Influence of the micro-oxygenation dose and supplementation with oak staves of different potential of ellagitannin release on wine color and composition

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Abstract. Aliquots of a wine of Merlot were micro-oxygenated at two doses of oxygen (2.5 and 5.0 mg of O_2/L.month) in the presence or not of oak staves of different potential ellagitannin release (PER) for three months. In general, micro-oxygenation increased the color intensity and stability probably because favor the formation of new pigments. The presence of staves increased the total phenolic index and the ellagitannin concentration, and this effect was higher when greater was the PER of the staves. Finally, the dose of microoxygenation only affects the concentration of total furanic compounds whereas the PER of the staves seems to determine the concentration of furanic compounds, volatile phenols and β-methyl-γ-octolactones.

1. Introduction

Wine aging in oak barrels is a complex process through which the wine gains complexity and stability. Oak wood releases volatile substances and phenolic compounds that improve their aromatic quality and also their texture sensations. All these volatile and non-volatile substances are released from oak wood into wine during barrel aging and the amount and proportion of them will depend on multiple factors such as the botanical and geographical origin of the oak, the seasoning technique, the degree of toasting and the number of times the barrel was previously used [1,2]. In addition, aging in oak barrels allows a moderate micro-oxygenation [3] that changes the wine phenolic composition which involves color stabilization and astringency reduction [4,5].

However, oak aging is an expensive process. For that reason, the use of oak alternatives coupled with micro-oxygenation is widely used to reproduce barrel aging more economically and quickly. It has also recently proposed a device using near-infrared spectroscopy (NIRS), the Oakscan system [6], to non-invasively determine the potential polyphenol index in wood. This procedure enables the classification of wood staves in function of their potential ellagitannin release (PER), making possible the selection of barrels or other wood alternatives according with a new criterion.

Therefore, the objective of this research was to study how the dosage of oxygen and supplementation with oak staves of different PER during three months of micro-oxygenation influences the color and composition of a red wine.

2. Materials and methods

2.1. Experimental design

Around 4000 L of a Merlot wine from the 2015 vintage of the AOC Tarragona were distributed in 24 stainless steel tanks of 165 L of capacity (Height: 2.5 m; Diameter: 0.30 m) equipped with a ceramic diffuser. Argon was used during the wine-racking process to ensure that the wine received oxygen only from the micro-oxygenation. Groups of 6 tanks were supplemented with French oak staves of low, medium and high PER while other 6 tanks were considered as controls. All staves groups only differ by their PER (same forest, maturation and toasting). 3 tanks of each group were micro-oxygenated at a low oxygen dose (2.5 ml/L.month) whereas other 3 tanks were treated with a high dose (5.0 ml/L.month) for three months and were kept at a temperature of $16 \pm 2\,^{\circ}$C.

2.2. Chemical analyses

The color intensity (CI), total phenolic index, total anthocyanins and PVPP Index were estimated using the methods described by Glories (1984) [7]. The CIELab coordinates, lightness (L*), chroma (C*), hue (h*), red-greenness (a*), and yellow-blueness (b*), were determined according to the method used by Ayala et al. (1997) [8] and data processing was performed with MSCV software (Ayala et al., 2001) [9].

The proanthocyanidins of the wines and their mean degree of polymerization (mDP) were analyzed by HPLC-DAD after acid depolymerization in the presence

Table 1. Color and phenolic compound composition.

