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Oak barrel maturation vs. micro-oxygenation: Effect on the formation of anthocyanin-derived pigments and wine colour

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ABSTRACT

The objective of this study was to check whether micro-oxygenation (MO) could mimic oak barrel ageing as regard the effect on wine colour. A red wine was submitted to micro-oxygenation for three months while another lot from the same wine was matured in oak barrels for three or six months. After these times, oak-matured and micro-oxygenated wines were bottled and analyzed six months later. The chromatic characteristics of these wines were also compared with those of a control wine that remained in a stainless steel tank all the time. Anthocyanins and anthocyanin-derived compounds were studied by LC–ESI-MS. Monomeric anthocyanins and other compounds including direct anthocyanin–flavanol adducts, ethyl-linked anthocyanin–flavanol compounds, and pyranoanthocyanins were detected. The application of MO for three months produced wines with a lower concentration of monomeric anthocyanins and a higher concentration of vitisin-related pigments than the control wine, the oak mature wines showing similar results than MO wines when aged for the same period of time. Differences were also observed in the chromatic characteristics, the micro-oxygenated and the oak matured wines showing a higher colour intensity than control wine. However, after six months in bottle differences were found between the micro-oxygenated wines and oak matured wines, the latter showing a more stable colour, probably due to the beneficial effects of compounds extracted from the wood (e.g. ellagitannins or wood aldehydes).

1. Introduction

Anthocyanins are the main compounds responsible for the colour of young wines. However, they are relatively unstable and tend to form new compounds during maturation and ageing, some of them more stable than genuine anthocyanins. These compounds include the products resulting from direct and acetaldehyde-mediated anthocyanin–tannin condensation reactions (Atanasova, Fulcrand, Le Guernevé, Cheynier, & Moutounet, 2002; Dallas, Ricardo da Silva, & Laureano, 1996; Fulcrand, Cameira dos Santos, Sarni Manchado, Cheynier, & Favre Bonvin, 1996; Fulcrand, Dueñas, Salas, & Cheynier, 2006; Remy, Fulcrand, Labarde, Cheynier, & Moutounet, 2000; Rivas-Gonzalo, Bravo-Haro, & Santos-Buelga, 1995), as well as the products originated from the C4/C5 cycloaddition reaction of anthocyanins with other molecules bearing a polarizable double bond, including pyruvic acid, 4-vinylphenols, vinylflavanols, acetaldehyde, etc., which conform the so called pyranoanthocyanins (Fulcrand, Benabdejalil, Rigaud, Cheynier, & Moutounet, 1997; Fulcrand et al., 1996; Rentzsch, Schwarz, & Winterhalter, 2007). Some of these reactions may be favoured by the presence of small quantities of oxygen or by the acetaldehyde produced by the effect of oxygen on ethanol. In this way, oxygen or reactive species seems to be involved in the formation of A type vitisins (Lee, Swinny, Asenstorfer, & Jones, 2004), while acetaldehyde seems to be involved in the formation of ethyl-linked anthocyanin and tannin adducts, B type vitisins, vinyl-flavanols and vinyl-pyranoanthocyanis (Es-Safi, Fulcrand, Cheynier, & Moutounet, 1999; Fulcrand, Doco, Es-Safi, Cheynier, & Moutounet, 1996; Morata, Calderón, González, Gómez-Cordoves, & Suárez, 2007; Pissarra et al., 2004; Saucier, Guerra, Pianet, Laguerre, & Glories, 1997; Timberlake & Bridle, 1996).

Small quantities of oxygen are usually present during oak maturation. Nevares and Del-Alamo (2008) stated that a barrel micro-oxygenation profile can be assumed to require a long ageing time during which the wine consumes practically all the oxygen it absorbs. These authors indicated that the natural rate of permeation of oxygen into new French oak barrels is between 1.66 ml l^{-1} $month^{-1}$ and 2.5 ml l^{-1} $month^{-1}$, but lower in American oak barrels. However it should not be forgotten that the age of the barrel will also affect the oxygen diffusion rate, the older the barrel, the slower the oxygen diffusion rate since most of the wood pores will be plugged with wine deposits.

