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Changes in the chromatic properties of red wines from *Vitis vinifera* L. cv. Merlot and Pinot Noir during the course of aging in bottle

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Abstract

Differences in color of red wines from *Vitis vinifera* L. cv. Merlot and Pinot Noir grapes (vintage 2005, winemaking center Recas) were examined during the course of aging in bottle for a period of two years. The parameters evaluated in our study included chromatic parameters (color intensity and tonality), color structure (color due to monomeric anthocyanins, polymeric pigments and copigmented anthocyanins), monomeric anthocyanins content, "chemical age" and ionization of anthocyanins for red wines as young and after 4, 10, 18 and 24 months of aging in bottle. During the aging, the color intensity decreased and the tonality increased. The highest value of color intensity was registered for the young red wine Merlot (8.708) and the lowest values for Pinot Noir aged for 24 months (6.611). For color tonality, the highest value was recorded for Merlot wine after ageing in bottles for 24 months (0.96) and the smallest for young red wine Merlot (0.64). During the course of aging in bottle, the monomeric anthocyanins content decreased from 179.44 to 122.29 mg L^{-1} for Merlot wine and from 132.81 to 85.72 mg L^{-1} for Pinot Noir. By ageing, the fraction of color due to polymeric pigment increased on the basis of decreasing of color percentage due to monomeric and copigmented anthocyanins. Percentage of color assigned of copigmented anthocyanins after ageing in bottles for 24 months decreased for both analyzed wines from 22.71% to 10.87% for Pinot Noir wine and from 35.49% to 19.19% in the case of Merlot wine. Pinot Noir aged in bottle for 24 months showed the greatest contribution of polymeric pigments (67.96%) to the wine color. The "chemical age" of the wines, assessed on the basis of I_1 and I_2 indices, increased for both analyzed red wines but in different manner according to the color stabilization phenomenon. The values of these indices are very different in rapport with grapes variety and the aging time. The results are important in anticipation of the red wine color evolution during the course of aging. It outlines the idea that the red wine color can be influenced by the choosing of the aging time.

Key words: Red wine, Merlot, Pinot Noir, chromatic parameters, anthocyanins, aging process, "chemical age".

Introduction

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. The color of red wine derives from the phenolic class of anthocyanidins and has been elusive to define because it is controlled by many factors, among the more important being grape variety, oenological treatments, temperature and aging period. Also, a big importance on the color of red wines presents the anthocyanins content, copigmentation phenomenon, procyanidins, acetaldehyde, free bisulfite, acids, polymeric pigments and tannins content [6, 7, 9, 20]. This level of complexity makes red wine color both intriguing and difficult to understand. Bottle aging of red wine is a result of many chemical reactions taking place over time. Over 30 years ago Somers observed as red wines aged they went through a change in spectral characteristics [16]. Malvidin-3-glucoside, the most abundant anthocyanin, principally responsible for wine's red color had declined over time [10, 13, 18]. The remaining colored compounds had unknown structures but were defined by their ability to resist bleaching bisulfite and became known as polymeric pigment. Work over the last thirty years trying to define the chemical structures of polymeric pigments has yielded very few conclusive results. Some of the results 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. As a wine ages, this process of direct condensation causes anthocyanidin pigment to accumulate in the polymeric form, leading to improved color stability. 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 polymeric pigment is more resistant to the change in pH than total anthocyanins [8, 12, 19]. Somers estimated that polymeric pigments retained more than 50% of their maximum color at wine pH, whereas anthocyanins only retained about 23% of their color [17]. 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 flavan-3-ols and flavanols, hydroxycinnamic acids and even anthocyanin molecules [2, 3, 11]. As wine ages the free anthocyanins react to form polymeric pigments, this shifts the equilibrium to replenish free anthocyanins by releasing them from the copigmented stacks. Therefore, as wine ages the stacks tend to break-up and co-pigmentation decreases as a result of this equilibrium [11]. During aging of the wine in bottles structural changes take place, and one of the most studied of those changes concerns red wine color evolution. 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 [1, 15]. On this basis, we investigated the changes of chromatic characteristics of red wine stored in bottles with the aging time since aging in bottle is a very important step in red wine manufacture and great physical and chemical changes take place during this period.

