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Influence of Copigmentation on the Chromatic Structure of Red Wine from the Recas Vineyard

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Abstract

Were characterized in relation to the chromatic properties the young and aged in bottle for 2, 6, 9 and 12 months, the red wines Cabernet Sauvignon and Pinot Noir from grapes harvested in 2005 year. During the ageing, the color intensity decreases from 8.20 to 7.89 for Cabernet Sauvignon and from 6.51 to 6.34 for Pinot Noir wine. In the ageing course, the tonality was increased from 0.79 to 0.97 for Cabernet Sauvignon and from 0.76 to 0.98 for Pinot Noir. The monomeric anthocyanins content decreases from 187.93 to 114.2 mg/L for Cabernet Sauvignon wines and from 131.16 to 88.16 mg/L for Pinot Noir wines. By ageing, the fraction of color due to polymeric pigment increases due to decreasing of color percent due to monomeric and copigmented anthocyanins. The "chemical wines age" was modified during the ageing in bottle due to color stabilisation.

Key words: red wines, copigmentation, chromatic structure, anthocyanins, ageing

Introduction

The establishing of chromatic characteristics of red wine is very important because these properties have a decisive role about the wines quality. Polyphenols from wine, particulary tannins and anthocyanins, even in small concentrations, have a great antioxidant capacity, assuring protection against cardiovascular diseases and cancer (Berke et al. 2003, Mazza et al. 1999). Through wines ageing in the bottle, due to oxidation and condensation processes, it was diminished the monomer polyphenols content; during the time of wine storage in bottle take place the structural changes, and one of the most studied of those changes concern red wine color evolution, called wine ageing. During aging, it has been demonstrated that initially present grape pigments slowly turn into new more stable red pigments. This phenomenon goes on for weeks, months and years (Mazza 1995, Monagas et al. 2006, Ollala et al. 1996, Pascu, 2005).

Anthocyanins are present in solution in several different forms. These forms exist in an equilibrium that is pH dependent. Based on an understanding of the pH equilibria and the different bleaching effect of SO2 on monomeric and polymeric anthocyanins, as well as the preferential binding of SO2 with acetaldehyde rather than anthocyanins, it was developed a set of spectral measures to determine the fraction of color due to each pigments: monomeric, polymeric and copigmented anthocyanins, the chemical age of the wine and the degree of pigment coloration (Somers and Evans 1974).

Copigmented anthocyanins are the complexes that result by reaction between anthocyanins and copigments molecules or co-factors. Co-factors are colorless compounds that when added to a solution containing anthocyanins will act to enhance the color of the solution. The most important copigments in wine are expected to be the flavan-3-ols and flavanols, hydroxycinnamic acids and even the antocyanins molecules. This phenomenon causes a hyperchromic effect and a bathochromic shift (Boulton 1996, Liao et al. 1992).

Material and method

The sample for analysis

In this study were analyzed red wines obtained in Recas vineyard from Cabernet Sauvignon (CS) and Pinot Noir (PN) grapes varieties harvested in 2005 year. Five red wines categories were analyzed: young red wines,

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immediately after conditioning (0-CS and 0-PN), aged in bottle for 2 months (2-CS and 2-PN), aged for 6 months (6-CS and 6-PN) aged for 9 months (9-CS and 9-PN) and aged in bottle for 12 months (12-CS and 12-PN).

Reagent and equipment

All chemicals and reagents were analytical grade or pure quality purchased from Merck, Fluka, Sigma and Chimopar.. Absorbance determination for color analysis were made using Spectrophotometer Specord 205 by Analitik Jena.

Total monomeric anthocyanin content will be determined by the pH-differential method, in accord with (Giusti and Wrolstad, 2005). Monomeric anthocyanins pigments (mg/L) will be calculated as cyanidin-3-glucoside.

Chromatic parameters: color intensity (IC), tonality (T) and contribution of yellow, red and blue pigments to the wine color were established by Glories method (Glories 1984).

