THE COLOR ANALYSIS AND ANTIOXIDANT PROPERTIES FOR RED WINE FROM SANGIOVESE GRAPES

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Were characterized in relation to the antioxidant and chromatic properties the red wines processing from Sangiovese grapes variety harvested in 2005. In this sense was determined the total antioxidant capacity, total polyphenols content, as the main chromatic characteristics resulted after red wines color analysis: monomeric anthocyanin pigment, fraction of color due to polymeric, monomeric and copigmented anthocyanins, color intensity, tonality, the hue, "chemical age" and the degree of pigments coloration. Total antioxidant capacity it was determined by FRAP method (expressed as mM Fe^{2+}/L). The polyphenols content it was determined by Folin-Ciocalteu method (expressed such as mM acid gallic/L). The chromatic parameters were obtained by standardized method and Glories method; monomeric antocyanins it was calculated by differential pH method and color composition by Boulton method. From the obtained data, it can be was observed that pigments structure reflect exactly the chromatic properties of analyzed red wines. For all Sangiovese red wines it was obtained the red shade and the chromatic structure was equilibrated. The values of color intensity were in the range 5.6-7.6, tonality between 0.89-0.95, and the values for monomeric anthocyanins content were situated between 41-85 mg/L. The fraction of color due to polymeric pigment was in the range 73-90%, fraction of color due to copigmented anthocyanins 6.5-15% and the fraction of color due to free anthocyanins between 4-12%. The chemical ages was characterized by two indices that give a measure of the extent to which polymeric pigments have replaced monomeric anthocyanins during the wine evolution. The degree of pigments coloration gives a measure of the amount of pigment in the colored form (for our case, this parameter present the values in the range 74-94%). The values for total antioxidant capacity were situated between 14-15.5 mM Fe^{2+}/L, the values for polyphenols between 10-13 mM gallic acid/L. The total antioxidant capacity has the same direction of evolution with polyphenols content. It was observed a linear correlation between antioxidant capacity and total polyphenols content (the correlation coefficient is R=0.98635).

***Keywords**: Sangiovese, color composition, chemical age, pigments, polyphenols, total antioxidant capacity.*

The establishing of chromatic characteristics of red wine is very important because these properties have a decisive role about the wine quality. Polyphenols from wine, even in small concentrations, have a great antioxidant capacity, assuring protection against cardiovascular diseases and cancer [2,6,7]. The majority of Romanian vineyards have heliothermic resources that permits the accumulation in grapes of an important content of phenolic compounds, but wine's antioxidant activity must be appreciated by taking in view the complex mixture of phenolic compounds and other compounds that can act as antagonist or in synergic way. At international level were made researches that certifies the fact that exist a strong correlation between polyphenols content and antioxidant capacity of wine [3,8,11]; also, it was established that origin place and grape's variety have a prominent influence about antioxidant and chromatic of red wines [6,8].

We know that for the wine color are responsible the monomeric or free anthocyanins, copigmented anthocyanins and polymeric pigments. Copigmentes anthocyanins are the complexes that result by reaction between anthocyanins and copigments molecules. Copigmentation is the enhancement of color due to the association of anthocyanins with co-factors. Co-factors are colorless compounds that when added to a solution containing anthocyanins will act to enhance the color of the solution. They can be one of several compounds: flavonoids, alkaloids, amino acids, metals or anthocyanins. This phenomenon causes a hyperchromic effect and a bathochromic shift. The hyperchromic effect is an increase in color intensity and the bathochromic shift results in a shift of the wavelength of maximum absorbance. Co-pigmentation permits greater extractability of anthocyanins and cofactors from the grape skins. There is an equilibrium that exists between the grape, the free anthocyanins and cofactors, and the co-pigmented stacksDuring winemaking and aging, anthocyanins from the skins are thought to react with tannins from the skins and seeds to give rise to polymeric pigments, the stable color compounds in wine [7,10].