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Micro-oxygenation (MO), which attempts to simulate in a tank the low uptake of oxygen that occurs in barrels, has become a very common practice. The technique involves treating a wine with well-controlled sub-saturation doses of oxygen over short periods of time. Nevertheless, the micro-oxygenation provides neither the flavours nor the ellagic tannins that the contact with the oak wood provides. Care should be taken to prevent an excess of oxygen, which can lead to the formation of large molecules of high molecular weight that are unable to stay in solution, causing the precipitation of polymeric material and leaving the wines with a reduced colour intensity.

Most of the studies on micro-oxygenation claim that the effect of this technique on wine colour can be compared to that which occurs during maturation in oak barrels (Atanasova, Fulcrand, Cheynier, & Moutounet, 2002; Castellari, Matricardi, Arfelli, & Amati, 2000; Celotti & Zucchetto, 2004; Parish, Wollan, & Paul, 2000; Cano-López, Pardo, López-Roca, & Gómez-Plaza, 2006; Du Toit, Lisjak, Marais, & du Toit, 2006; Cano-López, Pardo, López-Roca, & Gómez-Plaza, 2007; Perez-Magariño, Sanchez-Iglesias, Ortega-Heras, Gonzalez-Huerta, & Gonzalez-San Jose, 2007), although we have found no studies that actually compare both techniques. For this reason, we have studied the evolution of a wine's chromatic parameters during three months of MO, simultaneously ageing the same wine in American oak barrels for the same period of time. Since the age of the barrel influences the natural micro-oxygenation of the wines, both new and three years old barrels were used in this study.

MO periods longer than three months are not common in S.E. Spain, whereas it is not common for wines to spend less than six months in barrels. Due to this, we have also compared the three months MO wine with wines resulting after an ageing period of six months in new and old barrels. Wines were analyzed at the end of the ageing period (three and six months) and again six months after bottling.

2. Materials and methods

2.1. General

A red wine made from *Vitis vinifera* var. Monastrell was used for the experiment. When malolactic fermentation had finished, the wine was distributed into six 17,500 l tanks; three were used as control (C), and three were dispensed with oxygen doses of 3 ml l^{-1} $month^{-1}$. Another lot from the same wine was matured in new and used oak barrels during three months (three new and three years old French oak, medium toast barrels, Herfe, Spain). After this time, micro-oxygenated wines and part of the oak-matured wine were bottled. The remaining oak matured wine spent another three months in the barrel before being bottled. Wines were analyzed at the moment of bottling and analyzed again after six months in the bottle.

2.2. Colour determination of wine samples

Absorbance measurements were made in a Helios Alpha (Thermospectronic) with 0.2 cm path length glass cells. The samples were clean and contained no CO_2, after elimination by ultrasound and stirring.

Colour intensity (CI) and tint was calculated as described by Glories (1984). Other variables calculated were red, yellow and blue percentages, according to Glories (1984). Total phenols (OD280) were determined following the methods described by Ribéreau Gayon, Glories, Maujean, and Dubourdieu (1998). Determination of compounds resistant to SO_2 decolouration ($CDRSO_2$) were determined according to Levengood and Boulton (2004). HPLC analysis of wine phenolics were conducted according to Cano-López et al. (2006).

2.3. Identification and quantification of anthocyanins

The HPLC analyses were performed on a Waters 2690 liquid chromatograph (Waters, Milford, MA, USA), equipped with a Waters 996 diode array detector and a Lichrocart RP-18 column (Merck, Darmstadt, Germany), 25 × 0.4 cm, 5 μm particle size, using as the mobile phase water plus 4.5% formic acid (solvent A) and acetonitrile (solvent B) at a flow rate of 0.8 ml min^{-1}. Elution was performed with a gradient starting with 10% B to reach 14.5% B at 30 min, 15.2% B at 45 min, 18% B at 60 min, 25% B at 100 min and 25–100% B in 30 min. Chromatograms were recorded at 520 nm.

Compounds were identified by comparing their UV spectra recorded with the diode array detector and those reported in the literature. In addition, an HPLC–MS analysis was conducted to confirm each peak identity. An LC-MSD-Trap VL-01036 liquid chromatograph–ion trap mass detector (Agilent Technologies, Waldbronn, Germany) equipped with an electrospray ionization (ESI) system was used. Elution was performed with the HPLC analysis conditions detailed above. The heated capillary and voltage were maintained at 350 °C and 4 kV, respectively. Mass scans (MS) were measured from m/z 300 up to m/z 1100. Mass spectrometry data were acquired in the positive ionization mode.