The analysis of red wine color was determined in accord with Somers and Evans (1974) method. The fraction of red wine color due to monomeric, polymeric and copigmented anthocyanins was in order: MA (%), PA (%) and CA (%). The wine chemical age is quantified by two indices that give a measure of the extent to which polymeric pigments have replaced monomer anthocyanins during of wine evolution. The first index, I1 represent the ratio between color due to polymeric anthocyanins and color due to total anthocyanins and the second index I2 - the ratio between color due to polymeric anthocyanins and color due to monomeric anthocyanins. The degree of pigment coloration (α) gives a measure of the amounts of monomeric anthocyanins in the colored form (Somers and Evans 1974).

Results and discussion

The data from the Table 1 show the chromatic structure obtained by Glories method. By this method, it was determined the percent with that each pigments category (yellow, red and blue) contribute to the total red wine color. In general case, for wine with red shade, the red pigment class takes part in higher percent (more than 45%) to underline the wine color.

For aged red wine the yellow pigments percent increases and the red pigments percent decreases, the both pigments classes are more equilibrate in the aged wines. The class of blue pigments participate to the red wines color in low measure (in the range 8.69-10.08% for CS and 7.40-9.47% for PN wine). The red pigments category is preponderant in the all analysed wines. The yellow pigment contributed with less than 45% to the red wine color. Through wines ageing, the absorbance at λ=520 nm decreases, accompanied of the increasing of absorbance at λ=420 nm and 620 nm. As a rule, during the ageing of red wines, the absorbance at 520nm decreases while the absorbance at 420nm and 620nm increases, due to the shift from monomeric to polymeric anthocyanins (Pascu 2005).

The highest values of color intensity were registered in the case of young red wines, in particular, for the young red wine from Cabernet Sauvignon grapes. The smallest values for IC were observed for aged red wines (for 12-PN the IC value was 6.34).

From the data showed in the Table 2 it was observed that, by ageing the chromatic structure was modified, because the red wines are in the stabilisation course.

The percent of color due to polymeric pigments increased and the percent of color due to monomeric and copigmented anthocyanins decreased. For wines ageing, the monomeric anthocyanins turn into polymeric anthocyanins with different moleculare mass. In practice, the phenomenon of red wine color evolutions called "*wine ageing*". The color stabilization can be attributed to diminishing of monomeric and copigmented anthocyanins content and formation of combinations between tannin and anthocyanins, polymeric pigments, and intermolecular associations which have the red color. The polymeric pigments are the very stable compounds responsible for color of red aged wine. Copigmented anthocyanins are the complexes that result by reaction between anthocyanins and copigments molecules. This phenomenon causes a enhancement of color due to the association of anthocyanins with co-factors.

The class of monomeric and copigmented pigments participate to the total young red wine color with a percent in the range 15-27%. The polymeric pigments, that are predominate, are the stable color compounds

in wine. From these value results that the wine color is in the course of stabilisation. The small value of copigmented anthocyanins founded in Pinot Noir wine is due this grape variety specific that contain a little amounts of cofactor (Boulton 1996). Therefore, the color percent due to copigmented anthocyanins is low in Pinot Noir wine (15.21% for young wine and 7.52% for aged wine). In the case of Cabernet Sauvignon wine, the color percent due to copigmented antocyanins varies in the range 26.77-16.8%. For the wine Pinot Noir, by ageing the color percent due to polymeric pigments was reached to 86.40%. From these data results that the color of wine Pinot Noir is more stable than Cabernet Sauvignon wine. The Cabernet Sauvignon will need the more time for ageing in the view of color stabilisation. This process could be extended during several months or even years. From the data showed in the Table 1 and 2 it can be observed that, through ageing, the decreasing of color intensity it was correlated with the diminishing of color percent due to copigmented and monomeric anthocyanins.