Red wine is a complex solution and although its colour can be meaningfully measured rather easily by spectral techniques, the composition of the wine colour is more difficult to determine. Based on an understanding of the pH equilibria 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, Somers & Evans developed a set of spectral measures to evaluate young wines and determine the amount of monomeric, polymeric and copigmented anthocyanins, the chemical age of the wine and the degree of pigment coloration. The fraction of color due to each pigments categories will be determined throught rapport between fraction color and total color of wine [10].

In this study were characterized in relation to the antioxidant and chromatic properties the red wines processing from Sangiovese grapes variety harvested in 2005 in Italy (regions Romagna and Marche).

MATERIAL AND METHOD

In the present research, total five wine bottles were investigated. These wines were processed of Italy, from Sangiovese grapes variety harvested in 2005 year from Romagna region (Sangiovese di Romagna Brumale, Sangivese di Romagna La Rocca – Bernardi, Sangiovese di Romagna Ostro, Sangiovese di Romagna Vecchie Cantine Rove) and from Marche region – the red wine Marche Sangiovese.

For these wines it was determined: the chromatic parameters, the total polyphenols content, the total antioxidant capacity, the total monomeric anthocyanins, and the color analysis that supposes the determination of percent from color due to each anthocyanins fractions: monomeric, polymeric, copigmented anthocyanins. Also, it was determined the chemical age of wines and the degree of pigment coloration.

Reagent and equipment: All chemicals and reagents were analytical grade or purest quality purchased from Merck, Fluka, Sigma. Was used distilled water. Absorption determination for FRAP, total polyphenol content and for wine color analysis was made using Analitik Jena Specord 205 spectrophotometer.

Total antioxidant capacity, **TAC**, will be determinated by FRAP assay [1].

The total antioxidant capacity (TAC) in wine samples in mM Fe^{2+}/L was calculated. For antioxidant capacity analyse the dilution was 1/50. Correlation coefficient (r^2) for calibration curve was 0.998.

Total polyphenolic compounds content **(P)** was determined by spectroscopic modified method Folin-Ciocalteu [9] and was expressed in (mM gallic acid /L) [25]. For polyphenol analyse the dilution was 1/25. Correlation coefficient (r^2) for calibration curve was 0.995.

Chromatic properties were established by standardized method A and B [12] and by Glories method [4].

Total monomeric anthocyanin content **(AM)** will be determined by the pH-differential method [5]. Monomeric anthocyanin pigment (mg/L) will be calculated as cyanidin-3-glucoside.

The analysis of red wine color is realised in accord with Somers & Evans [10] method. The ffraction or percent of color due to monomeric, polymeric and copigmented anthocyanins was in order: **MA**, **PA** and **CA.**

The wine chemical age is cuantified 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 polymeric anthocyanins and total anthocyanins*) and the second index I2 - *the ratio between polymeric anthocyanins and monomeric anthocyanins*. ***The degree of pigment coloration*** (α) gives a measure of the amounts of pigments in the colored form [10].

RESULTS AND DISCUSSIONS

In the table 1 it was presented the chromatic parameters obtained by application of A and B standardized methods. The results obtained by using A and B methods are in perfect accordance: the wine shade identified by these methods is the same. The data from the table 2 show the chromatic structure obtained by Glories method. By this method application, it was determined the percent with that each pigment category (yellow, red and blue) contribute to the total wine color. On the base of each pigments category contribution to the wine color it can be appreciated the wine shade. From obtained data it was observed that the pigments

structure reflects exactly the chromatic features of analyzed red wines. In general case, for wine with red shade, the red pigment class takes part with biggest percent (over 40%) to underline the wine color: the red pigment class participates with 45-47%, the yellow pigments 40-447% and the blue pigments with 10-146% to the total wine color. IC and IC* have the same direction of evolution. The tonality present values in the range 0.89-0.95 for red wines Sangiovese.

