Behavior of Monosaccharides, Phenolic Compounds, and Color of Red Wines Aged in Used Oak Barrels and in the Bottle

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A red wine with appropriate basic quality characteristics for aging was stored in oak barrels for 12 months and then bottled and aged for a further 6 months. The same ambient conditions of temperature and humidity were maintained throughout the entire aging process. The barrels used were made from three different species of oak by four different cooperages and had been used for at least two years. Analysis of variance and principal component analysis were run on the values for hexoses, pentoses, total anthocyanins, *ortho*-diphenols, low- and high-polymer polyphenols, and color parameters to study the behavior of the monosaccharides and polyphenols in response to the factors of aging time, the oak variety employed, and the source cooperage where the barrels had been made. Time trends for all the phenolic components were directly related to aging time, with low-polymeric polyphenols (LPPs) being the most affected by wood type and source cooperage. Wine color was defined by a basic red color which decreased with aging time in the barrel and was altered by yellowish pigment components differing for each of the barrels in which oxidative aging took place and by increased stability of the blue copigments. Principal component analysis showed that samples of the same source wine aged in different barrels tended to be grouped together according to each of the aging intervals considered.

Keywords: *Red wine; aging; carbohydrates; polyphenols; color; Quercus robur; Quercus alba; Quercus sessilis*

INTRODUCTION

The role of carbohydrates (monosaccharides) in wine aging has generally received less attention than it has in the aging of brandies and spirits, in which the release of monosaccharides such as galactose and fructose has been observed as a consequence of the breakdown of hemicellulose, which is helped along by the use of temperatures in the range of 45−50 °C and 70−75 °C during distillation (Dzhanpoladyan et al., 1969). Hemicellulose breakdown has also been put forward to account for increases in sugars of up to 2000 mg/L in brandies aged for 40 years (Lafon, 1971) and up to 500 mg/L in cognacs aged in oak wood (Viriot et al., 1993).

The presence of arabinose, glucose, xylose, rhamnose, and fructose has been reported in a brandy aged in Limousin oak for 6 months (Belchior et al., 1972), whereas adding oak extracts to brandies has resulted in increases in both total polyphenols and carbohydrates (Bozhinov et al., 1984).

Changes in the substances present in wines and distillates that are of great importance in determining their sensory characteristics take place during aging in oak barrels. This phenomenon has resulted in a large body of research, normally focusing on phenolic compounds, which may originate both from the wine (Bourzeix and Saquet, 1975; Di Stefano and González-SanJosé, 1991) and the wood (Delgado and Gómez-Cordovés, 1986; Estrella et al., 1987; Gómez-Cordovés et al., 1995; Del Alamo, 1997). Such research has documented the variations undergone by certain phenolic compounds during aging as well as the bonding of phenolic components with other substances present in the wine.

Families of polyphenols such as *ortho*-diphenols (ODs), low- and high-polymer polyphenols (LPPs and HPPs), anthocyanins, and proanthocyanidins exert an important influence on both the sensory characteristics (Singleton and Trousdale, 1992; Jackson and Lombard, 1993; Gómez-Cordovés and Bartolomé, 1993; Gómez-Cordovés and González-SanJosé, 1995) and health aspects (Bourzeix, 1993) of wines and distillates.

There is a need to relate phenolic compounds to sugars because increased sugar contents may be, in part, due to hydrolysis of flavonols (Harborne et al., 1995) which can form O−glycoside bonds with glucose, galactose, xylose, rhamnose, and arabinose. Production of organic acids and sugars from the 3-glucoside and 3-*p*-coumaryl glucoside forms of anthocyanins has been considered in a red wine (Cameira dos Santos et al., 1996).

A major portion of the improvement in the quality of mature wines aged in wood is attributable to the quality of the barrel in which aging takes place and to ambient conditions in the wine cellar. Barrel quality is a function of oak species and variety and the barrel manufacturing process employed.