Material and Methods

Samples: Red wines of Merlot (M) and Pinot Noir (PN) were obtained in winemaking center Recas (Western part of Romania) from the grapes harvested in 2005. Five red wine categories were investigated: young wines (0-M and 0-PN) and wines aged in bottles at 18°C and kept in the dark for 4, 10, 18 and 24 months: 4-M, 4-PN, 10-M, 10-PN, 18-M, 18-PN, 24-M, 24-PN. The storage area for wine must be dark because ultraviolet (UV) light will damage wine by causing the degradation of otherwise stable organic compounds found in red wine. The initial wines (0-M and 0-PN) were elaborated following the same winemaking techniques.

Determination of chromatic parameters: Chromatic parameters were determined according to Glories method [5]. The color intensity (IC), expressed in AU-absorbance units, was given by the sum of the absorbance to 420, 520 and 620 nm or A_{420}, A_{520} and A_{620}. The color tonality or hue (T) was expressed by the ratio of the A_{420} and A_{520}. Chromatic structure of wine was expressed by the yellow, red and blue pigment contribution (%) to the red wine color.

Red wine color analysis: Color analysis was done spectrophotometrically in accordance with Boulton's method [3] using the UV-VIS spectrophotometer (Analytic Jena Specord 205). For each wine the following parameters were measured by spectrophotometric assay: fraction of color due to monomeric anthocyanins (MA), copigmented anthocyanins (CA) and polymeric pigments (PP).

The samples were filtered and the wine pH was adjusted to 3.60 before analysis, 0.1 mL of 10% (v/v) acetaldehyde was added to 5.0 mL of wine and after 45 min at room temperature the absorbance was measured at 520 nm in a 1mm cuvette. Reading was multiplied by10.2. This is $A_{520}^{CH_3CHO}$ and represents the total color of the wine. To another 5.0 mL of wine, 0.1 mL of 3% potassium metabisulfite was added, and then the value of absorbance was measured at 520 nm in a 1 mm cuvette. Reading was multiplied by 10.2. This is $A_{520}^{SO_2}$ and represents the color due to polymeric pigments.

For co-pigmentation evaluation, to a 10 mm cuvette containing 1.9 mL of buffer, 0.1 mL of wine was added and after 10 minutes the value of absorbance was measured at 520 nm. Reading was multiplied by 20. This is A^{20} and represents the color due to monomeric and polymeric pigments. The difference $A_{520}^{CH_3CHO} - A_{20}$ represents the color due to copigmented anthocyanins and the difference $A_{20} - A_{520}^{SO_2}$ the color due to monomeric anthocyanins. The percentage of each fraction of pigment color assigned was calculated as the ratio of color due to the fraction in question and the total wine color multiplied by 100.

Evaluation of "chemical age": Evaluation was done on the basis of two indices I_1 and I_2, according to Somers and Evans method [16]. To 0.1 mL of wine, 10 mL of 1 N HCl was added and the value of absorbance was measured at 520 nm in a 10 mm cuvette after 60 minutes. Reading was multiplied by 101. This is A_{520}^{HCl}. At this pH, all anthocyanins are in flavilium form. Somers and Evans [15] proposed the following relationships for "chemical age" evaluation: $I_1 = \frac{A_{520}^{SO_2}}{A_{520}^{CH_3CHO}}$ and $I_2 = \frac{A_{520}^{SO_2}}{A_{520}^{HCl}}$

Determination of anthocyanin ionization degree: The α (%) gives a measure of the amounts of monomeric anthocyanins in the red colored form (carbonium ion) and was calculated as:

$$\alpha(\%) = \frac{A_{520(pH=3.6)} - A_{520}^{SO_2}}{A_{520}^{HCl} - \frac{5}{3} \times A_{520}^{SO_2}} \times 100$$

The $A_{520(pH=3.6)}$ can be obtained by adjusting the wine pH to 3.6 and measuring the absorbance at 520 nm [16]. In accord with Bakker *et al.* [1], the $\frac{5}{3} \times A_{520}^{SO_2}$ term represents the absorbance due to polymeric pigments at pH =1.

