, since the intensity of the red component was reduced and the yellowish nuances increased [45]. In addition, it seems that the oxygen dose exerts a clear effect on wine colour, because CI and C* were significantly higher and L* significantly lower in the wines treated with 5 mg/L.month than in those treated with 2.5 mg/L.month. These results indicate that the higher the oxygen dose, the more intense the colour. In contrast, h* and b* were also significantly higher in the wines treated with the high dose of oxygen, which indicates that the colour had evolved more. These results are generally in line with the observed effect of oxygen on the evolution of wine colour (Atanasova *et al.*, 2002; De Llaudy *et al.*, 2006; Kontoudakis *et al.*, 2011; Oberholster *et al.*, 2015).

Supplementation with staves also seems to have some influence on wine colour, especially in the case of medium- and high-PER staves. In fact, CI and C* tended to be higher and L* lower in the wines supplemented with staves, although these differences were not always statistically significant. The effect was probably due to the ellagitannins released from the staves. This point will be discussed in more detail later when we describe the ellagitannins released by staves of different PERs.

2. Anthocyanins, tannins and related parameters

Table 2 shows the anthocyanin and PVPP index of the original wine and the different wines obtained after applying the different MOX conditions. As expected, the total anthocyanin concentration decreased over time when MOX was applied, and this decrease was greater when the oxygen dose was higher. These data confirm that oxygen can degrade anthocyanins, as has been reported before (King *et al.*, 1980). However, the PVPP index tended to increase over time in all of the MOX wines, and did so more rapidly when the higher oxygen dose was applied. Since the PVPP index indicates the percentage of anthocyanins combined with flavanols (Glories, 1984), these results confirm that MOX favours the unions between anthocyanins and flavanols via the formation of ethyl bridges (Atanasova *et al.*, 2002; Gómez-Plaza and Cano-López, 2011; Cejudo-Bastante *et al.*, 2011b). Indeed, it has been reported that MOX increases the concentration of malvidin-3-glucoside-ethyl-flavan-3-ol adducts and pyranoanthocyanins (B-type vitisins) (Pérez-Magariño *et al.*, 2007; Cejudo-Bastante *et al.*, 2011a). Since these new pigments are more stable than free anthocyanins, their formation has been associated with the stabilisation of red wine colour.

TABLE 2. Influence of the micro-oxygenation dose and supplementation with oak staves of different potential ellagitannin release (PER) on anthocyanins, tannins and related parameters.

Parameter	Original wine	Oxygen dose (mg O_2/L.month)	Control	Low PER	Medium PER	High PER
TA (mg/L)	574 ± 17 **C**	2.5	493 ± 15 **B α**	466 ± 18 **AB α**	444 ± 7 **A α**	437 ± 13 **A β**
		5.0	455 ± 11 **B β**	438 ± 27 **AB α**	425 ± 23 **AB α**	413 ± 7 **A α**
PVPP Index (%)	25.1 ± 4.3 **A**	2.5	47.7 ± 1.8 **A β**	48.2 ± 2.6 **AB α**	51.9 ± 3.6 **AB α**	53.2 ± 3.7 **B α**
		5.0	52.7 ± 1.5 **A α**	52.4 ± 2.0 **A α**	58.8 ± 2.9 **B β**	60.1 ± 2.6 **B β**
TPI	65.3 ± 0.1 **D**	2.5	60.3 ± 0.2 **A α**	60.1 ± 0.7 **A α**	61.4 ± 0.5 **B α**	62.9 ± 0.3 **C β**
		5.0	60.1 ± 0.4 **A α**	60.0 ± 0.6 **A α**	61.5 ± 0.1 **B α**	61.5 ± 0.3 **B α**
PA (mg/L)	881 ± 17 **B**	2.5	704 ± 66 **A α**	668 ± 42 **A α**	697 ± 97 **A α**	680 ± 95 A **α**
		5.0	683 ± 42 **A α**	690 ± 40 **A α**	691 ± 56 **A α**	701 ± 67 **A α**
mDP	5.56 ± 0.16 **A**	2.5	5.68 ± 0.38 **A α**	5.29 ± 0.29 **A α**	5.48 ± 0.14 **A α**	5.41 ± 0.16 **A α**
		5.0	5.46 ± 0.29 **A α**	5.31 ± 0.22 **A α**	5.46 ± 0.13 **A α**	5.08 ± 0.39 **A α**
% PD	15.6 ± 0.3 **A**	2.5	14.9 ± 0.3 **A α**	14.7 ± 0.1 **A α**	15.2 ± 0.4 **A α**	15.0 ± 0.3 **A α**
		5.0	14.9 ± 0.1 **A α**	14.8 ± 0.1 **A α**	15.2 ± 0.3 **A α**	14.8 ± 0.3 **A α**
% GAL	4.50 ± 0.34 **A**	2.5	4.30 ± 0.10 **A α**	4.20 ± 0.09 **A α**	4.21 ± 0.06 **A α**	4.36 ± 0.22 **A α**
		5.0	4.24 ± 0.09 **A α**	4.28 ± 0.21 **A α**	4.11 ± 0.15 **A α**	4.11 ± 0.13 **A α**