This paper presents some initial data compiled on the monosaccharide, total anthocyanin (ACY), OD, and LPP and HPP contents, as well as on percentage color intensity in a red wine aged for 18 months under the

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Table 1. Analytical Characteristics of Initial Red Wine

characteristic	value
total sugars (mg/l)	2000.00
total anthocyanins (mg/L)	196.00
O-diphenols (mg/L)	642.80
high-polymer polyphenols (mg/L)	211.00
low-polymer polyphenols (mg/L)	1557.00
sum of hexoses (mg/L)	777.74
sum of pentoses (mg/L)	67.02
percentage of red (%)	56.00
percentage of yellow (%)	32.50
percentage of blue (%)	11.50

Table 2. Characteristics of Barrels Used

barrel[a]	variety[c]	origin	cooperage
M1	*Q. alba*	american	A
M2	*Q. alba*	american	B
M3	*Q. alba*	american	B
M4	*Q. alba*	american	C
M5	*Q. alba*	american	D
M6	*Q. alba*	american	D
M7[b]	*Q. robur*	french	D
M8[b]	*Q. sessilis*	french	D
M9[b]	*Q. sessilis*	french	D

[a] All barrels 2 years old except M3 which was 4 years old. [b] From different regions of France. [c] *Q.*, Quercus.

same ambient conditions using barrels made from the woods of different oak species manufactured at four different cooperages, in an effort to ascertain possible differences in the development of the wine characteristics during aging.

This work intends to demonstrate that the red wine aging in used oak barrels seems to be influenced by species and origin of the oak as well as cooperage practices.

MATERIALS AND METHODS

Sampling. A red wine made from grapes of *Vitis vinifera* L., c.v. Tinto del País (Table 1), made in the Ribera del Duero "Appellation of Origin" to a basic level of quality suitable for aging was stored in nine Bordeaux barrels, each with a 225-L capacity, manufactured from different types of oak.

Alcoholic fermentation was conducted in stainless steel tanks where the temperature was controlled at 25 ± 2 °C. The wine was clarified with 400 mg/L bentonite and 10 mg/L gelatin, tartrate-stabilized by refrigeration at −4 °C, and sulfited with 33 mg of potassium metabisulfite ($K_2S_2O_5$) per liter of wine.

According to the suppliers, the 225-L barrels were made from American and French oaks. The wood was seasoned by 24 months of natural drying and given a medium toasting. The characteristics of the barrels are summarized in Table 2. The barrels were two years old except M3 which was 4 years old. The wines were aged at the same wine cellar in humidity conditions ranging between 80 and 90% and temperature conditions ranging between 10 and 14 °C over the aging period.

In total, ninety one samples were analyzed, including the initial wine (Table 1) before aging. Nine samples were taken from each barrel over an aging period of one year. The wines were then bottled, and another sample was taken six months later (at the end of February) after further bottle aging. The first sample was taken three months after the wine had been transferred to the barrels, to give the wine time to reach an equilibrium state after transfer. Over the next eight months, a sample was collected monthly from each barrel. Differences in composition caused by the wood during aging first become perceptible after three months (Gómez-Cordovés and González-SanJosé, 1995). The total aging time monitored over the sampling period was 18 months.

Monosaccharides. Monosaccharides were analyzed by HPLC using a pulse amperometer detector (Bernal et al., 1996; Del Alamo, 1997). A model CM 4000 pump from Milton Roy (Riviera Beach, FL) was used to propel the eluent, which consisted of Nanopure purified water and 0.2 M NaOH. The eluent was delivered at a flow rate of 1 mL/min and degassed with helium. A ConstaMetric III pump, also from Milton Roy, was used to propel a 0.3M NaOH solution at a flow rate of 0.6 mL/min after column to boost the detector signal. A Promis II autoinjector from Spark Holland (Emmen, The Netherlands) was furnished with a fixed loop of 20 μL. A 4 × 250 mm Carbo Pac PA column was used in conjunction with a 3 × 25 mm Carbo Pac Guard precolumn, both from Dionex Co. (Sunnyvale, CA). A Coulochem II 5040 pulsed amperometric detector from ESA, Inc. (Bedford, MA), was equipped with a gold working electrode that was set with measurement potential, $E_1 = 250$ mV; measurement time, $t_1 = 500$ ms; delay time, $t_D = 300$ ms; $E_2 = 700$ mV; $t_2 = 120$ ms; $E_3 = -900$ mV, $t_3 = 160$ ms; range, 5 μV.

