

CHANGES IN COMPOSITION AND SENSORY QUALITY OF RED WINE AGED IN AMERICAN AND FRENCH OAK BARRELS

COMPARAISON DE LA COMPOSITION ET DES CARACTÈRES SENSORIELS D'UN VIN ROUGE ÉLEVÉ DANS DES BARRIQUES EN BOIS DE CHÊNES AMÉRICAIN ET FRANÇAIS

M. POMAR¹ and L.A. GONZALEZ-MENDOZA²

¹Instituto Canario Investigaciones Agrarias (ICIA),
Apto 60, La Laguna, Tenerife (Spain)

²Dpt. of Chemical Engineering, University of La Laguna,
Tenerife (Spain).

Summary : Red wine produced from Listán Negro and Negramoll grapes from the Canary Islands (Spain) was firstly aged in new American and French (Allier) oak barrels in order to measure composition and sensory changes during 21 months. Aging resulted in an increase in titratable and volatile acidity and a decrease in ethanol concentration with a greater evaporation in the American oak samples. Initially, there was also an increase in color density due to the polymerization of anthocyanins. Extraction of total phenols was greater in the French barrels.

Résumé : L'étude effectuée porte sur un vin rouge élaboré dans les Iles Canaries à partir des cépages Listán noir (90 p. cent) et Negramoll (10 p. cent), élevé neuf mois en barriques de 228 litres, soit en chêne américain, soit en chêne français. Les vins sont ensuite mis en bouteilles et conservé douze mois à une température de 13 - 18°C.

Les barriques en chêne américain (*Quercus alba*) ont été fabriquées à partir de bois scié et séché 22 mois. Le chêne français (*Quercus petraea*) a subi le même séchage que le bois américain, mais il a été fendu.

On a suivi, au cours de l'élevage en barriques et du vieillissement en bouteilles, l'évolution de certains constituants (éthanol, acidité titrable, acidité volatile, intensité et teinte, anthocyanes, indice de phénols totaux). Parallèlement aux déterminations analytiques, on a effectué une analyse sensorielle.

On a noté une nette diminution de la teneur en éthanol au cours du premier mois d'élevage en barrique ; la forte humidité de la région favorisant l'évaporation de cette substance, le phénomène est plus sensible dans le vin logé en barriques en chêne américain. L'écart constaté pourrait avoir pour origine le mode de fabrication des douelles. Les acidités titrable et volatile ont tendance à augmenter dans les vins en barriques ; cette augmentation étant particulièrement marquée au début de l'élevage. Cette observation est en accord avec les résultats d'autres chercheurs.

La valeur de l'indice de polyphénols totaux oscille en fonction des équilibres entre les composés phénoliques du bois et ceux des vins. L'indice de polyphénols totaux est légèrement plus faible dans les vins stockés en barriques fabriquées en chêne américain.

Nos observations sur l'évolution de l'intensité colorante confirment les données obtenues par ailleurs. Il en est de même en ce qui concerne la diminution des anthocyanes libres au cours de l'élevage et de l'augmentation des combinaisons anthocyanes - tanins.

Mots clés : Iles Canaries, vin rouge, analyse sensorielle.

Key words : Canary Island, red wine, sensory analysis.

INTRODUCTION

Chemical changes in wines stored in oak barrels depend primarily upon the grapes used during vinification (LASZLAVIK *et al.*, 1995), the ethanol concentration (SINGLETON and DRAPER, 1961), the wood surface in contact with a unit of beverage and the barrel age (ROUS and ALDERSON, 1983; WILKER and GALLANDER, 1988). Moreover, test results have

considered not only species, but also the forest site as an important variable affecting the maturation achieved with barrels from different sources (MILLER *et al.*, 1992). Another important influence on the properties of aging wines is the difference in coopering methods. The way of drying the freshly cut wood (PONTALLIER *et al.*, 1982; CHATONNET *et al.*, 1994), the use of steam versus an open fire for bending the staves and the level of toasting and charring the bar-

rel wood (GUYMON and CROWELL, 1968; CHATONNET *et al.*, 1989; REAZIN, 1981) have large effects on the extractives and flavor of the beverage being matured. However, research about the influence of the procedure to obtain the staves (split or sawn) on wine composition has been limited.

