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THE ESTABLISHING THE QUALITY OF RED WINES ON THE BASIS OF CHROMATIC CHARACTERISTICS

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Abstract

In this paper it was determined the chromatic properties, monomeric anthocyanins amounts, and total polyphenols content from some red wines processing from black grapes variety Cabernet Sauvignon in different vineyards from Romania. This study presents a methodology for these characteristics analysis but and the influence of origin place about chromatic properties of red wines that contribute to the wines authenticity. Chromatic properties will be determined through high performance spectrophotometer analysis with a Analytic Jena Specord 205. It was used the standardized methods and Glories method. For polyphenols determination (expressed such as mg/l acid gallic) will be use the spectrophotometer method with the reactive Folin-Ciocalteu. The total monomeric anthocyanins will be determined by differential pH method. On the basis of these correlations we can be establishing the red wines quality and authenticity depending on the origin place.
Keywords: *red wines, monomeric anthocyanins, chromatic parameters, polyphenols*

Introduction

The studies made till this moment contain the fact that from all the foods and drink consumed by humans, the wine represents the most important source of substances with protective role against cardiovascular diseases that represent the principal cause of mortality in developed countries. The protective role is due to the non alcoholic component of the wine, which is represented by

monomer polyphenolic compounds, because of their antioxidant activity. The chemical structure of polyphenols is specially adapted for antioxidant activity (these are donators of hydrogen or electrons, or they capture free radicals present human organism that may cause oxidative degradation of some lipids molecules, proteins, nucleic acids, inducing in this way the appearance of degenerative diseases) (Burns, 2000; Tedesco, 2001; Berke, 2003). It may tell that the polyphenols contribute to the definition of organoleptic quality, to the food-hygiene and to the wines particularization (Landrault, 2001). Quality and quantity of polyphenols are related to the variety vineyard, weather, soil and cultivation practices. The level and quality of red wine's coloring can be determined based on spectrophotometric and chromatographic analyses (Glories, 1984). In Romania and at international level were made researches that certifies the fact that through wines ageing, because oxidation and condensation processes, it was diminished the monomer polyphenols content (which has the antioxidant properties); also, it was monitoring the evolution of substances with antioxidant role during wine's evolution, it was studied the influence of different factors (biological, biochemical, technological) about wine quality, but not made correlation between the content of compounds with antioxidant power, wine's antioxidant capacity, chromatic properties depending on the evolution stage of wine obtained from different wine variety and in different vineyards (Gomes-Cordoves, 1995; Fernandez, 2003; Pascu, 2005). At international level were made researches that certifies the fact that exist a strong correlation between polyphenols content and antioxidant capacity of wine; also, it was established that origin place (vineyard) and grape's variety have a prominent influence about antioxidant and chromatic of red wines (Gomes-Cordoves, 1995; Kennedy, 2001; Landrault, 2001; Ollala, 2005; Monagas, 2006).

Experimental

In the present research, it was investigated the bottled red wines processed of different Romanian vineyards obtained from Cabernet Sauvignon (CS) grapes harvested in 2004 year. The experimental study was structured in the next principal parts:

- color analysis of red wine (chromatic parameters and anthocyanins determination);
- investigation of antioxidant properties (total antioxidant capacity – TAC and total polyphenols determination).

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 total polyphenols content was made using Spectrophotometer Specord 205 by Analitik Jena.

Determination of total monomeric anthocyanins: The total monomeric anthocyanins will be spectrometric determined by differential pH method. Anthocyanins pigments undergo reversible structural transformations with a change in pH manifested by strikingly different absorbance spectra. The colored oxonium form predominates at pH 1.0 and the colorless hemiketal form at pH 4.5. The pH-differential method is based on this reaction, and permits accurate and rapid measurement of the total anthocyanins, even in the presence of polymerized degraded pigments and other interfering compounds. The pigments content was calculated *as cyanidin-3-glucoside* (Giusti, 2000).

Determination of phenolic compounds: (Singleton, 1965). The content of total polyphenolic compounds (P) was determined by Folin-Ciocalteu method. It was used: Folin-Ciocalteu′s phenol reagent solution 1:10 (v/v) in bidistilled water, Na_2CO_3 solution 7.5%; Standard solution - gallic acid 10mM/L: 1,8755 g acid galic in 1000 mL ethanol 96% (v/v). For the preparation of calibration curve 0.5 mL aliquot of 0.05; 0.1; 0.2; 0.3; 0.4; 0.5; 0.6 μM/mL aqueous gallic acid solution were mixed with 2.5 mL Folin-Ciocalteu reagent and 2.0 mL Na_2CO_3 solution. 1 mL from diluted 1:50 (v/v) wines was mixed with the same reagents as described above, and absorption was read after 2 h at λ= 750 nm in rapport with a blank solution (0,5 ml bidistilled water, 2,5 mL Folin-Ciocalteu′s phenol reagent and 2,0 mL Na_2CO_3 solution). Total content of polyphenols in wines in gallic acid equivalents (GAE) was calculated. The equation of calibration curve was:

$$Y = -0.10164 + 1.92242 \cdot X$$

Correlation coefficient (R) for calibration curve was 0.9980.

Chromatic properties were established by standardized method A and B (Culegere de standarde române comentate, 1987) and by Glories method (Glories, 1984).