Monosaccharides were grouped as sum of hexoses (SH: galactose, glucose, fructose, and mannose) and sum of pentoses (SP: arabinose, rhamnose, ribose, and xylose) based on the concentrations (mg/L) obtained by means of HPLC.

Families of Phenolic Compounds. High-polymeric polyphenols (HPPs), *o*-diphenols (ODs), low-polymeric polyphenols (LPPs), and total anthocyanins (ACYs) were assayed according to the traditional methods set out in Paronetto, 1975.

HPPs were calculated by difference between total polyphenols (TPs, analyzed using Folin Ciocalteau reagent (Folin and Ciocalteau, 1927)) and low-polymeric polyphenols (according to the method of Masquelier et al., 1965). *o*-Diphenols were determined by the method of Flanzy and Aubert (1969) and ACYs were determined by means of color changes according to the pH of the medium (Paronetto, 1975).

Phenolic compounds were measured directly in wine without any prior treatment.

Color Percentage Intensity. A direct measurement of wine absorbance to 420, 520, and 620 nm was carried out in a Du 70 Beckman Spectrophotometer with a quartz cell of 1 mm path length, according to the Glories procedure (Glories, 1984). The variables calculated were red (R), yellow (Y), and blue (B) percentages.

All samples were analyzed in duplicate. Statistical treatment was applied to the analytical results, and mean values, coefficients of variation, analysis of variance, and principal components analysis were calculated to establish the relationships between the variables considered. The program STATISTICA, Soft Inc. 1992 was employed.

RESULTS AND DISCUSSION

Mean Values and Coefficients of Variation. Table 3 sets out the mean values and the coefficient of variation (%CV) values for the parameters analyzed for each sample with aging time, irrespective of oak type. High values for %CV suggest differences between wines from different barrels.

Considering only the mean values, distinct decreases were observed in the ACYs and LPPs, though the decrease in the latter family was lower than might be expected in view of the condensation and polymerization reactions taking place during aging. On the whole, HPP levels increased. Hexose levels fell during the months of May and June, as they customarily do on account of residual yeast revival, and afterward rose continuously until the end of the sampling period.

The percentage of red color intensity decreased and the percentage of yellow pigment components increased, as is to be expected for an oxidative process such as barrel aging, though this process was not as pronounced in this wine as has been observed in other types of wine. The percentage of blue pigment components increased, a special characteristic of this type of wine. (Valdés et al., 1997).

Table 3. Characteristics of Wine Aged during 18 Months: Mean Content (mg/L) and Coefficient of Variation for each Compound and Color Percentages in the Different Months