Anthocyanins and anthocyanin-derived compounds were quantified at 520 nm as malvidin-3-glucoside, using malvidin-3-glucoside chloride as external standard (Extrasynthèse, Genay, France).

3. Results and discussion

3.1. General

Several studies have demonstrated that the application of the micro-oxygenation technique is beneficial for wine colour; indeed, one of the major claims of this technique, is that stabilizes wine colour similarly to oak barrel ageing (Cano-López et al., 2007, 2006; Perez-Magariño et al., 2007).

The results of the chromatographic analysis of the wines after three months of ageing under different conditions (tank, MO and barrel ageing) showed that the profile of MO wines clearly resembled that of barrel aged wines (especially those aged in new barrels), while the control wine clearly differed (Table 1). Anthocyanin monoglucosides (the monoglucosides of delphinidin, cyanidin, peonidin, petunidin and malvidin, together with their acetyl and coumaryl derivatives) barely changed in three months of tank storage (control wine), whereas they decreased when MO was applied and with oak ageing. MO and ageing in new barrels led to the largest decrease. This decrease can be attributed to condensation reactions and not to the degradation of red pigments since wine colour intensity increased during this period.

During these three months, ethyl-linked compounds (malvidin 3-glucoside-ethyl-dicatechin, and three isomers of malvidin-3-glucoside-ethyl-(epi)catechin as well as malvidin-3-coumaryl glucoside-ethyl-catechin) increased in the control wine in tank and in the wines aged in new barrels while decreased in MO wines and those aged in used barrels. These compounds are easily formed especially when oxygen is present, as stated previously. However, they are not very stable and tend to form new compounds through cleavage of the ethyl link (García-Puente Rivas, Alcalde-Eon, Santos-Buelga, Rivas-Gonzalo, & Escribano-Bailon, 2005). Decreases after few months in oak have been described previously (Alcalde-Eon, Escribano-Bailon, Santos-Buelga, & Rivas-Gonzalo, 2005).

Table 1
Effect of micro-oxygenation and oak barrel aging in the concentration of HPLC identified compounds in wines before bottling.

Identified compound	Control t0	Control3	MO3	NB3	UB3	NB6	UB6
Σ Monomeric anthocyanins (mg l^{-1})	252.3 ± 8.0	246.5 ± 3.7	178.7 ± 1.7	185.8 ± 2.1	215.1 ± 0.7	55.1 ± 1.7	101.5 ± 3.7
Σ Direct adducts (mg l^{-1})	2.4 ± 0.5	3.6 ± 1.7	1.6 ± 0.1	1.7 ± 0.1	1.5 ± 0.1	5.0 ± 0.2	2.6 ± 0.3
Σ Carboxypyranoanthocyanins (mg l^{-1})	8.5 ± 0.7	9.9 ± 0.3	10.5 ± 1.2	10.9 ± 0.2	11.0 ± 0.1	10.2 ± 0.4	9.6 ± 0.8
Σ Flavanylpyranoanthocyanins + vinylpyranoanthocyanins (mg l^{-1})	2.8 ± 0.1	4.5 ± 0.5	3.9 ± 0.4	4.2 ± 0.6	4.2 ± 0.4	2.8 ± 0.1	3.3 ± 0.1
Σ Ethyl-linked compounds (mg l^{-1})	7.8 ± 0.1	8.7 ± 0.3	6.5 ± 0.3	8.7 ± 0.2	6.7 ± 0.4	4.9 ± 0.1	4.7 ± 0.4
Polymeric peak (mg l^{-1})	8.8 ± 0.4	7.6 ± 0.2	9.9 ± 1.4	9.9 ± 1.6	8.2 ± 0.3	13.7 ± 1.1	10.7 ± 0.8

t0: Initial control wine, t3: control wine after three months of tank storage, NB3: wines aged in new barrels for three months, UB3: wines aged in used barrels for three months, MO3: micro-oxygenated wines for three months, NB6: wines aged in new barrels for six months, UB6 : wines aged in used barrels for six months.