All the oaks used for cooperage are white oaks. In Europe, two species, *Quercus robur* and *Quercus petraea*, are exclusively used. In America, 45 p. cent of the oak suitable for cooperage is *Quercus alba*. In comparing materials extracted from oak wood, European was found to be richer in phenols, whereas the American had more odorants (SINGLETON, 1974) with a particular « coconutty » smell due to the oak lactone isomers. Nevertheless, the components of the different oak species are similar, differing only in concentrations.

In this study, the influence of oak species and barrel coopering methods on the chemical composition and sensory properties of aging wine was researched.

MATERIALS AND METHODS

I - MATERIAL

Red wine was produced commercially from a Canary Islands winery (Spain) by Tacoronte-Acentejo standard practices (POMAR *et al.*, 1994) from Listán Negro (90 p. cent) and Negramoll (10 p. cent) grapes. Tacoronte-Acentejo is a viticultural region situated on the northern slope of the island of Tenerife (Canary Islands, Spain).

Two French and 2 American 228-L new oak barrels were filled with the red wine. All the barrels were coopered by different methods. The stave wood was air-dried for at least 22 months and bent over a small fire, leaving the inside of these recipients lightly charred. Nevertheless, French oak wood was split, whereas the American was sawn to obtain the staves. The American barrels were coopered from oak wood grown

in Missouri (*Quercus alba*) and the French barrels from the Allier area of France (*Quercus petraea*).

The wine was aged in barrels for 9 months and then bottled into 750 mL bottles and stored for 12 months. Storage temperature ranged from 13 to 18°C.

At zero, one month and every three months of storage there after, two 750 mL samples from each barrel were removed for chemical analysis.

II - CHEMICAL ANALYSIS

Titrate acidity, ethanol, absorbance at 420 nm and 520 nm, color density and color hue were determined as described by AMERINE and OUGH (1980). Volatile acidity was analyzed by the method of García-Tena (GARCÍA BARCELÓ, 1976) and total polyphenols index by the procedure described by RUIZ (1994). Monomeric anthocyanins were quantified by the method of RIBÉREAU-GAYON and STONESTREET (1965) and polymeric anthocyanins were estimated as described by SOMERS and EVANS (1977).

III - SENSORY ANALYSIS

The sensory analysis has been developed by the sensory chart recommended by the O.I.V. This chart gives higher mark to better wine, taking consideration the visual phase, taste, smell, the pair taste-smell, and de total mark as an addition of the individual mark

RESULTS AND DISCUSSION

The results of the sensory analysis are shown in table 1 (french oak) and in table 2 (american oak). The sensory analysis has been the indicate of the procedure of vinification and aged, found that the American oak is better for short aged similar to bottles and the French oak for longer aged.

The ethanol content of the red wine significantly decreased during the first month of aging with losses of about 0,3 p. cent. This was mainly the result of the

TABLE I
Sensory analysis results for aged in french oak barrel, and then in bottles

Tableau I - Analyse sensorielle pendant l'élevage du vin dans des barriques en bois de chêne français, puis au cours du vieillissement en bouteilles

Sensory analysis/month	Élevage en barriques			Mise en bouteilles		
	3	6	9	12	15	21
Total	71,33	62,16	75,40	77,50	80,75	78,00
Visual phase	13,66	13,83	14,80	15,50	14,25	13,00
Smell	24,00	17,30	23,30	24,50	27,00	27,00
Taste	11,33	10,33	12,00	12,50	13,50	13,00
Taste-Smell	22,33	20,66	25,30	25,00	26,00	25,00

evaporative loss of ethanol and its diffusion through the staves, which are higher than that of water during storage. This is related to the high humidity of the Tacoronte-Acentejo region. If humidity is low the ethanol concentration in the residual beverage can rise, but if it is high a drop would be expected (VENTER and BAUMGARTEN, 1987). The ethanol content was also found to be higher in French oak-aged wine than in American barrels. This highly significant decrease

could be due to the different methods used to obtain the staves. With American oak the staves were sawn which caused a greater thickness impregnation inside the wood (RUIZ, 1994) than in split wood (French oak). The fiber saturation point (where free water ceases to be present, extraction stops and evaporation becomes primary) (SINGLETON, 1995) is then nearer to the outer American barrel surface and ethanol would have less difficulty in diffusing through the staves.