month (number of months of aging)		ACY[a]	OD[b]	LPP[c]	HPP[d]	SP[e]	SH[f]	% yellow	% red	% blue
Dec. (3)	mean	207.33	682.31	1585.00	372.00	62.02	109.94	32.70	55.82	11.47
	CV %	10.82	5.10	3.39	36.57	31.75	47.89	0.48	0.67	4.31
Jan. (4)	mean	204.41	661.82	1490.89	356.78	71.52	95.08	32.74	55.10	12.14
	CV %	6.43	2.40	5.23	38.69	34.34	45.25	0.33	1.33	6.79
Feb. (5)	mean	201.92	649.13	1475.22	346.11	79.69	75.96	32.70	55.28	12.03
	CV %	6.86	2.95	4.71	33.62	25.25	21.64	0.72	1.14	5.70
Mar. (6)	mean	193.51	667.07	1384.89	425.78	76.36	88.64	32.93	55.36	11.71
	CV %	9.72	3.92	4.32	22.31	19.84	24.78	0.38	1.77	7.87
Apr. (7)	mean	184.56	673.11	1499.22	416.22	73.01	102.30	33.11	54.46	12.44
	CV %	7.12	2.67	6.68	24.12	14.28	17.51	2.52	1.21	3.76
May (8)	mean	186.54	672.29	1470.78	407.89	71.72	90.42	33.44	54.86	11.69
	CV %	8.74	3.19	6.96	31.96	16.39	40.06	1.22	1.01	3.94
June (9)	mean	178.57	703.40	1446.67	387.33	76.98	79.78	33.67	54.73	11.60
	CV %	7.37	3.17	8.18	30.94	17.12	36.14	0.28	0.87	4.12
July (10)	mean	173.04	698.49	1450.11	409.44	78.67	126.74	33.91	54.18	11.91
	CV %	7.72	5.16	5.94	24.64	20.36	30.73	0.43	1.08	5.43
Sept. (12)	mean	147.86	651.96	1445.78	641.00	67.04	116.80	34.07	53.32	12.59
	CV %	7.17	2.70	8.10	17.07	13.25	24.37	0.66	0.95	5.26
Feb. (18)	mean	139.40	727.80	1473.56	487.78	65.28	119.37	33.76	53.41	12.81
	CV %	4.12	2.67	6.68	24.12	14.28	17.51	2.52	1.21	3.76

[a] ACY, total anthocyanins. [b] OD, *o*-diphenols. [c] LPP, low-polymer polyphenols. [d] HPP, high-polymer polyphenols. [e] SP, sum of pentoses. [f] SH, sum of hexoses.

Table 4. ANOVA Results[a]

	component								
	ACY	OD	LPP	HPP	SP	SH	Y	R	B
	Factor: aging time								
fcal	18.93	8.24	2.50	3.95	1.16	2.09	19.70	13.67	3.97
fcríti	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96
sig.	***	***	**	***	N. S.	*	***	***	***
	Factor: type of wood								
fcal	3.29	0.83	2.61	1.13	1.60	2.45	0.27	2.29	7.61
fcríti	2.02	2.02	2.02	2.02	2.02	2.02	2.02	2.02	2.02
sig.	**	N. S.	*	N. S.	N. S.	*	N. S.	*	***
	Factor: barrelmaking								
fcal	5.22	0.66	4.24	1.48	3.28	4.46	0.67	2.04	6.91
fcríti	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68
sig.	**	N. S.	**	N. S.	*	**	N. S.	N. S.	***

[a] N. S.,*,**,*** = Not significant, significance at $P < 0.05$, $P < 0.01$, and $P < 0.001$ respectively.

The different coefficient of variation values are indicative of the influence of barrel type on the wine, because the wine in all the barrels was identical at the start of the aging period.

Analysis of Variance. An analysis of variance was run on the parameters indicated above using the factors aging time, barrel wood type, and source cooperage in order to monitor changes in wine composition during aging. Monosaccharides were grouped as sum of hexoses (SH) and sum of pentoses (SP) based on the concentrations obtained by means of HPLC (Bernal et al., 1996).

The results have been tabulated in Table 4. Figures 1, 2, and 3 present bar charts graphically illustrating the mean values and %CV values for the samples by six-month interval, namely, (1) months 1−6 of barrel aging; (2) months 7−12 of barrel aging; and (3) the six months of bottle aging.

Carbohydrates. Table 4 shows source cooperage to be the only factor that affected the SP values. Similarly, Figure 1 shows that there was no variation in SP during the period of barrel aging and a slight decline during the period of bottle aging. However, %CV values were higher during the first six months of aging, indicating that there were differences in the release of pentoses into the wine from wood hemicelluloses according to barrel type during that period, but that leaching of pentoses from the wood later leveled off.