Among carboxypyranoanthocyanins, the anthocyanin–pyruvic acid adducts detected in our samples (petunidin 3-glucoside pyruvate, malvidin 3-glucoside pyruvate (Vitisin A), malvidin 3-acetylglucoside pyruvate (acetilVit A), malvidin 3-coumarylglucoside pyruvate (CumarilVit A)) increased in all the samples, especially in the MO and oak aged wines. As regards vinylphenolpyroanthocyanins (malvidin-3-glucoside-4-vinyl-catechol (Pinotina A) and malvidin-3-glucoside-4-vinyl-phenol), and the flavanylpyranoanthocyanins (malvidin 3-glucoside-vinyl-(epi)catechin) detected in our samples, they increased during the three months in all the samples, including control wine. No effect of MO or barrel ageing was observed.

Two direct adducts, that is, two compounds whose mass spectra allowed their identification as malvidin 3-glucoside-(epi)catechin, were detected. They decreased with time in MO and oak aged.

A broad peak at the end of the chromatogram was observed. It absorbed at around 540 nm, indicating that it contained flavylium units, probably formed from polymerisation of the pigments present in earlier samples. Its concentration increased in oxygenated samples.

For those wines that aged up to six months in oak, and since the natural MO continued, monomeric anthocyanins kept decreasing whereas the polymeric peak kept increasing. The concentration of direct adducts increased after six months in new barrels. Alcalde-Eon et al. (2005) stated that the presence of ellagitannins could probably speed up the formation of these direct adducts. Carboxypyranoanthocyanins maintained their concentrations and flavanylpyranoanthocyanins fell slightly as did ethyl-linked compounds, probably due to a conversion into more stable polymerised compounds, as an increase in the area of the polymeric peak was detected.

As regards their chromatic characteristics (Table S1 in supplementary material), oxygenated wines showed higher colour intensity, especially MO wines and those aged in new barrels. The percentages of red colour was lower than that of the control wine but the percentages of yellow and blue were higher. Also, much higher was the colour due to pigments resistant to SO_2 decolouration. The main difference between the MO wine and those aged in barrels was the total phenol content (expressed as optical density at 280 nm), which decreased in the control wine and MO wine but increased in barrel aged wines due to the extraction of phenolic compounds from oak. It is well known that wines extract compounds from wood (phenolic acids, ellagitannis, etc.), which increases the total phenol content (Gómez-Cordoves, Gonzalez-San Jose, Junquera, & Estrella, 1995; Jindra & Gallander, 1987; Perez-Prieto et al., 2003).

3.2. Phenolic compounds and wine colour after six months in bottle

After six months in bottle (Table 2), the phenolic compounds that more clearly decreased (as compared with their respective wines before bottling) were monomeric anthocyanins, the sum of flavanyl and vinylpyranoanthocyanins and ethyl linked compounds. In wines that were previously aged six months in new barrels, also a decrease in direct adducts and carboxypyranoanthocyanins was observed. The polymeric peak increased in all the wines, the highest values being detected in MO wines.

As regard chromatic characteristics (Table S2), colour intensity decreased in MO wines and was maintained in barrel aged wines. The protective effect of some of the wood extracted compounds, mainly ellagitannins, and/or the formation of some newly detected coloured compounds, named oaklins, arising from the reaction between wine phenolic compounds and some wood aldehydes (Sousa, Mateus, Pérez-Alonso, Santos-Buelga, & De Freitas, 2005) could explain the higher colour intensity of these wines. Also the pigments resistant to SO_2 decolouration were lower in the MO wine than in barrel aged wines, although higher than in the control wine. Total phenol content decreased slightly in MO wines but was maintained in barrel aged wines.

A PPC analysis using the chromatographic and spectrophotometric data of the wines showed how MO wines were very similar to wines aged three months in barrels and how these three wines were different from control wines and those aged for six months. When a discriminant analysis was carried out (data not shown) and the discriminant functions were used to classify the micro-oxygenated wines, these were classified as wines aged in new barrels. However, micro-oxygenated wines and oak barrel aged wines evolve differently while in bottle. Colour evolved faster in micro-oxygenated wines, which showed a higher tint and percentage of yellow colour (See Figs. 1 and 2).

Table 2
Effect of micro-oxygenation and oak barrel aging in the concentration of HPLC identified compounds in wines after six months in bottle.