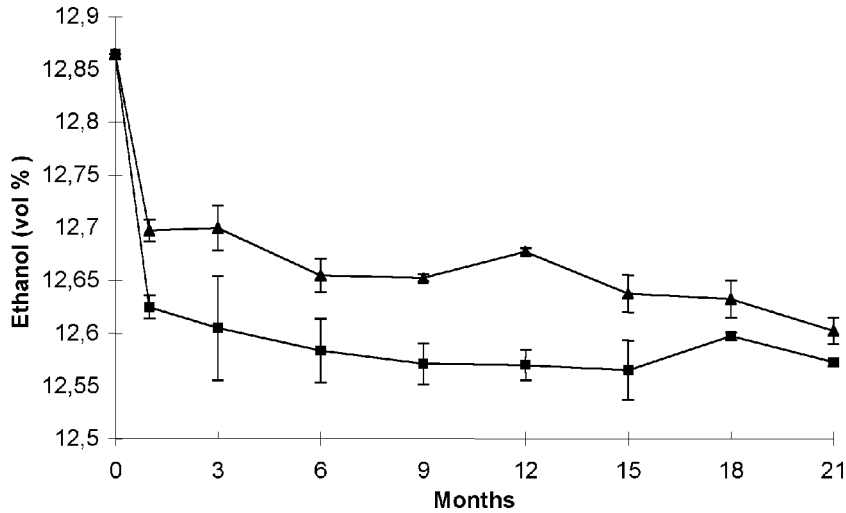


Fig. 1 - Ethanol content evolution during the aging of red wine in French (▲) and in American oak barrels (■).

Promedial values and standard deviations (n=4).

Fig. 1 - Évolution de l'éthanol au cours du vieillissement du vin rouge dans barriques de bois de chênes français (▲) et américain (■).

Valeurs moyennes et écart-type (n=4)

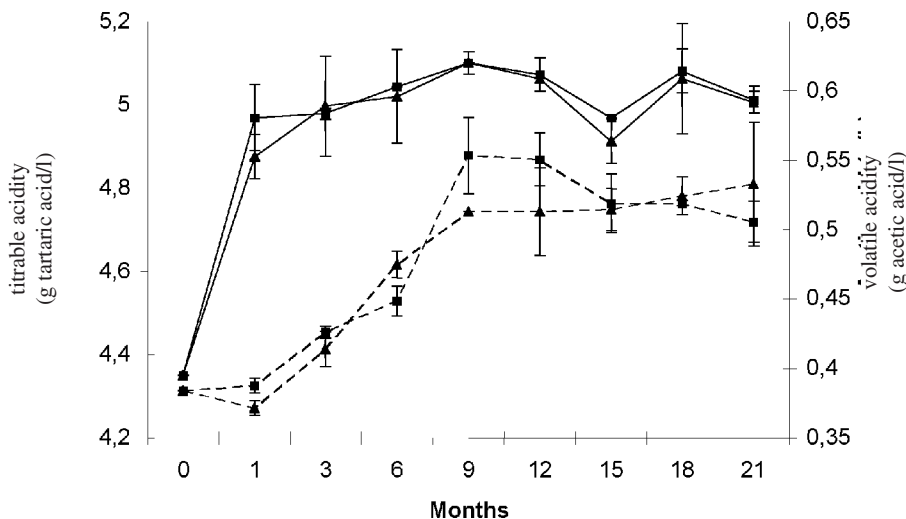


Fig. 2 - Evolution of titratable acidity (—) and volatile acidity (---) during the ageing of red wine in French (▲) and in American oak barrels (■).

Promedial values and standard deviations (n=4). Titratable acidity in tartaric acid (g/L) and volatile acidity in acetic acid (g/L).

Fig. 2 - Évolution de l'acidité titratable (—) et de l'acidité volatile (---) au cours du vieillissement du vin rouge dans des barriques en bois de chêne français (▲) et américaine (■).

Valeurs moyennes et écart-type (n=4). L'acidité titratable est exprimée en acide tartarique (g/L) et l'acidité volatile en acide acétique (g/L).