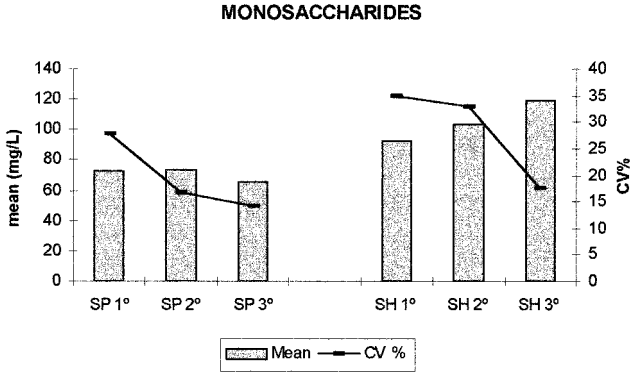

Figure 1. Average values (mg/L) and CV % of pentoses and hexoses. (SP, sum of pentoses; SH, sum of hexoses).

Conversely, the SH values presented statistically significant differences during the aging period (Table 4) according to aging time, wood type, and source cooperage, this last being the factor with the highest level of significance. Figure 1 depicts a gradual increase in SH values during each of the three aging periods considered. The %CV values fell slightly during the second six-month barrel-aging interval with respect to the first and underwent an appreciable decrease during the period of bottle aging. As in the case of the pentoses, influence of barrel wood type was discernible during the first six months of barrel aging. Therefore, aging time and source cooperage would appear to be the most important factors affecting changes in carbohydrate concentration.

Families of Phenolics. The four families of phenolic compounds considered underwent statistically significant differences in concentration during aging (Table 4), with the changes in the LPPs exhibiting the lowest level of significance.

Figure 2 reflects progressive decreases in both ACY levels and %CV values. This trend was expected because polymerization and copigmentation processes involving

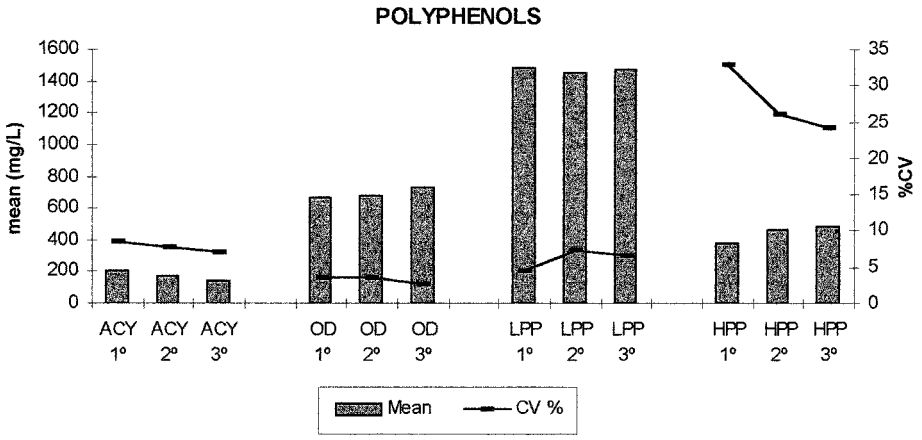

Figure 2. Average values (mg/L) and CV % of families of phenolic compounds. ACY, total anthocyanins; OD, *o*-diphenols; LPP, low-polymeric polyphenols; HPP, high-polymeric polyphenols.

these components are known to take place (Gómez-Cordovés et al., 1995). In addition, the ACY estimation methods were based on spectrophotometric readings of color intensity produced by the flavylium ion (red), and noncopigmented and/or low-polymer anthocyanins are the sole source of formation or decolorization of that ion.

The ODs are sensitive to oxidation and thus are substrates for browning reactions. These components increased slightly during aging, though %CV values decreased. Neither wood type nor source cooperage appeared to exert any significant influence on the variations taking place during aging.

