THE INFLUENCE OF GRAPES VARIETY ON THE CHROMATIC STRUCTURE AND "CHEMICAL AGE" OF THE RED WINES

INFLUENȚA SOIULUI DE STRUGURI ASUPRA STRUCTURII CROMATICE ŞI "VÂRSTEI CHIMICE" A VINURILOR ROŞII

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Abstract.. *Red wines of Merlot and Pinot Noir from Recas vineyard (from the grapes harvested in 2005 years), young and aged in bottle were characterized due to their chromatic structure, monomeric anthocyanins content, chemical age and the degree of pigment coloration during the ageing (3, 6, 12 and 18 months). The chromatic structure was evaluated by percent of monomeric anthocyanins, copigmented anthocyanins and polymeric pigments from the wine color. The monomeric anthocyanins content decreased from 179.44 to 122.29 mg/L for Merlot wine and 132.81 to 85,72 mg/L for Pinot Noir wine. By ageing, the fraction of colour due to polymeric pigment increased on the basis of decreasing of colour percent due to monomeric and copigmented anthocyanins. During the ageing the value of indices on the basis was quantified the red wines chemical age was increasing for all analysed wines due to colour stabilisation. The value of these indices is very different in rapport with grapes variety and the age of analysed red wines.*

Rezumat.. *Au fos caracterizate din punct de vedere al structurii cromatice, conținutului de antociani monomeri, vârstei chimice şi gradului de colorare al pigmenților, vinuri roşii tinere şi invechite in butelii de sticlă (3, 6, 12 şi 18 luni). Vinurile au fost obținute în podgoria Recaş în anul de recoltă 2005 din struguri Merlot şi Pinot Noir. Structura cromatică s-a evaluat pe baza ponderii diferitelor categorii de pigmenți antocianici: monomeri, copigmentați şi polimeri din culoarea totală a vinului. Conținutul de antociani monomeri scade de la 179,44 la 122,29 mg/L în cazul vinului Merlot şi de la 132,81 to 85,72 mg/L în cazul vinului Pinot Noir. Prin învechire, fracțiunea de culoare datorată pigmenților polimeri creşte prin diminuarea ponderii antocianilor monomeri şi copigmentați la culoarea vinului. De asemenea, prin învechire, valoarea indicilor prin care se exprimă vârsta chimică a vinului au crescut pentru toate probele analizate, datorită stabilizării culorii. Valorile acestor indici au fost foarte diferite în raport cu soiul de struguri şi vârsta vinurilor analizate.*

The color of red wines is one of the most important qualities yet it has proven itself to be one of the most poorly understood. Red wine color has been elusive to define because it is controlled by many factors. The factors include anthocyanin content, co-pigmentation, procyanidins, acetaldehyde, free bisufite, acids and polymeric pigments which all contribute to the color of red wines. This level of complexity makes red wine color both intriguing and difficult to understand. Over 30 years ago Somers observed as red wines aged they went through a change in spectral characteristics [12]. The wine color

changed from red to brick red as it aged. Malvidin-3-glucoside, the most abundant anthocyanin, principally responsible for wine's red color had declined over time [11, 12]. The remaining colored compounds had unknown structures but were defined by their ability to resist bisulfite bleaching and became known as polymeric pigment. Work over the last thirty years trying to define the chemical structures of polymeric pigment has yielded very few conclusive results. Some of the results have demonstrated that anthocyanins are not lost during wine aging; in fact anthocyanins form covalent adducts with tannin, undergo derivatization by keto-acids, and are linked to tannins by acetaldehyde. The color of red wine derives from the phenolic class anthocyanidins. As a wine ages, this process of direct condensation causes anthocyanidin pigment to accumulate in the polymeric form, leading to improved color stability [9]. Polymeric pigments are known to have different characteristics than malvidin-3-glucoside. They are resistant to bisulfite bleaching and are not as pH dependent as malvidin-3-glucoside. These two combined features spawned the term "stable color." The olymeric pigment is more resistant to the change in pH than total anthocyanins. Somers estimated that polymeric pigments retained more than 50% of their maximum color at wine pH, whereas anthocyanin only retained about 23% of their color [12]. This demonstrates that at wine pH a significant portion of the color is coming from polymeric pigment.