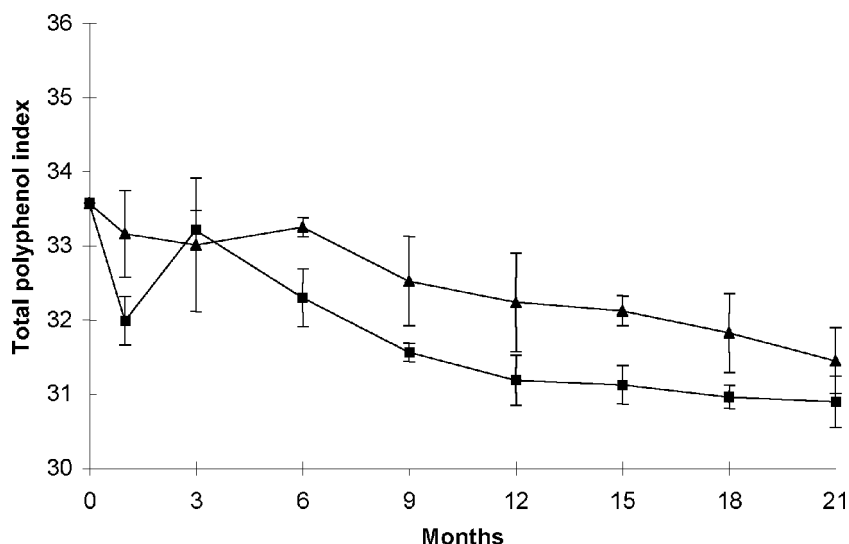


Fig. 3. -Total polyphenols index evolution during the aging of red wine in French (▲) and in American oak barrels (■).

Promedial values and standard deviations (n=4).

Fig. 3 - Évolution de l'index de polyphénols totaux au cours du vieillissement du vin rouge dans des barriques EN bois de chêne français (▲) et américain (■).

Valeurs moyennes et écart-type (n=4).

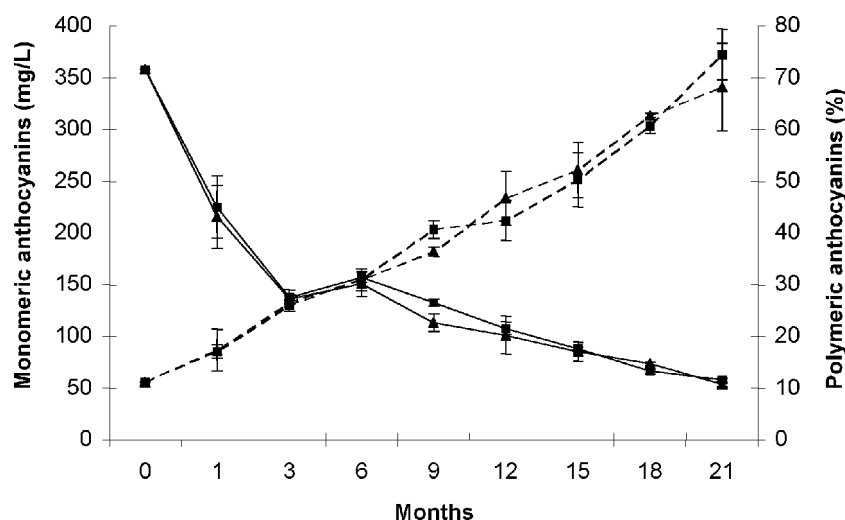


Fig. 4 - Evolution of monomeric anthocyanins (—) and polymeric anthocyanins (---) during the aging of red wine in French (▲) and in American oak barrels (■).

Promedial values and standard deviations (n=4). The monomeric anthocyanins are expressed in mg/l and polymeric anthocyanins in %

Fig. 4 - Évolution des anthocyanines monomériques (æ) et polymériques (—) au cours du vieillissement du vin rouge dans barriques EN bois de chêne français (▲) et américain (■).

Valeurs moyennes et écart-type (n = 4). Les anthocyanines monomériques sont exprimées en mg/L et les polymériques en pourcentage.

TABLE II
Sensory analysis results for aged in french oak.

Sensory analysis/month	Élevage en barriques			Vieillessement en bouteilles		
	3	6	9	12	15	21
Total	72,66	76,66	63,48	79,00	73,25	69,50
Visual phase	13,66	13,66	14,50	15,50	14,25	13,50
Smell	24,33	25,66	17,66	24,50	23,50	23,00
Taste	12,00	12,66	10,66	13,00	12,50	12,00
Taste-Smell	22,66	24,66	20,66	26,00	23,00	21,00