The LPPs underwent slight variations throughout the aging period, with the highest concentration values and lowest %CV values after six months of aging (Figure 2). The differences in concentration were statistically significant for all the factors, i.e., aging time, barrel wood type, and source cooperage, though the levels of significance for each of those factors varied. Because these components come not only from the wine itself but also from ethanolysis of the barrel wood, both the latter factors affected concentration; however, source cooperage appeared to exert a greater influence than the type of oak employed. (Table 4).

The HPPs increased during all three aging intervals considered (Figure 2), while the %CV values decreased more between the first two aging intervals. The factors wood type and source cooperage did not have any significant effect on concentration trends (Table 4).

Percentage Color Intensity. The passage of time affected wine color expressed as percentage color intensity, with statistically significant differences at the highest level of significance (Table 4). The wines were characterized by a basic red color, the percentage intensity of which decreased both during the period of oxidative aging when the wine was stored in the barrel and during the aging period when reduction took place in the bottle (Figure 3), though the %CV values remained similar over the entire period. This means that, as expected, reactions involving yellow and blue pigment components that modified the red pigments took place over the entire aging period, resulting in alterations in the red color of the wines.

After red, yellow pigment components made the greatest contribution to wine color. Although the percentage color intensity and %CV values for these pigments underwent a slight increase during the second half of oxidative barrel aging (Figure 3), the greatest increase took place during the period of bottle aging,

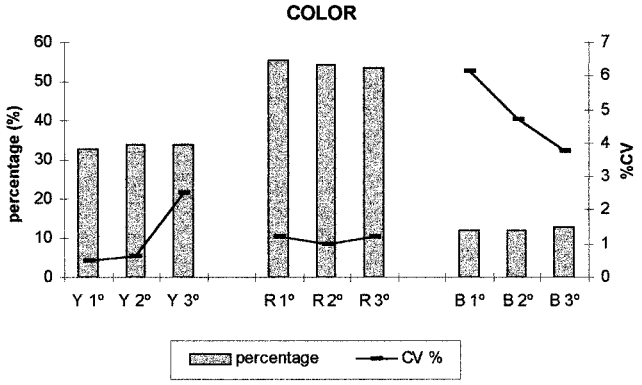

Figure 3. Average values (%) and CV % of color percentages. (R, percentage of red; Y, percentage of yellow; B, percentage of blue)

indicating that the yellow co-pigment components (nature or quantity) fluctuated during the reducing period, with color component levels varying according to the barrel in which oxidative aging took place.

As already mentioned above, the percentage color intensity values for blue pigment components underwent statistically significant differences at the highest level of significance in response to each of the three factors considered in this study (Table 4). These blue color components exhibited a greater tendency to increase slightly, a tendency that was somewhat more pronounced during the reducing period. Conversely, during the first six months of aging, the %CV values were higher than for the red and yellow color components (Figure 3), which would seem to indicate greater differences in the formation of copigments or polyphenols at the lower end of the HPP range depending on barrel type. This corroborates the findings for the HPPs already reported above. The subsequent decrease in the %CV values would appear to be indicative of greater stability of copigment types in the wine and smaller differences in the structure of such copigments in response to source cooperage.

Principal Component Analysis. PCA was applied to a total of 27 samples, according (1), (2), and (3) based on nine parameters (SP, SH, ACY, HPP, LPP, OD, R, B, Y). From this analysis, two components with eigenvalues greater than unity were selected (the first eigenvalue 3.51 and the second eigenvalue 2.15), accounting for 60% of the total variance.