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. This phenomenon causes a hyperchromic effect and a bathochromic shift. The most important copigments in wine are expected to be the flavan-3-ols and flavanols, hydroxycinnamic acids and even the antocyanins molecules [1,5]. As wine ages the free anthocyanins react to form polymeric pigments, this shifts the equilibrium to replenish free anthocyanins by releasing them from the co-pigmented stacks. So therefore, as wine ages the stacks tend to break-up and co-pigmentation decreases as a result of this equilibrium [4]. During the wine ageing in bottle take place the structural changes, and one of the most studied of those changes concern red wine colour evolution, called wine ageing. In the ageing time, 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 [6-10]. 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 equilibrium and the different bleaching effect of SO_2 on monomeric and polymeric anthocyanins, as well as the preferential binding of SO_2 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 [12].

MATERIALS AND METHODS

The sample for analysis. In this study were analyzed red wines of Merlot (M) and Pinot Noir (PN) harvested in 2005, from Recas vineyard. Five red wines categories were analyzed: young red wines, immediately after conditioning (0-M, 0-PN), and aged in bottle for: 3, 6, 12 and 18 months, respectivelly: 3-M, 3-PN, 6-M, 6-PN, 12-M, 12-PN, 18-M, 18-PN.

Reagents and equipment. All chemicals and reagents were analytical grade or pure quality purchased from Merck, Fluka, Sigma and Chimopar. For color analysis it was used Specord 205 by Analitik Jena.

The pH-differential method [2] it was used for *total monomeric anthocyanin determination.* Monomeric anthocyanins pigments (mg/L) will be calculated as cyanidin-3-glucoside.

Glories method [3] it was used for *chromatic parameters evaluation.* By this method, followed parameters it were quantified: color intensity (IC), tonality (T) and yellow, red and blue pigments contribution, expressed in percent (%) to the wine color.

The red wine color analysis was effectuated in accord with Boulton method [1]. The red wine color fraction due to monomeric, polymeric and copigmented anthocyanins was in order: MA (%), PA (%) and CA (%).

The red wine "chemical age" is quantified by two indices. 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 [12].

RESULTS AND DISCUSSIONS

From the Table 1 it can be observed the chromatic structure obtained by Glories method. From these data results that, during the wine ageing, the yellow pigments percent increased and the red pigments percent decreased, but the both pigments categories are more equilibrated in the aged wines. The class of blue pigments participate to the red wines color in low measure (in the range 8.43-9.26% for M and 7.93-9.55% for PN). The most red pigments percent were registered in the case of yong red wines. The yellow pigment class contributed with less than 45% to the red wine colour. By ageing, the absorbance values at λ=520 nm decreased, accompanied of the increasing of absorbance at λ=420 nm and 620 nm. This phenomenon is responsible for shift of anthocyanins from monomeric to polymeric form [11].

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-M	3.231	4.298	0.693	8.22	0.75	39.30	52.27	8.43
3-M	3.255	4.187	0.705	8.15	0.78	39.95	51.39	8.65
6-M	3.306	4.103	0.713	8.12	0.81	40.70	50.52	8.78
12-M	3.349	4.007	0.724	8.08	0.84	41.45	49.59	8.96
18-M	3.563	3.704	0.742	8.01	0.96	44.49	46.25	9.26
0-PN	2.566	3.379	0.512	6.46	0.76	39.74	52.33	7.93
3-PN	2.629	3.247	0.519	6.40	0.81	41.11	50.77	8.12
6-PN	2.677	3.153	0.536	6.37	0.85	42.05	49.53	8.42
12-PN	2.732	3.078	0.548	6.36	0.89	42.97	48.41	8.62
18-PN	2.773	2.805	0.589	6.17	0.99	44.97	45.48	9.55

The highest values of colour intensity were registered in the case of young red wines, in particular, for the Merlot young red wine (8.22). The smallest values for IC were observed for aged red wines (for 18-PN the IC value was 6.17). By ageing the chromatic structure was modified, because the colour stabilisation phenomenon. From the data present in the table 2 results that, the monomeric anthocyanins content decreased from 179.44 to 122.29 mg/L for Merlot wine and 132.81 to 85,72 mg/L for Pinot Noir wine.

Table 2.