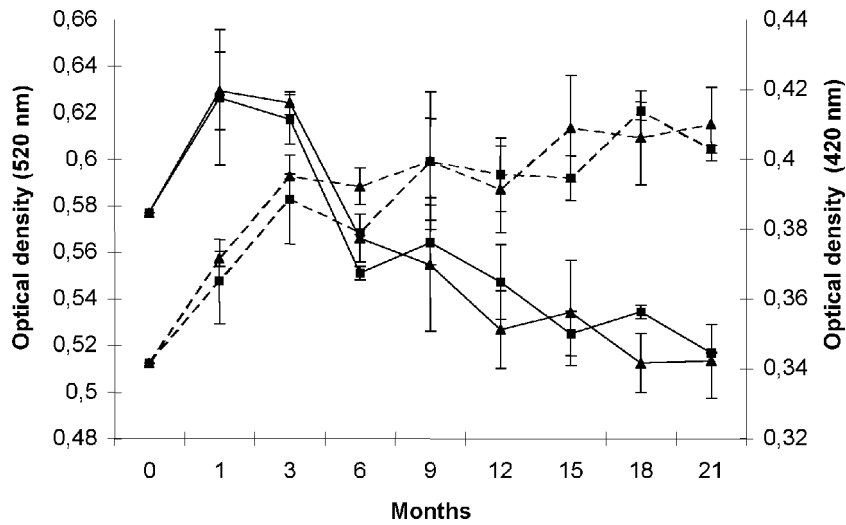


Fig. 5 - Evolution of O.D. 520 nm (—) and O.D. 420 nm (---) during the aging of red wine in French (▲) and in American oak barrels (■).

Promedial values and standard deviations (n=4).

Fig. 5 - Évolution de la D.O. 520 nm (—) et la D.O. 420 nm (---) au cours du vieillissement du vin rouge dans des barriques en bois de chênes français (▲) et américain (■).

Valeurs moyennes et écart-type (n=4).

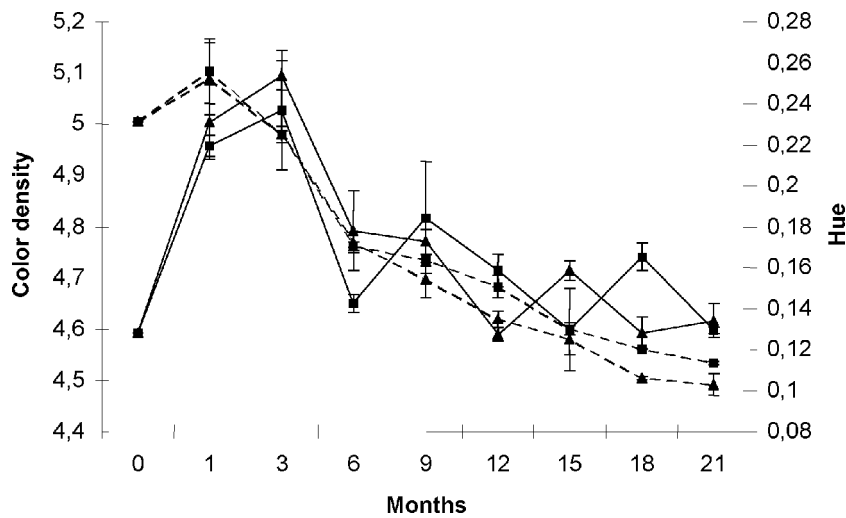


Fig. 6 - Evolution of color density (—) and hue (---) during the aging of red wine in French (▲) and in American oak barrels (■).

Promedial values and standard deviations (n = 4).

Fig. 6 - Évolution de la densité decouleur (—) et de la teinte (---) au cours du vieillissement du vin rouge dans des barriques en bois de chênes français (▲) et américain (■).

Valeurs moyennes et écart-type (n = 4).

As shown in figure 2, there was a consistent increase in volatile acidity during barrel storage, which could be primarily due to the extraction of volatile acids from the oak (AIKEN and NOBLE, 1984; WILKER and GALLANDER, 1988; VIVAS *et al.*, 1995) and to ethanol oxidation. Although barrels are different in coopering methods, there was no difference in volatile acidity between the two types of oak. In bottles, volatile aci-

dity showed slight alterations during storage, due to the use of manual corking which allowed a higher oxygen diffusion across the cork than with automatic corking.