Results are expressed as mean ± standard deviation of three replicates. Different letters in a row indicate the existence of statistical difference ($p < 0.05$). First row (capital letters) indicates the influence of the PER of the staves. Second row (Greek letters) indicates the influence of the oxygen dose. TA: Total anthocyanins; PVPP Index (%): the percentage of anthocyanins combined with flavanols; TPI: total phenolic index; PA: Proantocyanidins; mDP: Mean degree of polymerisation; % PD: Percentage of prodelfinidins; % GAL: Percentage of galloylation

These results agree with previous published data (De Llaudy *et al.*, 2006; Kontoudakis *et al.*, 2011).

Supplementation with staves also seems to exert an effect on the total anthocyanin concentration and the PVPP Index. In short, the higher the PER the lower the anthocyanin concentration and the greater the PVPP index. These results suggest that the presence of ellagitannins released from the staves favours the combination of anthocyanins with flavanols. This is in agreement with the results from García-Estévez *et al.* (2017), who reported that supplementation of a model wine solution with oenological tannins, mainly composed of ellagitannins and proanthocyanidins, favours the formation of A-type and B-type vitisins and flavanol-anthocyanin compounds obtained by direct condensation.

Table 2 also shows the tannin concentration and some related parameters of the original wine and the different wines obtained after applying the different MOX conditions. As expected, the total phenolic index (TPI) and the proanthocyanidin concentration tended to decrease over time in all of the MOX wines, probably as a result of the precipitation of large polymers that took place during the three months that the experiment lasted. Similar results have been previously described for wines treated with micro-oxygenation (De Llaudy *et al.*, 2006; González-del Pozo *et al.*, 2010). However, the differences observed in TPI were not as great as in the case of proanthocyanidins, especially in the wines supplemented with staves of medium and high PER. This is probably because of the dissolution of ellagitannins and other phenolic compounds from the wood staves. In fact, it can be seen that the TPI tends to be higher in those wines supplemented with staves than in the control wine, and that the higher the PER of the staves, the higher the TPI tends to be, although the differences are not always statistically significant.

No significant differences were found in the mean degree of polymerisation (mDP), the percentage of prodelphinidins (% PD) or the percentage of galloylation (% GAL). The lack of differences in % PD and % GAL can be considered logical since these parameters are conditioned by the initial wine composition. However, in the case of the mDP these results might be considered somewhat surprising, because it was thought that MOX would induce the polymerisation of proanthocyaninidins, and mDP was therefore expected to increase with this treatment.

Nevertheless, the fact that phloroglucinolisis, the analytical procedure used for determining mDP, has some limitations should be taken into account. It is generally considered suitable for analysing

native condensed tannins from plants, but not for analysing condensed tannins in advanced or oxidised forms. In fact, this procedure cannot cleave certain interflavanic links such as A-type bonds, bonds involving anthocyanin or those involving ethyl bridges (Foo *et al.*, 2000; Zeng, 2015). Other authors have also been unable to find micro-oxygenation causing an increase in mDP (Atanasova *et al.*, 2002; Kontoudakis *et al.*, 2011).

3. Ellagitannins

Table 3 shows the ellagitannin content of the different wines. As expected, no ellagitannins were found in the control wine since it had not been in contact with oak staves. In contrast, they were detected in all the wines supplemented with staves. Castalagin was the major ellagitannin (around 75 % of total ellagitannins) in all the samples. The data also show that the higher the PER of the staves, the higher the ellagitannin content of the wine, which confirms that the Oakscan system efficiently classifies the staves according to how rich they are in ellagitannins. Other authors have also detected a reliable relationship between ellagitannins released from barrels, staves or oak chips and the PER classification of the wood using the Oakscan system (Michel *et al.*, 2010; Michel *et al.*, 2013; Navarro *et al.*, 2016b.