From the Table 3, on the base of I1 value results that the color of polymeric pigments represents 52-71% from total anthocyanins for Cabernet Sauvignon and 65-86% for Pinot Noir wine. On the basis of I2 values results that the polymeric pigments have replaced the monomeric anthocyanins in a measure in the range 47-60% for Cabernet Sauvignon wine and between 53-73% for Pinot Noir wine. On the basis of these indices, it can be observed the gradual conversion of monomeric anthocyanins to polymeric form during the wine ageing. From obtained "α"values results that, for Cabernet Sauvignon wine, 78-86% from total anthocyanins are in flavilium form, and for Pinot Noir wine, between 71-90%.

Table 1 Chromatic parameters of red wines determined by Glories method

Wine type	A_{420}	A_{520}	A_{620}	I.C	T	Chromatic structure		
						(%), yellow pigments	(%), red pigments	(%), blue pigments
0-CS	3.301	4.183	0.712	8.20	0.79	40.28	51.04	8.69
2-CS	3.365	3.974	0.735	8.07	0.85	41.68	49.22	9.10
6-CS	3.412	3.806	0.751	7.97	0.90	42.82	47.76	9.42
9-CS	3.452	3.701	0.772	7.93	0.93	43.56	46.70	9.74
12-CS	3.487	3.608	0.795	7.89	0.97	44.20	45.73	10.08
0-PN	2.613	3.418	0.482	6.51	0.76	40.12	52.48	7.40
2-PN	2.705	3.281	0.502	6.49	0.82	41.69	50.58	7.73
6-PN	2.785	3.146	0.513	6.44	0.89	43.22	48.82	7.96
9-PN	2.824	3.071	0.521	6.42	0.92	44.02	47.87	8.12
12-PN	2.839	2.901	0.600	6.34	0.98	44.77	45.75	9.47

Table 2. The evolution of monomeric anthocyanins content and the wines color structure during the ageing

Wine type	PA (%)	MA (%)	CA (%)	Monomeric anthocyanins (mg/L)
0-CS	52.05	21.18	26.77	187.93
2-CS	56.18	17.92	25.9	175.16
6-CS	65.15	15.88	18.97	151.22
9-CS	69.09	13.22	17.69	130.78
12-CS	71.52	11.68	16.80	114,21
0-PN	65.28	19.51	15.21	131.16
2-PN	70.14	15.65	14.21	122.08
6-PN	79.16	8.63	12.21	111.37
9-PN	83.09	8.40	8.51	100.62
12-PN	86.40	7.52	6.08	88.16

Table 3 The values for wine "chemical age" indices and for degree of pigment coloration

Wine type	Chemical age (I1)	Chemical age (I2)	α (%)
0-CS	0.5205	0.4712	78.61
2-CS	0.5618	0.5045	80.12
6-CS	0.6515	0.5473	82.36
9-CS	0.6909	0.5822	85.13
12-CS	0.7152	0.6071	86.33
0-PN	0.6528	0.5311	71.16
2-PN	0.7014	0.5516	75.22
6-PN	0.7916	0.6427	80.12
9-PN	0.8309	0.7216	85.47
12-PN	0.8640	0.7501	90.22

Conclusions

The ageing process affects the chromatic structure of red wines: the percent of yellow pigments from aged wines is higher than in the young wines for both red wines varieties. The values of color intensity decreased by ageing and the tonality values were increased. The highest value of color intensity was registered for the young red wine Cabernet Sauvignon (8.20), and the smallest values for tonality was registered for young red wine Pinot Noir (0.76). By ageing, the percent of color due to polymeric pigments increased and the percent of color due to monomeric and copigmented anthocyanins decreased. The percent of color due to copigmented anthocyanins is low in Pinot Noir wine (15.21% for young wine and 7.52% for aged wine), because these grapes contain a little amounts of cofactor. For Cabernet Sauvignon wine, the percent of color due to copigmented antocyanins is in the range 26.77-16.8%. By ageing of Pinot Noir wine, the color percent due to polymeric pigments was reached to 86.40%. The color of wine Pinot Noir is more stable than Cabernet Sauvignon wine. The values for I1 and I2 were increased by ageing.

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