Determination of total monomeric anthocyanins content: Total monomeric anthocyanins were quantified by the pH-differential method [4] Anthocyanin pigments undergo reversible structural transformations with a change in pH. The colored oxonium form predominates at pH = 1.0 and the colorless hemiketal form at pH=4.5. The anthocyanin content (mg L^{-1}) was calculated as cyanidin-3-glucoside.

Results and Discussion

For simple and total characterization of Merlot and Pinot Noir red wine color, on the basis of optic densities at bandwidth characteristics, we foresaw a series of indices, out of which we recall color intensity, color tonality or hue and the chromatic structure expressed by the weight of every color. Red wine color can be evaluated by adding the three components: red, yellow and blue. The yellow component (absorbance to 420 nm or A_{420}) is ascribed to tannin and anthocyanin degradation products. The red component (A_{520}) is ascribed to the free anthocyanins under flavilium cations form and anthocyanins-tannins combinations in older wines. The blue component (A_{620}) is ascribed to free anthocyanins under the chinonic form or combinations between tannins and anthocyanins[14].

Table 1 shows the chromatic structure obtained by Glories method. During the wine aging, the percentage of color due to

Table 1. The changes in the chromatic parameters of red wines during the course of aging.

Wine sample	A_{420}	A_{520}	A_{620}	IC	T	Chromatic structure (%) yellow	(%) red	(%) blue
0-M	3.117	4.898	0.693	8.708	0.64	35.79	56.25	7.96
4-M	3.184	4.476	0.705	8.365	0.71	38.06	53.51	8.43
10-M	3.352	3.973	0.713	8.038	0.84	41.70	49.43	8.87
18-M	3.449	3.831	0.724	8.004	0.90	43.09	47.86	9.05
24-M	3.528	3.671	0.742	7.941	0.96	44.43	46.23	9.34
0-PN	2.711	3.979	0.512	7.202	0.68	37.64	55.25	7.11
4-PN	2.749	3.647	0.519	6.915	0.75	39.75	52.74	7.51
10-PN	2.777	3.353	0.536	6.666	0.83	41.66	50.30	8.04
18-PN	2.832	3.278	0.548	6.658	0.86	42.54	49.23	8.23
24-PN	2.903	3.119	0.589	6.611	0.93	43.91	47.18	8.91

Table 2. Dynamics of red wines color structure during the course of aging in bottle.

Wine type	PP (%)	MA (%)	CA (%)
0-M	10.33	54.18	35.49
4-M	18.71	48.92	32.37
10-M	27.96	43.88	28.16
18-M	44.55	32.68	22.77
24-M	53.99	26.82	19.19
0-PN	26.68	50.61	22.71
4-PN	34.39	46.16	19.45
10-PN	51.1	32.52	16.38
18-PN	53.8	34.17	12.03
24-PN	67.96	21.17	10.87

yellow component increased and the fraction of color due to red component decreased, but the chromatic structure was more equilibrated in the aged red wines. The blue component participates to the red wines color in low measure (in the range of 7.96-9.34% for Merlot and 7.11-8.91% for Pinot Noir wine). In the case of young red wines, the largest share of color is attributed to red components and the yellow component contributed with less than 40% to the red wine color. It can be said that during aging the red wine color components recorded changes: the values registered for A_{520} decreased, accompanied by increasing of A_{420} and A_{620}. The highest values of color intensity were registered in the case of young red wines, in particular, for the Merlot young red wine (8.708). The smallest values for IC were observed for aged red wines (for 18-PN the IC value was 6.611). The results presented in Table 1 reveal the fact that the color intensity drops for aged red wines, while the wine color hue intensifies. The IC diminuation is due to the disappearance of monomeric anthocyanins in the aging time. In this phase, due to the fact that A_{420} is increasing and A_{520} is decreasing, the color tonality is emphasized, so that it increased from 0.64 and 0.68, values which correspond to young red wines 0-M, respectively 0-PN, to 0.96 and 0.93, values corresponding to wines aged for 24 months. The decrease of A_{520} is due to condensed tannins precipitation.

The decrease of monomeric anthocyanins content in the aging time is shown in the Figs. 1 and 2. The monomeric anthocyanins content decreased from 179.44 to 122.29 mg L^{-1} for Merlot wine and from 132.81 to 85.72 mg L^{-1} for Pinot Noir wine.