The different ellagitannin content also explains some of the results concerning wine colour discussed above. It has been reported that ellagitannins can enhance the colour of anthocyanins because of their effect as copigments (Vignault *et al.*, 2019; Gombau *et al.*, 2019), and that they can also directly consume oxygen and then protect the wine colour against oxidation (Pascual *et al.*, 2017; Vignault *et al.*, 2018). In addition, the presence of ellagitannins can favour the formation of new pigments (Vivas and Glories, 1996; García-Estévez *et al.*, 2017) that increase colour intensity and stability (Bakker and Timberlake, 1997; He *et al.*, 2012). Consequently, supplementation with staves during MOX seems to exert a positive effect on wine colour, most likely because they release ellagitannins.

4. Volatile substances released by oak wood

Table 4 shows the concentrations of the volatile substances released by the oak wood into the different wines. As mentioned earlier, the different volatile substances released from oak staves were grouped into four families (furanic compounds, vanillin, β-methyl-γ-octalactones and volatile phenols) in order to facilitate the discussion of the results.

As expected, the levels of furanic compounds were very low in the control wine and clearly increased in the presence of staves. These compounds originate from carbohydrates and nitrogen compounds by means of the Maillard reaction, and for that reason their concentration in wines which have had no contact with oak wood is very small.

TABLE 3. Influence of the micro-oxygenation dose and supplementation with oak staves of different potential ellagitannin release (PER) on ellagitannin content.

Compound (mg/L)	Oxygen dose (mg O_2/L.month)	Control	Low PER	Medium PER	High PER
Vescalagin	2.5	n.d.	0.04 ± 0.02 **A α**	0.13 ± 0.03 **B α**	0.14 ± 0.02 **B β**
	5.0	n.d.	0.03 ± 0.01 **A α**	0.08 ± 0.01 **B α**	0.18 ± 0.01 **C α**
Castalagin	2.5	n.d.	0.27 ± 0.03 **A α**	0.74 ± 0.06 **B α**	1.15 ± 0.12 **C β**
	5.0	n.d.	0.23 ± 0.01 **A α**	0.68 ± 0.11 **B α**	1.34 ± 0.09 **C α**
Grandinin	2.5	n.d.	n.d.	0.13 ± 0.02 **B β**	0.12 ± 0.01 **B β**
	5.0	n.d.	n.d.	0.08 ± 0.01 **B α**	0.11 ± 0.03 **B α**
Roburin E	2.5	n.d.	n.d.	0.13 ± 0.02 **B β**	0.12 ± 0.02 **B β**
	5.0	n.d.	n.d.	0.08 ± 0.01 **B α**	0.11 ± 0.03 **B α**
Total Ellagitannins	2.5	n.d.	0.31 ± 0.04 **A α**	1.13 ± 0.12 **B α**	1.53 ± 0.13 C **α**
	5.0	n.d.	0.26 ± 0.01 **A α**	0.92 ± 0.12 **B α**	1.74 ± 0.12 **C α**

Results are expressed as mean ± standard deviation of three replicates. Different letters in a row indicate the existence of statistical difference ($p < 0.05$). First row (capital letters) indicates the influence of the PER of the staves. Second row (Greek letters) indicates the influence of the oxygen dose.

TABLE 4. Influence of the micro-oxygenation dose and supplementation with oak staves of different potential ellagitannin release (PER) on the volatile substances released by wood.

Compound (mg/L)	Oxygen dose (mg O_2/L.month)	Control	Low PER	Medium PER	High PER
TF	2.5	142 ± 10 **A α**	1019 ± 74 **B β**	2532 ± 276 **C β**	2871 ± 403 **C β**
	5.0	144 ± 18 **A α**	660 ± 37 **B α**	1498 ± 176 **C α**	1234 ± 159 **C α**
t-BMGO	2.5	n.d.	115 ± 20 **B α**	35 ± 4 **A α**	43 ± 4 **A α**
	5.0	n.d.	118 ± 13 **B α**	37 ± 6 **A α**	37 ± 10 **A α**
c-BMGO	2.5	n.d.	190 ± 38 **B α**	137 ± 21 **B α**	48 ± 6 **A α**
	5.0	n.d.	121 ± 21 **C α**	143 ± 28 **B α**	40 ± 8 **A α**
Total BMGO	2.5	n.d.	304 ± 58 **C α**	171 ± 24 **B α**	91 ± 7 **A α**
	5.0	n.d.	313 ± 32 **C α**	180 ± 33 **B α**	77 ± 18 **A α**
Vanillin	2.5	n.d.	467 ± 84 **A α**	449 ± 86 **A α**	412 ± 50 A **α**
	5.0	n.d.	536 ± 43 **B α**	591 ± 175 **B α**	322 ± 40 **A α**
TVP	2.5	326 ± 61 **A α**	597 ± 49 **B α**	1219 ± 244 **C α**	1333 ± 44 C **α**
	5.0	385 ± 31 **A α**	591 ± 69 **B α**	1052 ± 242 **C α**	1043 ± 264 **C α**