Identified compound	Control3+6	MO3 + 6	NB3 + 6	UB3 + 6	NB6 + 6	UB6 + 6
Σ Monomeric anthocyanins (mg l^{-1})	33.8 ± 1.9	18.7 ± 3.2	55.1 ± 2.6	42.6 ± 0.9	37.5 ± 0.8	37.6 ± 0.9
Σ Direct aducts (μg l^{-1})	2.6 ± 1.2	2.1 ± 0.8	3.1 ± 1.2	3.5 ± 1.2	3.5 ± 0.4	2.9 ± 0.2
ΣCarboxypyranoanthocyanins (mg l^{-1})	9.4 ± 1.3	13.3 ± 2.5	10.7 ± 3.5	12.1 ± 4.3	8.8 ± 0.7	8.0 ± 1.1
Σflavanylpyranoanthocyanins + Vinylpyranoanthocyanins (μg l^{-1})	2.1 ± 1.8	2.7 ± 0.4	2.6 ± 0.5	2.2 ± 0.6	1.1 ± 0.3	2.6 ± 0.6
Σ Ethyl-linked compounds (μg l^{-1})	2.2 ± 1.2	2.5 ± 8.1	4.6 ± 2.2	4.2 ± 2.9	3.8 ± 0.7	4.4 ± 0.3
Polymeric peak (mg l^{-1})	10.5 ± 0.4	14.0 ± 1.2	12.6 ± 0.8	11.7 ± 1.0	12.1 ± 0.8	12.6 ± 0.1

Control: wine aged in tank, NB: wines aged in new barrels, UB: wines aged in used barrels, MO: micro-oxygenated wines, 3: three months of aging time, 6: six months of aging time, 3 + 6: three months of aging time and six months of bottle storage, 6 + 6: six months of aging time and six months of bottle aging.

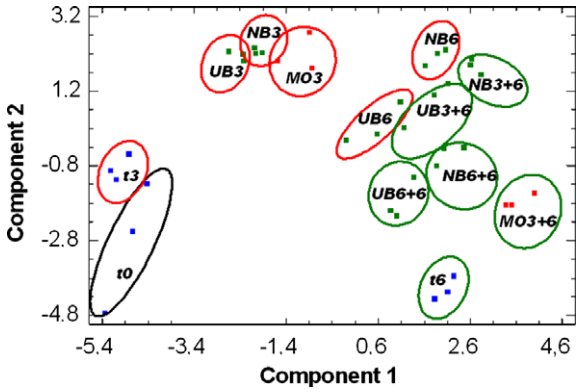

Fig. 1. Distribution of the wines in the two dimensional coordenate system defined by the first two principal components (t0: initial control wine, t3: control wine after three months of tank storage, t3 + 6: control wine after three months of tank storage and six months in bottle, NB: wines aged in new barrels, UB: wines aged in used barrels, MO: micro-oxygenated wines, 3: three months of storage time, 6: six months of aging, 3 + 6: six months of bottle aging, 6+6: six months of bottle aging.

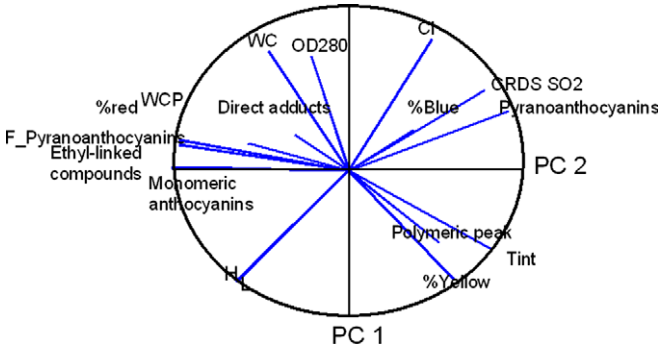

Fig. 2. Representation of the components weight in the principal component analysis.

4. Conclusion

Micro-oxygenation improves wine colour in a similar way as oak barrel ageing does, phenolic and chromatic characteristics of a three months micro-oxygenated wines being very similar to that of a three month oak aged wine. However, they do not evolve similarly during bottle ageing. After six months in the bottle, micro-oxygenated wines were chromatically different from wines aged in new barrels, showing higher percentage of yellow colour and tint, that is, a more evolved colour. Probably, the phenolic compounds extracted from the wood during barrel ageing (ellagitannins, phenolic acids and wood aldehydes) play an important role in protecting barrel-aged wine colour.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.foodchem.2009.06.018.