Initially, titratable acidity (figure 2) presented a consistent increase, which has been reported previously in oak-aged alcoholic beverages (ONISHI *et al.*, 1977;

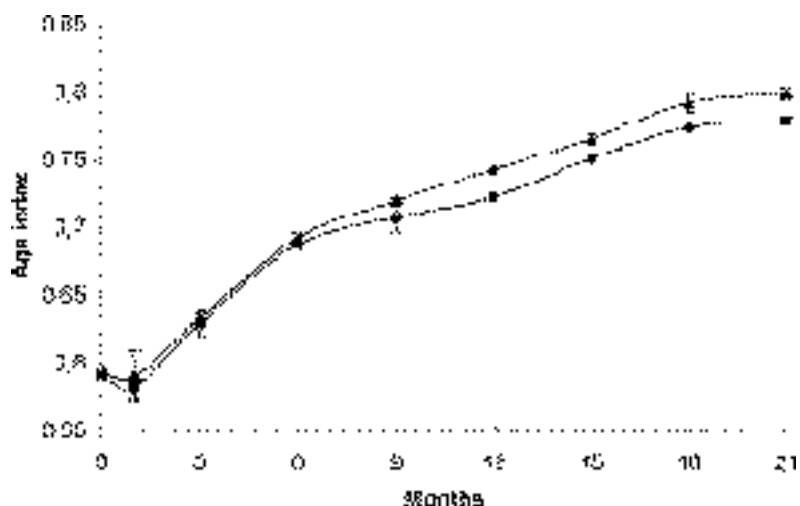


Fig. 7 - Age index evolution during the aging of red wine in French (▲) and in American oak barrels (■).
Promedial values and standard deviations (n=4).

Fig. 7 - Évolution de l'index de l'âge au cours du vieillissement du vin rouge dans des barriques en bois de chêne français (▲) et américain (■).

Valeurs moyennes et écart-type (n=4).

AIKEN and NOBLE, 1984; WILKER and GALLANDER, 1988). Whereas the rest of the increase in titratable acidity is due to the rise in volatile acidity, during the first month this rise indicated the extraction of carboxylic, phenolic and volatile acids from wood, as suggested by AIKEN and NOBLE (1984). Moreover, this initially high increase agrees with other previous researches who similarly found that extraction of substances from oak-wood was greater during the first aging stage (SINGLETON and DRAPER, 1961; NYKÄNEN *et al.*, 1984).

The total polyphenol index showed slight fluctuations (figure 3), probably due to a complex equilibrium between phenolic substances extracted from wood, and coloring material precipitated in red wine during the storage time. A decrease in the index over time in the bottle was observed as previously reported by RUIZ (1994). Moreover, phenolic extraction was not marked because of the use of lightly charred barrels, poor in extractives (ARTAJONA, 1991). However, the index was higher in wine stored in French barrels, as other researchers observed in phenolic compounds in oak extracts and alcoholic beverages (SINGLETON, 1974; HENDERSON, 1983; AIKEN and NOBLE, 1984; SCHUETZ, 1986).

Results for monomeric anthocyanins (figure 4) are similar to those of NAGEL and WULF (1979). These compounds presented a decrease over time, while polymeric anthocyanins (figure 4) showed a continuous rise during the aging period in barrel and bottle, consistent with previous reported data (BAKKER *et al.*, 1986; DALLAS and LAUREANO, 1994). In effect, a polymerization look place between monomeric anthocyanins (the red colored pigments of wine) themselves and

with tannins along the maturation. These anthocyanin-tannin polymers in wine give a more stable (to SO₂ and pH changes) red color and astringency loss (MARGUERI *et al.*, 1980; SINGLETON and TROUSDALE, 1992; MAZZA, 1995). The drop in monomeric forms is higher in the first months of oak-aged wine since polymerization is favoured by the presence of oxygen (SOMERS, 1983), which is more abundant during the maturation process in barrique than in bottle.

As shown in figure 5, a consistent increase in 420 nm and 520 nm absorbances up to three months of storage time was observed, which could be due to the extraction of colored substances from oak wood (AIKEN and NOBLE, 1984), polymerization of anthocyanins and to the drop in wine pH, which increased the proportion of anthocyanins in the red form (the flavylium ion) (RIBÉREAU-GAYON, 1974). After three months of storage, a constant loss in 520 nm absorbances and a slight increase in 420 nm values were observed. Initially, these changes provoked a rise in color density and hue (figure 6), but during the rest of the storage time a decrease was found as a result of wine color turning from purple to brick red and from dark to lighter tones. In other research work on aging wine, not only the increase in color density has been found (AIKEN and NOBLE, 1984; LAZSLAVIK *et al.*, 1995), but also a drop in this index for long maturations (RUIZ, 1994).