Table 1

Chromatic properties of red wine determined by standardized A and B methods

Variety	Method A		Method B			
	λd	Wine color	I.C	tgα	α	Wine color
Brumale	616	red	5.95	0.32	17.83	red
La Rocca – Bernardi	616	red	5.07	0.12	6.90	red
Marche	615	red	6.09	0.23	13.11	red
Ostro	615	red	6.55	0.39	21.13	red
Vecchie Cantine Rove	611	red	5.77	0.33	18.42	red

Table 2

Chromatic properties of red wine determined by Glories method

Variety	Glories Method				
	I.C*	T	Chromatic structure		
			%, yellow pigments	%, red pigments	%, blue pigments
Brumale	6.73	0.90	41.84	46.62	11.54
La Rocca – Bernardi	5.64	0.95	43.88	46.02	10.10
Marche	6.91	0.93	42.35	45.72	11.94
Ostro	7.60	0.89	40.57	45.66	13.77
Vecchie Cantine Rove	6.49	0.89	41.87	47.01	11.12

The own technology applied for wines making leaded to differences between chromatic paameters. The high value for IC and IC* it was registered for wine Sangiovese di Romagna Ostro (7.6) while the small value in the case of wine Sangivese di Romagna La Rocca – Bernardi (5.64). The others wine have the value of IC in the range 6.5-6.9.

The color stabilization can be attributed the diminishing of anthocyanins content and formation of combinations between tannin and anthocyanins, polymeric compounds, and intermolecular associations which have the red color.

From the data showed in the table 3 it was observed that for all analysed wine from 2005 harvest year's (bottled as young wine but aged through keeped in the bottle for 1 year) the majority color is due to polymeric pigment class (in the range 73-90%). The class of monomeric and copigmented pigments participate to the total wine color with a percent between 3-12% for monomeric anthocyanins and 6.5-15% for copigmented anthocyanins. The polymeric pigments, that are prepominats, 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 is due the specificy of Sangiovese grapes variety that contain a litle amounts of cofactor (especially flavan-3-ols and flavanols). From the table 4, on the base of value for I1 results that the polymeric pigments represent 73-90% from total anthocyanins, while on the base of I2 values, polymeric pigments have replaces monomeric anthocyanins in a measure between 55-78%. Results, that the color stabilisation of these wine is not ready, the process of transformation the monomeric anthocyanins into polymeric forms can be continued. From the value of α results that the 74-94% from anthocyanins are in coloured form, as flavilium form or ionised anthocyanins.

Table 3

The wine color structure

No. crt.	Variety	PA (%)	MA (%)	CA (%)
1	Brumale	73.05	12.18	14.77
2	La Rocca – Bernardi	78.17	6.55	15.29
3	Marche	84.39	4.00	11.61
4	Ostro	90.11	3.38	6.51
5	Vecchie Cantine Rove	83.44	4.07	12.49

Table 4

The values for chemical age indices and for degree of pigment coloration

No. crt.	Variety	Chemical age I1	Chemical age I2	α (%)
1	Brumale	0.7305	0.5518	74.28
2	La Rocca – Bernardi	0.7817	0.6960	88.28
3	Marche	0.8439	0.6908	80.20
4	Ostro	0.9011	0.7576	82.36
5	Vecchie Cantine Rove	0.8343	0.7860	94.06

In the table 5 are presented the values of total antioxidant capacity, total polyphenols content and total monomeric anthocyanins. For these wines, the total monomeric anthocyanins amount, are in the range 41-85 mg/L – for this reason the wines from Sangiovese grapes are the wine types with midle pigmentation. The TAC value is in the range 14.1-15.5 mM Fe^{2+}/L while polyphenols content, between 10.38-13 mM gallic acid /L.

After processing the obtained data with Origin Program it was established the linear correlations, between TAC and P: **$TAC=A+B\cdot P$,** where A=-13,8263, B=1,7196 with the correlation coefficient R=0.98635. From this correlation results that, the decreasing of TAC is highly correlated to **P** content diminishing.