References

Alcalde-Eon, C., Escribano-Bailon, M. T., Santos-Buelga, C., & Rivas-Gonzalo, C. (2005). Changes in the detailed pigment composition of red wine during maturity and ageing. A comprehensive study. *Analityca Chimica Acta, 513*, 305–318.

Atanasova, V., Fulcrand, H., Cheynier, V., & Moutounet, M. (2002). Effect of oxygenation on polyphenol changes occurring in the course of wine-making. *Analytica Chimica Acta, 458*, 15–27.

Atanasova, V., Fulcrand, H., Le Guernevé, C., Cheynier, V., & Moutounet, M. (2002). Structure of a new dimeric acetaldehyde malvidin 3-glucoside condensation product. *Tetrahedron Letters, 43*, 6151–6153.

Cano-López, M., Pardo, F., López-Roca, J. M., & Gómez-Plaza, E. (2006). Effect of micro-oxygenation on anthocyanin and derived pigment content and chromatic characteristics of red wines. *American Journal of Enology and Viticulture, 57*, 325–331.

Cano-López, M., Pardo, F., López-Roca, J. M., & Gómez-Plaza, E. (2007). Chromatic characteristics and anthocyanin profile of a micro-oxygenated red wine after oak or bottle maturation. *European Food Research and Technology, 225*, 125–132.

Castellari, M., Matricardi, L., Arfelli, G., & Amati, A. (2000). Level of single bioactive phenolics in red wine as a function of the oxygen supplied during storage. *Food Chemistry, 69*, 61–67.

Celotti, E., & Zucchetto, M. (2004). Exemple de gestion raisonnee de la micro-oxygenation appliquee a un vin rouge. *Wine Internet Technical Journal, 14*, 1–9.

Dallas, C., Ricardo da Silva, J. M., & Laureano, O. (1996). Products formed in model wine solutions involving anthocyanins, procyanidin B2 and acetaldehyde. *Journal of Agriculture and Food Chemistry, 44*, 2402–2407.

Du Toit, W., Lisjak, K., Marais, J., & du Toit, M. (2006). The Effect of Micro-oxygenation on the phenolic composition, quality and aerobic wine-spoilage microorganisms of different South African red wines. *South African Journal for Enology and Viticulture, 27*, 57–67.

Es-Safi, N., Fulcrand, H., Cheynier, V., & Moutounet, M. (1999). Studies on the acetaldehyde-induced condensation of (−)-epicatechin and malvidin-3-glucoside in model solution systems. *Journal of Agriculture and Food Chemistry, 47*, 2096–2102.

Fulcrand, H., Benabdejalil, C., Rigaud, J., Cheynier, V., & Moutounet, M. (1997). A new class of wine pigments generated by reaction between pyruvic acid and grape anthocyanins. *Phytochemistry, 47*, 1401–1407.

Fulcrand, H., Cameira dos Santos, P., Sarni Manchado, P., Cheynier, V., & Favre Bonvin, J. (1996). Structure of new anthocyanin-derived wine pigments. *Journal Chemical Society PT, 1*(7), 735–739.

Fulcrand, H., Doco, T., Es-Safi, N., Cheynier, V., & Moutounet, M. (1996). Study of the acetaldehyde induced polymerisation of flavan-3-ols by liquid chromatography–ion spray mass spectrometry. *Journal of Chromatography, 752*, 85–91.

Fulcrand, H., Dueñas, M., Salas, E., & Cheynier, V. (2006). Phenolic reactions during winemaking and aging. *American Journal of Enology and Viticulture, 57*, 289–297.

García-Puente Rivas, E., Alcalde-Eon, C., Santos-Buelga, C., Rivas-Gonzalo, C., & Escribano-Bailon, M. T. (2005). Behaviour and characterization of the colour during red wine making and maturation. *Analytica Chimica Acta, 563*, 215–222.

Glories, Y. (1984). La coleur des vins rouges: 1 Partie "les equilibres des anthocyanes et des tanins". *Connaisance Vigne Vin, 18*, 195–217.

Gómez-Cordoves, C., Gonzalez-San Jose, M., Junquera, B., & Estrella, I. (1995). Correlation between flavonoids and color in red wines aged in wood. *American Journal of Enology and Viticulture, 46*, 295–298.