The changes in wine color reflected the increase in age index (the yellow-red color ratio) (figure 7). This behavior is consistent with previous data observed in alcoholic beverages (CRUZ *et al.*, 1996). From the second sampling onwards, the age index was higher

in French oak wine suggesting the existence of a faster oxidation process in Allier barrels.

CONCLUSIONS

Spanish red wine aged in French and American oak barrels presented an increase in titratable acidity and total phenolic compounds, primarily due to the wood extraction whereas oxidation processes resulted in a rise in volatile acidity and in age index. The increase in total phenols extracted from the barrels was higher in French than in American oak-aged wines, as changes in age index.

Ethanol content decreased during the aging period resulting in a higher concentration in wines stored in French barrels than in American ones, probably due to the different coopering methods of obtaining the staves.

Acknowledgements : Authors are grateful to Mr. Felipe Blanco Pinilla (Bodegas Insulares S.A.), to Mr. Eugenio Díaz Díaz (I.C.I.A.) and to Mr. Julian Suberbiola Ripa (E.V.E.N.A.) for their inestimable assistance and collaboration in this research.

BIBLIOGRAPHY

- AIKEN J.W. and NOBLE A.C., 1984. Composition and sensory properties of Cabernet Sauvignon wine aged in French versus American oak barrels. *Vitis*, **23**, 27-36.
- AMERINE M.A. y OUGH C.S., 1980. *Análisis de mostos y vinos*. Ed. Acibia.
- ARTAJONA J., 1991. *Estudio de la caracterización de roble según su origen y grado de tostado mediante utilización de GC y HPLC*. *Jornadas Técnicas Internacionales*. FIRAVI 91.
- BAKKER J., PRESTON N.W. and TIMBERLAKE C.F., 1986. The determination of anthocyanins in aged red wines: comparison of HPLC and spectral methods. *Am. J. Enol. Vitic.*, **37**, n° 2, 121-126.
- CHATONNET P., BOIDRON J.N., DUBOURDIEU D. et PONS M., 1994. Évolution des composés polyphénoliques du bois de chêne au cours de son séchage. Premiers résultats. *J. Int. Sci. Vigne Vin*, **28**, n° 4, 337-357.
- CHATONNET P., BOIDRON J.N. et PONS M., 1989. Incidence du traitement thermique du bois de chêne sur sa composition chimique. 2° partie : évolution de certaines composés en fonction du intensité de brûlage. *J. Int. Sci. Vigne Vin*, **23**, n° 4, 223-250.
- CRUZ M., SARABIA A., SYMINGTON C., SANTAMARÍA F. and INIGHEZ M., 1996. Analysis of ageing and typification of vintage ports by partial least squares and soft independent modeling class analogy. *Analyst*, **121**, n° 8, 1009-1013.
- DALLAS C. and LAUREANO O., 1994. Effects of pH, sulphur dioxide, alcohol content, temperature and storage time on colour composition of a young Portuguese red table wine. *J. Sci. Food Agric.*, **65**, 4, 477-485.
- GARCÍA BARCELÓ J., 1976. *Metodología de análisis de vinos y derivados*. Sepsa, Villafranca del Penedés.
- GUYMON J.F. and CROWELL E.A., 1968. Separation of vanillin, syringaldehyde, and other aromatic compounds in the extracts of french and american oak woods by brandy and aqueous solutions. *Qual. Plant. Mater. Veg.*, **16**, 320-333.
- HENDERSON C.E., 1983. Cooperage lignin M.S. Thesis, University of California, Davis.
- LASZLAVIK M., GAL L., MISIK S. and ERDEI L., 1995. Phenolic compounds in two Hungarian red wines matured in *Q. Robur* and *Q. Petraea* barrels. HPLC analysis and diode array detection. *Am. J. Enol. Vitic.*, **46**, n° 1, 67-74.
- MARGUERI G., TONON D. and TREPIN P. (1980) Modification of composition of wine polyphenol compounds during rapid ageing. *Vini Ital.*, **22**, n°125, 77-82.
- MAZZA G., 1995. Anthocyanins in grapes and grape products. *Critical Reviews in Food Sciences and Nutrition*, **35**, n° 4, 341-371.
- MILLER D.P., HOWELL G.S., MICHAELIS C.S. and DICKMANN D.I., 1992. The content of phenolic acid and aldehyde flavor components of white oak as affected by site and species. *Am. J. Enol. Vitic.*, **43**, n° 4, 333-337.
- NAGEL C.W. and WULF L.W., 1979. Changes in the anthocyanins, flavonoids and hydroxycinnamic acid esters during fermentation and aging of merlot. *Am. J. Enol. Vitic.*, **30**, n° 2, 111-116.
- NYKÄNEN L., NYKÄNEN I. and MORING M., 1984. Aroma compounds dissolved from oak chips by alcohol. In: *Progress in flavour research*. Ed. J. Adda, 339-346. Elsevier, Amsterdam.
- ONISHI M., GUYMON J.F. and CROWELL E.A., 1977. Changes in some volatile constituents of brandy during aging. *Am. J. Enol. Vitic.*, **28**, 192-198.
- POMAR M., GONZÁLEZ L.A. and DÍAZ F., 1994. Analytic characteristics of red wine from the Canary Islands (SPAIN). *J. Int. Sci. Vigne Vin*, **28**, n° 2, 173-179.
- PONTALLIER P., SALAGOÏTY-AUGUSTE M-H. and RIBÉREAU-GAYON P., 1982. Intervention du bois de chêne dans l'évolution des vins rouges élevés en barrique. *Connaissance Vigne Vin*, **16**, 45-61.
- REAZIN G.H., 1981. Chemical mechanisms of whiskey maturation. *Am. J. Enol. Vitic.*, **32**, 283-289.