Parameter	Original wine	O_2 dose	CONTROL	Low PER	Medium PER	High PER
CI	15.1 ± 0.0	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 ± 0.2 **A** β	14.2 ± 0.5 **A** α	14.2 ± 0.7 **A** α	14.9 ± 0.3 **A** β
*L**	42.1 ± 0.1	2.5	44.5 ± 0.6 **A** β	45.4 ± 0.9 **A** α	44.1 ± 0.6 **A** α	45.0 ± 0.9 **A** β
		5.0	43.1 ± 0.6 **A** α	43.9 ± 0.9 **A** α	43.3 ± 1.5 **A** α	42.2 ± 0.1 **A** α
*C**	62.2 ± 0.2	2.5	57.7 ± 0.4 **A** α	58.0 ± 0.7 **A** α	58.8 ± 0.5 **A** α	58.5 ± 0.4 **A** α
		5.0	58.9 ± 0.2 **A** β	58.5 ± 0.4 **A** α	58.7 ± 0.3 **A** α	59.2 ± 0.0 **B** β
h*	13.3 ± 0.1	2.5	15.1 ± 0.7 **A** α	14.4 ± 0.9 **A** α	16.2 ± 1.1 **A** α	15.0 ± 1.6 **A** α
		5.0	20.2 ± 0.7 **A** β	19.3 ± 0.2 **A** β	20.8 ± 1.0 **A** β	19.9 ± 0.4 **A** β
TA (mg/L)	574 ± 17	2.5	493 ± 15 **B** β	466 ± 18 **AB** α	444 ± 7 **A** α	437 ± 13 **A** β
		5.0	455 ± 11 **B** α	438 ± 27 **AB** α	425 ± 23 **AB** α	413 ± 7 **A** α
PVP P Index (%)	25.1 ± 4.3	2.5	47.7 ± 1.8 **A** α	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** β	52.4 ± 2.0 **A** α	58.8 ± 2.9 **B** β	60.1 ± 2.6 **B** β
TPI	65.3 ± 0.1	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	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	5.6 ± 0.2	2.5	5.7 ± 0.4 **A** α	5.3 ± 0.3 **A** α	5.5 ± 0.1 **A** α	5.4 ± 0.2 **A** α
		5.0	5.5 ± 0.3 **A** α	5.3 ± 0.2 **A** α	5.5 ± 0.1 **A** α	5.1 ± 0.4 **A** α

Results are expressed as mean ± standard deviation of three replicates. Different letters indicate a statistical difference ($p < 0.05$). Roman capital letters are used to compare between the wines supplemented or not oak chips of different PER. Greek letters are used to compare the influence of the different oxygen dose.

of an excess of phloroglucinol according with the method described by Kennedy and Jones (2001) [10].

The ellagitannins were analyzed by HPLC [11]. The ellagitannins were identified by matching the retention time and spectral data (DADUV–vis and MS/MS) with those of authentic standards.

Volatile compounds released from the oak wood were analyzed by GC/MS according with the method described by Ibartz et al. (2006).

3. Results and discussion

3.1. Color and phenolic compounds

Table 1 shows the results corresponding to the color and phenolic compound composition of the wines.

As it was expected, the color was significant more intense (higher CI and C*, lower L*) and the hue (h*) was more evolved when the oxygen dose was higher. However, no significant differences were found in color parameters in function of the presence or not of staves of different PER.

Total anthocyanins (TA) tended to decrease and the PVPP index to increase when the oxygen dose was higher. These results seem to indicate that micro-oxygenation increase the formation of new pigments, contributing in this way to a more intense and stable color.

The presence of staves, especially when the PER was higher, originated wines with lower total anthocyanin concentration and higher PVPP Index. This data suggest that the presence of ellagitannins released by oak staves (data confirmed by the results presented below) favor the formation of new pigments (probably flavanol-ethyl-anthocyanin).

Neither micro-oxygenation nor the presence of staves of any PER caused significant differences in the concentration of proanthocyanidins or in their mDP. However, the TPI value tended to increase when the PER of the staves was higher confirming that the higher the PER of the oak staves the higher the release of phenolic compounds.

3.2. Ellagitannins

Table 2 shows the results corresponding to the ellagitannin concentration of the different wines.

The results are very clear and confirm that the higher the PER the higher the ellagitannin concentration. These differences were found in all the analyzed ellagitannins. Consequently, it can be asserted that the Oakscan system really allows classifying the staves according to their potential ellagitannin release capacity.