Results are expressed as mean ± standard deviation of three replicates. Different letters in a row indicate the existence of statistical difference ($p < 0.05$). First row (capital letters) indicates the influence of the PER of the staves. Second row (Greek letters) indicates the influence of the oxygen dose. TF: Total Furanic Compounds; t-BMGO: trans-β-methyl-γ-octalactone; c-BMGO: cis-β-methyl-γ-octalactone; Total BMGO: Total β-methyl-γ-octalactones; TVP: Total Volatile Phenols.

However, they are formed from the pyrolysis of carbohydrates during oak wood toasting, and so the wines in contact with staves had higher concentrations of these compounds (Navarro *et al.*, 2018; Robinson *et al.*, 2014; Zamora, 2019). In addition, it seems that the PER of the staves also plays an important role as regards the concentration of total furanic compounds (TF) in the wines, since those supplemented with medium or high PER have significantly higher levels than those supplemented with low-PER staves.

MOX also seems to exert a clear effect on the TF content, since all the wines supplemented with staves and treated with the high dose of oxygen had significantly lower concentrations of these compounds than the corresponding wines treated with the low dose. It would seem, therefore, that oxygen caused a decrease in the TF content. Similar results have been previously reported (Ortega-Heras *et al.*, 2008). However, the role of TFs in wine aroma does not seem to be of great importance, because they are usually found at levels below their perception threshold (Navarro *et al.*, 2018). Nevertheless, it has been reported that furfural is a precursor of furfurylthiol, an interesting volatile substance with a very pleasant coffee aroma (Tominaga *et al.*, 2000) and therefore its presence cannot be neglected.

Unsurprisingly, the content of total β-methyl-γ-octalactones (BMGO) in the control wine was below the detection limit of the analytical method, whereas all the wines supplemented with staves contained substantial concentrations of these substances. MOX does not appear to have any effect on BMGOs or any of their isomers, since no significant differences were detected. Nevertheless, the BMGO content of the wines changes substantially depending on the PER of the staves. Specifically, the lower the PER of the staves, the higher the BMGO concentration. This is very interesting, since wines supplemented with low-PER staves have around 75 % more BMGO content than those supplemented with medium-PER staves, and around 250 % more than those supplemented with low-PER staves. This effect was observed in both BMGO isomers, but was more marked for the isomer with the lowest perception threshold (Abbott *et al.*, 1995) (i.e., the *trans* isomer (*t*-BMGO)) than for the *cis* isomer (*c*-BMGO). The differences are so big that the changes in sensory impact (coconut notes) can be very obvious (Zamora, 2019).