The factor 1 (Figure 4) was clearly associated with OD, HPP, Y, R, and B which is related with color

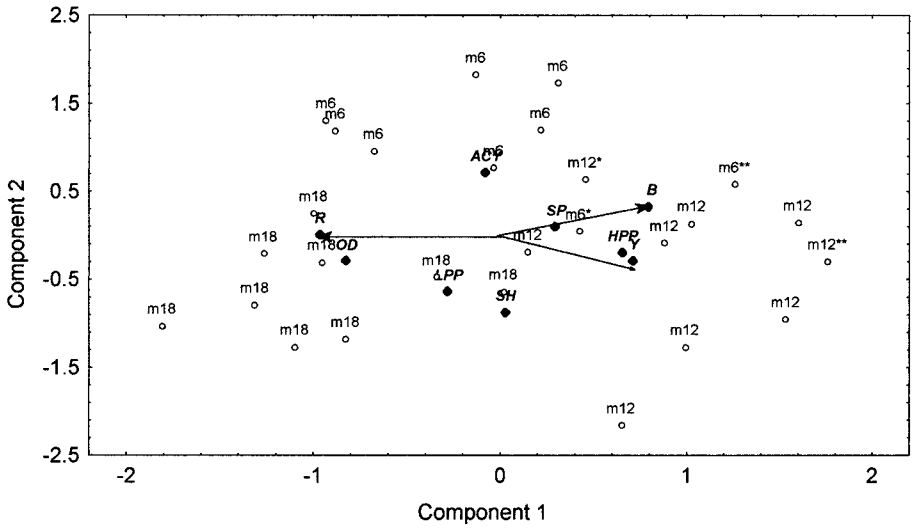

Figure 4. Distribution of wines in the two-coordinate system defined by two Principal Components with eigenvalues greater than unity.

evolution and copigmentation process; the factor 2 was associated with ACY, SH and LPP, related with wood extraction.

On the coordinate grid defined by the first two principal components, the samples taken after the first six months of aging were clustered closer together. This was to be expected, because the source wine in all the barrels was the same, and the barrel wood had not yet exerted sufficient influence to bring about changes in the wine. The location of these samples in the angle formed by the red and blue color components confirms that the samples retained the bluish hues characteristic of the young wine. The samples taken after 12 months of aging were also grouped together, though the values display a greater spread, indicative of larger differences in wine characteristics on the basis of the different parameters considered. After one year in the wood the wine took on different characteristics in each barrel, and dispersion of the samples in the vicinity of the angle formed by the pigment components affecting color was greater. This indicates that copigment formation was highest during that period.

The period of bottle aging yielded a separate sample cluster, indicative of similar development over the reducing period. The wine became smoother, more balanced, and more rounded. The location of the samples in the angle formed by the red and yellow color components is normal in wines that have undergone aging in wood. However, grouping of these samples along the vector for red color (negative values) suggests that greater influence of color components is a factor in stabilization, indicative of oxidation reactions and copigmentation.

In addition to these overall trends, certain individual samples displayed special behavior. Wines 8 (aged in *Q. sessilis* from Allier, marked as * in Figure 4) and 9 (*Q. sessilis* from Nevers, marked as ** in Figure 4) underwent very rapid development, in that both the samples taken at six months (m6) and the samples taken at 12 months (m12) were located close to each other, within the group of data points for the second aging interval.

The results for the carbohydrates suggest that the pentoses were more closely related to the period of oxidative aging and copigment (HPP) formation, whereas the hexoses were more closely related to the LPPs and stabilization of the wine during bottle storage.

CONCLUSIONS

Carbohydrate concentrations were significantly affected by aging time (hexoses $p < 0.05$) and source cooperage (hexoses $p < 0.01$ and pentoses $p < 0.05$). This different pattern between hexoses and pentoses during wine aging could be attributed to the different location and role of these carbohydrates in wood.

Time trends for all the phenolic components were directly related to aging time, with LPPs being the most affected by wood type and source cooperage.

Wine color was defined by a basic red color which decreased with aging time in the barrel. Wine color was altered by yellowish pigment components differing for each of the barrels in which oxidative aging took place and by increased stability of the blue copigments.

Principal component analysis showed that samples of the same source wine aged in different barrels tended to be grouped together according to each of the aging intervals considered. After one year in the wood, the wine had taken on different characteristics in each of the different barrels used, and dispersion of the samples increased, with greater spread in the vicinity of the angle formed by the color components, indicating that copigment formation was highest during that period.

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