Total wine color was an aggregate number of three components: copigmentation, free anthocyanins or monomeric anthocyanins and polymeric pigment (Table 2). The contribution to color due to copigmented anthocyanins in these aged red wines remained at 19.19% for 24-M and 10.87% for 24-PN and monomeric anthocyanins at 26.82% for 24-M and 21.17% for 24-PN. From these data results that during aging the fraction of color due to polymeric pigments increased. In parallel, the color assigned monomeric and copigmented anthocyanins decreased with aging time advance. In this period, the monomeric anthocyanins turn into polymeric anthocyanins with different molecular mass. In practice, the phenomenon of red wine color evolution is known as the aging of wine [16]. These changes are attributed to the red wine color stabilization.

The color stabilization can be attributed to diminishing of monomeric and copigmented anthocyanin contents. As a result of these changes the combinations between tannin and anthocyanins, polymeric pigments and intermolecular associations that have red color appear. The polymeric pigments are very stable compounds responsible for color of aged red wine [1, 10, 13]. Copigmented anthocyanins are the complexes that result by reaction between anthocyanins and copigment molecules. This phenomenon causes an enhancement of young red wine color due to the association of anthocyanins with co-factors with the effect of a bathochromic and a hyperchromic shift. These associations cause the pigments to exhibit far greater color than it would be expected from their concentration [2, 3, 16].The small value of copigmented anthocyanins in the case of 0-PN (22.71% comparatively with 34.49% registered for 0-M) is due to the specifics of Pinot Noir grape variety that contains a little amount of cofactor (especially flavan-3-ols and flavanols). From Table 2 it can be observed that the copigmented anthocyanins are destroyed by ageing. The co-pigmented anthocyanins also act as a reservoir for free flavylium ion, and we see a decrease in the contribution of co-pigmentation to color over time. Therefore, as wine ages the stacks tend to break-up and co-pigmentation decreases as a result of this equilibrium [3]. The polymeric pigments are present in a low measure in the young red wine Merlot (10.33) and their contribution to the total red wine color increases with aging in the bottle. The time for color stabilization is different in rapport with grape variety, maturation and ageing conditions [12, 14]. Lower degree of copigmentation identified for Pinot wines is due to the grapes of this variety which contain a small quantity of cofactor [2]. Percentage of color assigned copigmented anthocyanins after ageing in bottles for 24 months decreases for both analyzed wines from 22.71% to 10.87% for Pinot Noir wine and from 35.49% to 19.19% in the case of Merlot wine. By aging of Pinot Noir wine, the color due to polymeric pigments increased until 67.96%. From these data

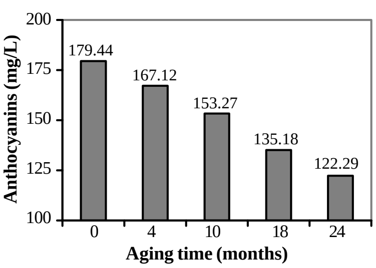

Figure 1. Evolution of monomeric anthocyanins content during the course of Merlot wine aging.

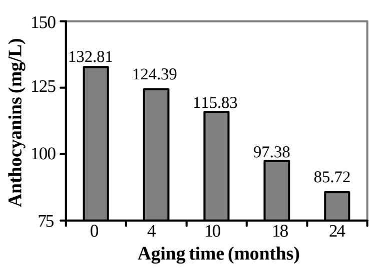

Figure 2. Evolution of monomeric anthocyanins content during the course of Pinot Noir wine aging.

it results that the Pinot Noir color is more stable thanthat of Merlot. Merlot requires more ageing time for color stabilization. This process could be extended during several months or even years. From the data presented in the Tables 1 and 2 we can see that by ageing the decrease of color intensity was correlated with the diminishing of copigmented and monomeric anthocyanins.

Fig. 3 and 4 present the "chemical age" evolution registered by ageing wine. The so-called "chemical age" of wine was quantified by two indices, I_1 and I_2. 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 [16]. Based on the I_1 values the contribution of polymeric pigments to total red wine color can be appreciated. For the young wines, I_1 and I_2 showed reduced values for both 0-M and 0-PN wines and, once with the ageing the value of these indices reached to 0.54 and 0.51, for 24-M 0.68 and 0.64 for 24-PN. These data show that after 24 months of aging, the color due to polymeric pigments represents 54% from the total wine color for wine Merlot and 68% for wine Pinot Noir. On the basis of I_2 values, the color due to polymeric pigments represents 22-51% from the color of anthocyanins in flavilium form for Merlot wine and 32-64% for Pinot Noir. On the basis of these indices, it can be observed the gradual conversion of monomeric anthocyanins to polymeric form in relation to wine aging.