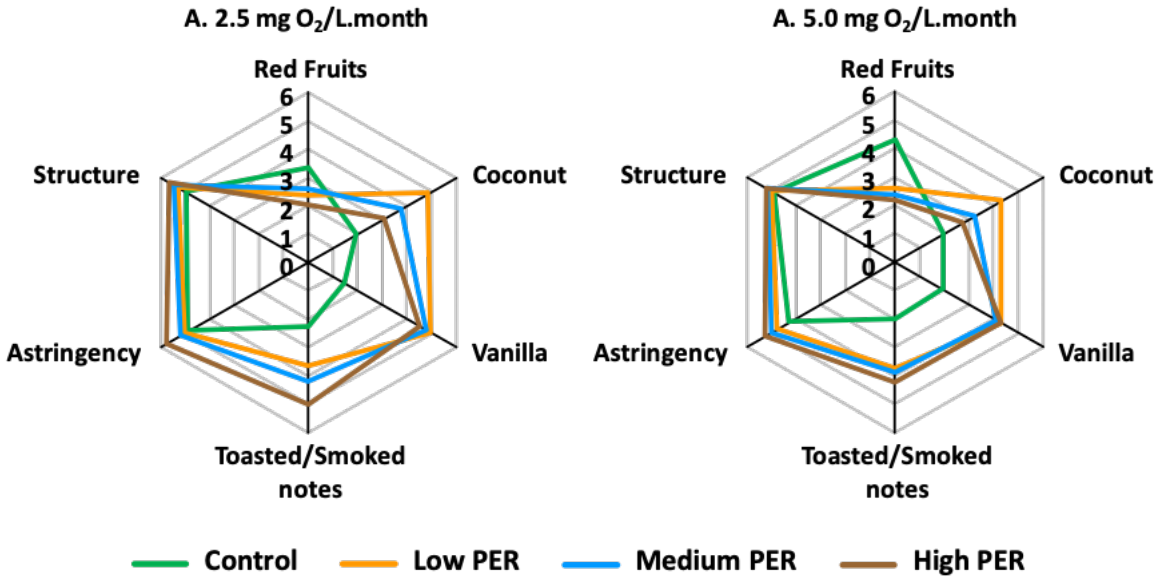

FIGURE 2. Influence of the micro-oxygenation dose and supplementation with oak staves of different potential ellagitannin release (PER) on the sensory perception of the wines.

As might be expected, the vanillin concentration of the control wine was below the detection limit, since this wine was not in contact with oak staves. In contrast, all the wines supplemented with staves contained substantial concentrations of this volatile substance. However, in this case, no clear trend was observed due to neither the effect of the MOX treatment nor the PER of the staves. What was observed was that the levels of vanillin were significantly lower in the case of wine supplemented with high-PER staves and subjected to the high dose of oxygen. All in all, the levels of vanillin do not appear to be substantially affected by MOX or by the PER of the staves.

The levels of total volatile phenols (TVP) were relatively low in the control wine and clearly increased with the presence of staves. These results are very logical, since some volatile phenols originate from the microbiological decarboxylation of coumaric acids (Chatonnet *et al.*, 1992), whereas other volatile phenols are mainly produced from lignin during barrel toasting (Chira and Teissedre, 2013; Zamora, 2019).

MOX treatment does not seem to have any effect on phenol levels since there is no clear trend in connection with the oxygen dose. However, it appears that the PER of the staves exerts a clear effect on the TVP concentration of the wines. Specifically, wines supplemented with medium- and high-PER staves had significantly higher levels of TVP than wines supplemented with low-PER staves.

5. Sensory analysis

Figure 2 comprises two spider web charts to illustrate the results obtained by sensory analysis. Figure 2A compares all the wines treated with the low dose of oxygen. Generally speaking, the astringency, structure and smoked notes were lowest in the control wine and tended to increase in the wines supplemented with staves, with the values of these sensory attributes being greater when the PER of the staves was higher. In contrast, the intensity of red fruits was maximal in the control wine and tended to decrease in the wines supplemented with staves, with this decrease being more pronounced when the PER of the staves was higher. Coconut perception was minimal in the control wine and increased considerably in the wines supplemented with staves, with the intensity of this perception being clearly influenced by the PER of the staves. Specifically, the lower the PER of the staves, the higher the perception of coconut. No differences could be appreciated in vanilla intensity.

Figure 2B compares all the wines treated with the high dose of oxygen. Overall this spider web chart shows a trend similar to the previous one, although the differences are not so clear.

The results of the sensory analysis are very much in line with the analytical results discussed earlier. The perception of astringency and structure was greater in the wines when the PER of the staves was higher, which is in agreement with the concentration of ellagitannins released by the staves. In addition, the perception of coconut was higher when the PER of the staves was lower, which is in agreement with the concentration of BMGO released by the staves. Finally, the perception of smoked notes was greater when the PER of the staves was higher, which is in agreement with the concentrations of TVP and TFC released by the staves.

CONCLUSIONS

This work confirms that supplementation with oak staves during micro-oxygenation treatment is a useful tool for improving the intensity and stability of the colour and aromatic complexity of red wines. It also confirms that the classification of oak staves using the Oakscan system enables staves to be selected according to their richness in ellagitannins, which allows producers choose the contribution from ellagitannins that they want for their wine much more precisely. However, the main conclusion is that this non-invasive measurement method based on infrared spectrometry can also select oak staves according to their potential release of different volatile substances. More specifically, the lower the PER of the staves the higher the release of β-methyl-γ-octalactones (coconut notes) and the lower the release of volatile phenols (smoked notes) and furanic compounds (toasted nut notes). Consequently, by selecting the PER of the staves, winemakers can modulate not only the structure of their wines, but also their aromatic profile.

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