Table 5

The values of polyphenols and total antioxidant capacity for analyzed wine

No. crt.	Variety	P (mM gallic acid / L)	TAC (mM Fe^{2+}/L)	MA (mg/L)
1	Brumale	10.38	14.10	52.14
2	La Rocca – Bernardi	12.51	15.45	68.31
3	Marche	12.18	15.15	85.25
4	Ostro	12.15	15.00	50.65
5	Vecchie Cantine Rove	13.05	15.55	41.13

CONCLUSIONS

The pigments structure, evaluated by Glories method reflects exactly the chromatic features of analyzed wines obtained by A and B standardized methods. For all red wines it was obtained the red shade. IC and IC* have the same direction of evolution. The tonality present values in the range 0.89-0.95 for red wines Sangiovese.

The polymeric pigment class participates to the total wine color in a 73-90% measure. The class of monomeric pigments participates with 3-12%, while copigmented anthocyanins with 6.5-15%. The polymeric pigments represent 73-90% from total anthocyanins, while on polymeric pigments have replaces monomeric anthocyanins in a measure of 55-78%. Results, that these wines found in the stabilisation course. From total anthocyanins, a percent of 74-94% are in flavilium form. The wines from Sangiovese grapes are the wine types with midle pigmentation because the Sangiovese grapes contain a litle amounts of copigments.

The polyphenols content has the same evolution direction of with total antioxidant capacity. Between these parameters it was observed a linear correlation (R=0.98635).

BIBLIOGRAFIE

1. Benzie, I.F.F., Strain, L., 1996, Ferric reducing ability of plasma (FRAP) as a measure of antioxidant power: The FRAP assay, *Analytical Biochemistry*, 239, p. 70-76.
2. Berke B, Vauzour D, Castagnino C, Arnaudinaud V, Nay B, Cheze C, Vercauteren J., 2003 - *Vin et santé: découvertes récentes*, Journal de Pharmacie de Belgique, 58(3), p. 57-74.
3. Burns J, Peter T. Gardner, Jennifer O'Neil, et al.,2000 - *Relationship Amoung Antioxidant Activity, Vasodilation Capacity and Phenolic Content of Red Wines*, J. Agric. Food Chem., 48(2), p. 220-230.
4. Glories Y., 1984, La couler des vins rouges in: *Connaisance Vigne Vin*, 18(4), p.253-271.
5. Giusti Monica, Wrolstad R.E., 2000, *Characterization and Measurement of Anthocyanins by UV-Visible Spectroscopy*, Current Protocols in Food Analytical Chemistry.
6. Landrault N, Poucheret P, Ravel P, Gasc F, Cros G, Teissedre PL., 2001 - *Antioxidant capacities and phenolics levels of French wines from different varieties and vintages*., *Journal* of Agricultural and Food Chemistry, 49(7), p. 3341-3348.
7. Mirabel, M., C. Saucier, 1999 - Copigmentation in model wine solutions: Occurrence and relation to wine aging, *Am. J. Enol. Vitic.*, 50, p. 211-218.
8. Simonetti P., Pietta P. G., Testolin G., 1997 - *Polyphenol content and total antioxidant activity potential of selected Italian wines,* J. Agric. Food Chem. , 45, p. 1152-1155.
9. Singleton, V. L., Rossi, J. A., 1965 - *Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents*, Am. J. Enol. Vitic., 16, p. 1644-1658.
10. 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. Fd. Agric., 25, p. 1369-1379.
11. Tsai, P.J., Huang, H. P., Huang, T. C., 2004 - *Relationship between anthocyanin patterns and antioxidant capacity in mulberry wine during storage*, J. Food Quality, 27(6), p. 497-505.
12. *****Culegere de standarde române comentate. Vin. Metode de analiză,* Editura S.C.C.O.P.C.I.A.S.A., Bucureşti, 1997.