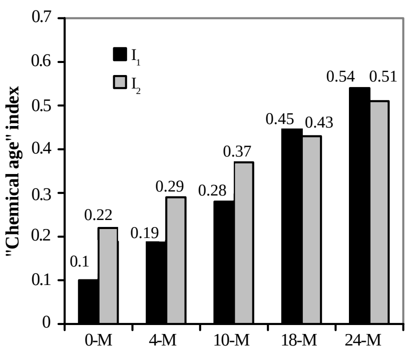

Figure 3. Evolution of "chemical age" indices for Merlot during aging in bottle.

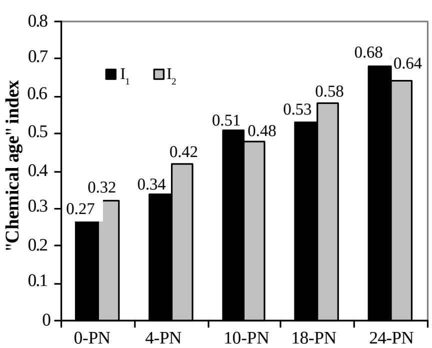

Figure 4. Evolution of "chemical age" indices for Pinot Noir during aging in bottle.

Fig. 5 shows that in the ageing time the degree of pigment coloration (α) registered a significant increase from 46.79% for 0-M to 75.37% for 24-M and from 33.545 for 0-PN to 68.19 for 24-PN. This value indicates the percentage of anthocyanins found in the flavilium or ionized form, being associated with the power of anthocyanin coloration.

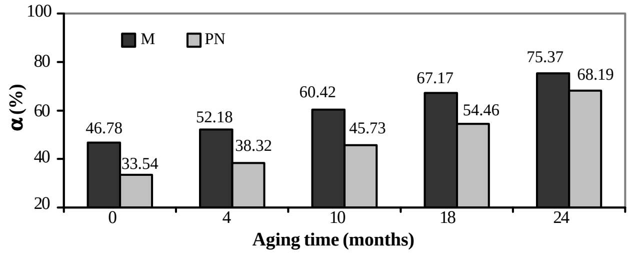

Figure 5. The changes of degree of anthocyanin ionization from Merlot and Pinot Noir wine during the course of aging.

Conclusions

The color components of red wines were changed during the aging: the percentage of color due to polymeric pigments increased and due to monomeric and copigmented anthocyanins decreased. The polymeric pigments, that are prevalent in the aged wines, are the stable color compounds. Along with the aging process forward, the proportion of yellow pigments contributed most to the total wine color, while red pigments contribution was reduced. During the ageing of both Merlot and Pinot Noir red wines, the color intensity decreased and the tonality increased.The magnitude of these changes is influenced by the grapes variety and the aging time. The color intensity is correlated with quantitative variation of free anthocyanin content. For young Merlot and Pinot Noir red wines, copigmentation seems to result in both a higher pigment concentration and an enhancement in the color of those pigments. The "chemical age" of the wines assessed on the basis of I_1 and I_2 indices proportionally increases with the color evolution of red wine to form more stable chemical structure. From these data we can say that red wine color stabilization involves transformation of free anthocyanins into polymeric forms. This process can continue with increasing aging time. The class of monomeric anthocyanins participates in the highest measure to the young red wines color and their contribution decreases in rapport with the aging time. Polymerization reactions of anthocyanins prevailed over pigment degradation reactions, and copigmentation was still relevant after two years of bottle aging. These might provide a substantial basis for the further researches on control of wine color during winemaking.

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References

[1]Bakker, J., Preston, N. W. and Timberlake, C. F. 1986. The determination of anthocyanins in aging red wines: Comparisons of HPLC and spectral methods. Am. J. Enol. Vitic. **37**:121-126.