Jindra, J. A., & Gallander, J. F. (1987). Effect of American and French oak barrels on the phenolics composition and sensory quality of Seyval blanc wines. *American Journal of Enology and Viticulture, 38*, 133–138.

Lee, D., Swinny, E., Asenstorfer, R., & Jones, G. (2004). Factors affecting the formation of red wine pigments. In A. Waterhouse & J. A. Kennedy (Eds.), *Red wine color. Revealing the mysteries. ACS symposium series 886* (pp. 125–142). Washington: American Chemical Society.

Levengood, J., & Boulton, R. (2004). The variation in the color due to copigmentation in young Cabernet Sauvignon wines. In A. Waterhouse & J. A. Kennedy (Eds.), *Red wine color. Revealing the mysteries. ACS symposium series 886* (pp. 35–52). Washington: American Chemical Society.

Morata, A., Calderón, F., González, M. C., Gómez-Cordoves, M. C., & Suárez, J. A. (2007). Formation of the highly stable pyranoanthocyanins (Vitisina A and B) in red wines by the addition of pyruvic acid and acetaldehyde. *Food Chemistry, 100*, 1144–1152.

Nevares, I., & Del Alamo, M. (2008). Measurement of dissolved oxygen during red wines tank aging with chips and micro-oxygenation. *Analytica Chimica Acta, 621*, 68–78.

Parish, M., Wollan, D., & Paul, R. (2000). Micro-oxygenation. A review. *Australian Grapegrower and Winemaker, 438a*, 47–50.

Perez-Magariño, S., Sanchez-Iglesias, M., Ortega-Heras, M., Gonzalez-Huerta, C., & Gonzalez-San Jose, M. L. (2007). Colour stabilization of red wines by micro-oxygenation treatment before malolactic fermentation. *Food Chemistry, 101*, 881–893.

Perez-Prieto, L. J., De la Hera Orts, M. L., López-Roca, J. M., Fernández-Fernández, J. I., & Gómez-Plaza, E. (2003). Oak matured wines. Influence of the characteristics of the barrell on wine colour and sensory characteristics. *Journal of the Science of Food and Agriculture, 83*, 1445–1450.

Pissarra, J., Lourenco, S., González-Paramás, A. M., Mateus, N., Santos-Buelga, C., & De Freitas, V. (2004). Formation of new anthocyanin-alkyl/aryl-flavanol pigments in model solutions. *Analytica Chimica Acta, 513*, 215–216.

Remy, S., Fulcrand, H., Labarde, B., Cheynier, V., & Moutounet, M. (2000). First confirmation in red wine of products resulting from direct anthocyanin–tanin reactions. *Journal of the Science of Food and Agriculture, 80*, 745–751.

Rentzsch, M., Schwarz, M., & Winterhalter, P. (2007). Pyranoanthocyanins – An overview on structures, occurrence, and pathways of formation. *Trends in Food Science and Technology, 18*, 526–534.

Ribéreau Gayon, P., Glories, Y., Maujean, A., & Dubourdieu, D. (1998). *Traité d'Oenologie. 2. Chimie du vin. Stabilisation et traitements*. Paris: Dunod.

Rivas-Gonzalo, J., Bravo-Haro, S., & Santos-Buelga, C. (1995). Detection of compounds formed through the reaction of malvidin-3-monoglucoside and catechin in the presence of acetaldehyde. *Journal of Agriculture and Food Chemistry, 43*, 1444–1449.

Saucier, C., Guerra, C., Pianet, I., Laguerre, M., & Glories, Y. (1997). (+)Catechin-acetaldehyde condensation products in relation to wine-ageing. *Phytochemistry, 46*, 234–239.

Sousa, C., Mateus, N., Pérez-Alonso, J., Santos-Buelga, C., & De Freitas, V. (2005). Preliminary study of oaklins, a new class of brick-red catechinpyrylium pigments resulting from the reaction between catechin and wood aldehydes. *Journal of Agricultural and Food Chemistry, 53*, 9249–9256.

Timberlake, C. F., & Bridle, P. (1996). Interactions between anthocyanins, phenolic compounds, and acetaldehyde and their significance in red wines. *American Journal of Enology and Viticulture, 27*, 97–105.