On the other hand, micro-oxygenation does not seem to exert any effect on the concentration of ellagitannins.

3.3. Volatile substances released by oak wood

Table 3 shows the results corresponding to the main volatile substances released by oak wood.

In general, micro-oxygenation, regardless of the oxygen dose, does not affect the concentration of β-methyl-γ-octolactones (BMGO), vanillin or total volatile phenols (TVP). However, it seems to exert an effect on the total furanic compounds (TF) because their concentration is significantly lower in wines treated with the high dose of oxygen.

In contrast, the PER of the staves seems to exert a clear influence on the concentration of total furanic compounds, total volatile phenols and β-methyl-γ-octolactones. Specifically, the higher is the PER the higher is the concentration of total furanic compounds, total volatile phenols and the lower is the concentration of β-methyl-γ-octolactones, especially of the more intense *cis* isomer. In contrast the PER of the staves has not an influence of the vanillin concentration.

4. Conclusions

It can be concluded that the contact of wine with staves during micro-oxygenation really enrich the wine in ellagitannins and this enrichment is really higher when greater is the PER of the staves. This data confirms that Oakscan system really allows classifying the staves according to their potential ellagitannin release capacity.

Moreover it seems that staves with different PER also exert a different effect on the wine aromatization because when the higher is the PER the higher is the release of furanic compounds and volatile phenols. In contrast, when the higher is the PER the lower is the release of β-methyl-γ-octolactones, especially of the *cis* isomer. This data indicates that the selection of the PER of the staves is a key point because it is very important for the final sensory impact on the wine.

Specifically, low PER staves will provide mainly coconut notes (high BMGO concentration, especially the *cis* isomer), very few smoky/toasted notes (low TF and VF concentration) and a slight impact on wine mouthfeel (low ellagitannin concentration). In contrast, high PER staves will provide mainly smoked/toasted notes (high TF and VF concentration), very few notes of coconut (low BMGO concentration, especially the *cis* isomer) and a high impact on wine mouthfeel (high ellagitannin concentration). Further studies are needed to deep in the knowledge of the impact of the staves of different PER on the chemical composition and sensory quality of wines.

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Table 2. Ellagitannins.

Compound	O_2 dose	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
(mg/L)	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
(mg/L)	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
(mg/L)	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
(mg/L)	5.0	n.d.	n.d	0.08 ± 0.01 **B** α	0.11 ± 0.03 **B** α
Total Ellagitannin	2.5	n.d.	0.31 ± 0.04 **A** α	1.13 ± 0.12 **B** α	1.53 ± 0.13 **C** α
(mg/L)	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 indicate a statistical difference ($p < 0.05$). Roman capital letters are used to compare between the wines supplemented or not oak chips of different PER. Greek letters are used to compare the influence of the different oxygen dose.

Table 3. Volatile compounds released by oak wood.

Compound	O_2 dose	CONTROL	Low PER	Medium PER	High PER
TF (mg/L)	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
(mg/L)	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
(mg/L)	5.0	n.d.	194 ± 21 **C** α	143 ± 28 **B** α	40 ± 8 **A** α
Ratio	2.5	n.d.	1.7 ± 0.1 **B** α	3.9 ± 0.3 **C** α	1.1 ± 0.2 **A** α
cis/trans	5.0	n.d.	1.6 ± 0.1 **B** α	3.8 ± 0.3 **C** α	1.1 ± 0.1 **A** α
Total BMGO	2.5	n.d.	304 ± 58 **C** α	171 ± 24 **B** α	91 ± 7 **A** α
(symg/L)	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
(µg/L)	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
(µg/L)	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 indicate a statistical difference ($p < 0.05$). Roman capital letters are used to compare between the wines supplemented or not oak chips of different PER. Greek letters are used to compare the influence of the different oxygen dose.

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