The wines color structure evolution during the ageing

Wine type	PA (%)	MA (%)	CA (%)	Monomeric anthocyanins (mg/L)
0-M	10.33	54.18	35.49	179.44
3-M	18.71	48.92	32.37	167.44
6-M	27.96	43.88	28.16	153.27
12-M	44.55	32.68	22.77	135.18
18-M	53.99	26.82	19.19	122.29
0-PN	26.68	50.61	22.71	132.81
3-PN	34.39	46.16	19.45	124.39
6-PN	51.1	32.52	16.38	115.83
12-PN	53.8	34.17	12.03	97.38
18-PN	67.96	21.17	10.87	85.72

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

The class of monomeric pigments participate in the highest measure to the young red wines and their contribution decrease in raport with ageing. From the data showed in the table 2 it can be observe that the copigmented anthocyanins are distroyed by ageing. The polymeric pigments are present in a low measure in the young red wine Merlot (10.33) and the participation percent to the total red wine color for this category increases by ageing. From these value results that the young red wines colour is unstable. The time for colour stabilisation is different in raport with grape variety, maturation and ageing conditions. The small value of copigmented anthocyanins founded in Pinot Noir is due to grape variety specific that contain a little amounts of cofactor [1]. Therefore, the colour percent due to copigmented anthocyanins is low in

young wine Pinot Noir (22.71%). In the case of Merlot, the colour due to copigmented antocyanins is in the range 19.19-35.49%. By ageing of Pinot Noir wine, the color due to polymeric pigments increased until 67.96%. The polymeric pigments is the stable compounds responsible of the aged red wine. From these data results that the Pinot Noir colour is more stable than Merlot. The Merlot requires more ageing time for colour 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, by ageing, the colour intensity decreasing was correlated with the diminishing of copigmented and monomeric anthocyanins.

The data of the Table 3, showed the "chemical age" evolution through red wine ageing. This parameter were quantified by two indices I1 and I2. The ratios are close to zero in new wine, but increase to about 1.0 and 0.9, respectively, for wines older than 10 years.

Table 3

Chromatic The values of "chemical age" indices and degree of pigment coloration

Wine type	Chemical age (I1)	Chemical age (I2)	α (%)
0-M	0.1033	0.2734	46.78
3-M	0.1871	0.35.15	52.18
6-M	0.2796	0.41.30	60.42
12-M	0.4455	0.5312	71.33
18-M	0.5399	0.6487	82.38
0-PN	0.2668	0.3578	33.54
3-PN	0.3439	0.4236	41.32
6-PN	0.5110	0.4997	48.73
12-PN	0.5380	0.6669	57.46
18-PN	0.6796	0.7743	68.19

It can be observed that I1 represent the measure on the base it we can be apreciatte the percent of polymeric pigments from red wines. From these data results that the color due to polymeric pigments represents 5.99% from colour due to total anthocyanins for Merlot and 67.96% for Pinot Noir. On the basis of I2 values results that the polymeric pigments replaced the monomeric anthocyanins in a measure in the range 27.34-64.87% for Merlot and between 35.783-77.43% for Pinot Noir. On the basis of these indices, it can be observed the gradual conversion of monomeric anthocyanins to polymeric form during the wine ageing. The "α"values indicate that, 46-82% from total anthocyanins are in flavilium form for Merlot, and in the range 33-68% for Pinot Noir wine.

CONCLUSIONS

The color structure of red wines were changed during the ageing. In the ageing wines the yellow pigments percent is higher than in the young wines so Merlot and Pinot Noir. During the ageing, the colour intensity decreased and the tonality increased. The highest value of colour intensity was registered for the young red wine Merlot (8.22) and the smallest values for 18-PN (6.17). In the tonality case, the highest value was registered for 18-PN (0.99) and the smallest for 0-M (0.75). By ageing, the percent

of colour due to polymeric pigments increased and due to monomeric and copigmented anthocyanins decreased. The percent of colour due to copigmented anthocyanins is lower in Pinot Noir so young wine (22.71%) and aged wine (10.87%), because the Pinot Noir grapes contain a little amounts of cofactor. For Merlot wine, the percent of colour due to copigmented antocyanins is in the range 35.49-19.19%. In the case of Pinot Noir, during the ageing for 18 months, the percent of colour due to polymeric pigments increased to 67.96%. By ageing, the values for I1 and I2 increased in different manner in accord with the grape variety; the stabilisation time for Pinot noir colour is lower comparativelly with Merlot wine.

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