[2]Boulton, R. 2001. The copigmentation of anthocyanins and its role in the color of red wine: A critical review. Am. J. Enol. Vitic. **52**(2):67-87.

[3]Boulton, R. 1996. A method for the assessment of copigmentation in red wines. Am. J. Enol. Vitic. **47**:346.

[4]Giusti, M. M. and Wrolstad, R. E. 2001. Unit F1.2: Anthocyanins.

Characterization and measurement with UV-visible spectroscopy. In Wrolstad, R. (ed.). Current Protocols in Food Analytical Chemistry. John Wiley & Sons, New York, pp. 1-13.
[5]Glories, Y. 1984. La couleur des vins rouges. Conn. Vigne Vin. **18**(4):253-271.
[6]Gonzalez Neves, G., Gomez Cordoves, C. and Barreiro, L. 2001. Anthocyanic composition of Tannat, Cabernet Sauvignon and Merlot young red wines from Uruguay. J. Wine Res. **12**:125-133.
[7]Liao, H., Cai, Y. and Haslam, E. 1992. Polyphenol interactions. Anthocyanins: Co-pigmentation and colour changes in red wines. J. Sci. Food Agric. **59**:299-305.
[8]Maletic, E., Kontic, J. K., Preiner, D., Jeromel, A., Patz, C. D. and Dietrich, H. 2009. Anthocyanin profile and antioxidative capacity of some autochthonous Croatian red wines. Journal of Food, Agriculture & Environment **7**(1):48-51.
[9]Mateus, N., Silva, A., Freitas, V. and Vercauteren, J. 2001. Occurrence of anthocyanins-derived pigments in red wines. J. Agric. Food Chem. **49**:4836-4840.
[10]Mazza, G., Fukumoto, L., Delaquis, P., Girard, B. and Ewert, B. V. 1999. Anthocyanins, phenolics, and color of Cabernet Franc, Merlot, and Pinot Noir wines from British Columbia. J. Agric. Food Chem. **47**(10):4009-4017.
[11]Mirabel, M. and Saucier, C. 1999. Copigmentation in model wine solutions: Occurrence and relation to wine aging. Am. J. Enol. Vitic. **50**:211-218.
[12]Monagas, M., Martín-Álvarez, P. J., Bartolomé, B. and Gómez-Cordovés, C. 2006. Statistical interpretation of the color parameters of red wines in function of their phenolic composition during ageing in bottle. Eur. Food Res. Tech. **222**(5-6):702-710.
[13]Ollala, M., Lopez, M. C., Lopez-Garcia, H., Villalon, M. and Gimwerez, L. 1996. Chromatic characterization of the wine produced in the Spanish region Alpujara-Contraviesa. Ars. Pharm. **37**(1):53-62.
[14]Pascu, L. 2005. Red wine quality establishing on the basis of chromatic properties. Rev. Chim. **56**(7):703-707.
[15]Pérez-Maragińo, S. and Gonzáles-San José, M. L. 2004. Evolution of flavanols, anthocyanins and their derivates during the aging of red wines, elaborated from grape harvested and different stages of ripening. J. Agric. Food Chem. **52**:1181-1189.
[16]Somers, T. C. and Evans, M. E. 1974. Wine quality: Correlations with colour density and anthocyanin equilibria in a group of young red wines. J. Sci. Food Agric. **25**:1369-1379.
[17]Somers, T. C. and Evans, M. E. 1986. Evolution of red wines. Ambient influences on colour composition during early maturation. Vitis **25**:31-39.
[18]Revilla, E., García-Beneytez, E., Cabello, F., Martín-Ortega, G. and Ryan, J. M. 2001. Value of high-performance liquid chromatographic analysis of anthocyanins in the differentiation of red grape cultivars and red wines made from them. J. Chromat. **915**:53-60.
[19]Versari, A., Parpinello, G. P. and Mattioli, A. U. 2007. Characterisation of colour components and polymeric pigments of commercial red wines by using selected UV-VIS spectrophotometric methods. S. Afr. J. Enol. Vitic. **28**(1):6-10.
[20]Vivar-Quintana, A. M., Santos-Buelga, C., Francia-Aricha, E. and Rivas-Gonzalo, J. C. 2002. Anthocyanin derived pigments and colour of red wines. Anal. Chim. Acta **458**:147-155.