- RIBÉREAU-GAYON P., 1974. *The chemistry of wine making*. Ed. A.D. Webb, American Chemical Soc., Washington.
- RIBÉREAU-GAYON P. and STONESTREET E., 1965. Le dosage des anthocyanes dans le vin rouge. *Bull. Soc. Chim. Fr.*, **9**, 2649.
- ROUS C. and ALDERSON B., 1983. Phenolic extraction curves for white wine aged in French and American oak barrels. *Am. J. Enol. Vitic.*, **34**, 211-215.
- RUÍZ HERNÁNDEZ M., 1994. *Crianza y envejecimiento del vino tinto*. Ed. Madrid Vicente.
- SCHUETZ R.C., 1986. *Humidity effects on evaporation and penetration in american and french white oak and its ethanol extract*, pp. 54 .M.S. Research Report. University of California, Davis.
- SINGLETON V.L., 1974. Some aspects of the wooden containers as a factor in wine maturation. *Adv. Chem. Ser. (ACS)*, **137**, 254-277.
- SINGLETON V.L., 1995. Maturation of wines and spirits: comparison, facts, and hypotheses. *Am. J. Enol. Vitic.*, **46**, n° 1, 98-115.
- SINGLETON V.L. and DRAPER D.E., 1961. Wood chips and wine treatment; the nature of aqueous alcohol extracts. *Am. J. Enol. Vitic.*, **12**, 152-158.
- SINGLETON V.L. and TROUSDALE E.K., 1992. Anthocyanin-tannin interactions explaining differences in polymeric phenols between white and red wines. *Am. J. Enol. Vitic.*, **43**, n° 1, 63-70.
- SOMERS T.C., 1983. Influence of conservation time on the physico-chemical and organoleptic characteristics of wines. *Food Technology in Australia*, **35**, n° 1, 38-43.
- SOMERS T.C. and EVANS M.E., 1977. Spectral evaluation of young red wines: anthocyanins equilibria, total phenolics, free and molecular SO₂, «chemical age». *J. Sci. Food Agric.*, **28**, 279-287.
- VENTER W.P. and BAUMGARTEN G.F., 1987. Influence of relative humidity and temperature on the chemical composition of brandy during maturation. *Proc. 8th Int. Enol. Symp., Cape Town*, 1-13.
- VIVAS N., LONVAUD A. and GLORIES Y., 1995. Observations concerning the increase of volatile acidity in red wines whilst ageing in barrels. *J. Sci. Tech. Tonnellerie*, **1**, 81-122.
- WILKER K.L. and GALLANDER J.F., 1988. Comparison of Seyval blanc wine aged in barrels and stainless steel tanks with oak chips. *Am. J. Enol. Vitic.*, **39**, n° 1, 38-43.

Reçu le 15 juillet 2000
accepté pour publication le 1e 10 septembre 2000