Chromatic properties will be determined by high performance spectrophotometer analysis with an Analytic Jena Specord 205. Because the Beer's law is not respected, the determinations will be done on undiluted samples. It will be done the following determinations depending on used method:

Standard method A determines transmittances at the following length wave: 445, 495, 550, 625 in ratio with blank sample (distillated water). With determined values will be determinate chromatic tristimulus X, Y, Z for point coordination (x,y) and in colors spectral representation it will be determined length wave dominant (***λd***). In the basis of this ***λd*** can be established the hue of wine color. In conformity with this method brawny wines have ***λd*** between 585 and 598 nm. For red wines ***λd*** is between 599 nm and 650 nm, for red–scarlet ***λd*** is 540, 585 nm (Romanian standards collection. Wine. Methods of analysis).

Standard methods B permits color expression through intensity and hue. Color intensity, I.C, is based on the relation $IC = A_{420} + A_{520}$, where: A_{420} – absorption at 420 nm and A_{520} – absorption at 520 nm. The hue is expressed on angle value as follow: the wines with angles between 0˚-51˚ are red wines, the wines with angles between 52-80˚ is red scarlet wines; the wines with negative angles are brawny wines (Romanian standards. Wine. Method of analysis).

Glories method is much more exact, has in calculation the contribution of blue-mauve pigments to the total color of wines. Determination of chromatic characteristics through this method is for maturated red wines and for young ones where blue compound has an important role to the total wine color. This method establishes other parameters for red wine color evaluation: color intensity (IC*), color tonality (T), and the contribution of each color (red, yellow and blue) to wine color.

Results and Discussions

In the table 1 it was presented the chromatic parameters obtained by application of A and B standardized methods. The dates 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. The results obtained for these methods are in perfect accord, namely, the wine shade identified by these methods is the same. For majority cases it was obtained the red shade, but for red wine Cabernet Sauvignon from Minis vineyard it was obtained the brown shade.

For red wine proceeded from different wine making centers, from same grape's variety and from dame harvest year, it can be observed that color intensity have the values very different (little values for wine from Murfatlar and Valley-Prahova vineyard and high for wine from Oprisor-Mehedinti, Minis and Recas vineyards).

From the dates showed in the table 2 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 participates in more measure (over 40%) to underline of wine color, for wine with brawny shade, the red pigments percent decrease (<40%) being accompanied of yellow-orange pigments percent increasing (over 45%). For wine from Minis vineyard the percent of yellow pigment is over 45% while the red pigment percent is <40%), therefore the shade is brawny; for the others analyzed wines the shade was red.

The class of blue pigments participates at total color of wine in measure of 10-15%. The biggest percent of blue pigment was founding in wine from Oprisor - Mehedinti and Minis and the smaller percent it was observed for wine proceed from Murfatlar and Valley - Prahova.

As a rule, for red wines age, the absorbance at 520nm decreases while the absorbance at 420nm increases, due to the shift from monomeric to polymeric anthocyanins (Pascu, 2005).

Though all analysed red wine proceed from same harvest year – 2004, the wine from Minis vineyard has the brawny shade because

ageing in oak cask. For wine that was aged a long tine period the percent of yellow pigments is more than red pigments percent. Regarding the influence of evolution stages of the wine on sensorial quality and food-hygienic value of wine it was observed that the structure of phenolic compounds varies very much during wine's maturation and ageing. Phenolic compounds proceed from grapes as well as those proceed from cask's wood participate at different reactions, which, although being slow, produce important transformation in wine. In this way, there take place condensation and polycondensation reactions between phenolic compounds from wine (leucoanthocyanidins, anthocyanidins, tannins, substances from flavones group) and other compounds extracted from the stave of the cask, represented especially by hydrolysable tannins (pirogalolic).

Also, the oxidative reactions of phenolic compounds with the elaboration of some xantiliu derivates, with yellow coloring determines, in the case of red wines, color modifications from red-violet to red-brick color.

For all cases, IC and IC* have the same direction of evolution. Wine tonality present values between 0.6-1.0 for wines with red shade and more 1 for brawny wines.

For wines proceed from Oprisor and Recas are visible the aging in bottle, more then the others analyzed red wines. This can be observing from the tonality values (0.97-0.98) and from chromatic structure (the yellow-orange and red pigments participate approximate in the same measure at total color of red wine).

For wine from Murfatlar, Valea Călugăreasca and Valley-Prahova the percent of red pigments participates in biggest measure at total color of red wine. The yellow pigment participates with less 13-15% than red pigments; in these cases the wine color it was perceptible as intensive red.

Between wine tonalities expressed by α angle (in conformity with B method) and red pigment percent not founding the correlations. Only for red wine Cabernet Sauvignon precedes from Valea Călugărească vineyard the biggest value of red pigments percent corresponds with the biggest value of α angle.

In the table 3 are presented the values of total polyphenols content and total monomeric anthocyanins.

Table 1. Chromatic properties of red wine determined by standardized A and B methods

Grape variety/Vineyard	Method A	Method B						
	λd	Wine color	A_{420}	A_{520}	I.C	tgα	α	Wine color
CS – Murfatlar	625	red	1.5057	2.0335	3.5392	0.5278	27.83	red
CS – La Cetate, Oprisor, Mehedinti	613	red	3.5194	3.5767	7.0961	0.0573	3.28	red
CS – Dealu Mare, Valea Calugareasca	618	red	2.3271	3.3636	5.6907	1.0365	46.03	red
CS – Uricani, Iasi	615	red	2.7476	3.3497	6.0973	0.6021	31.05	red
CS – Prahova, Valley	615	red	1.9495	2.6217	4.5712	0.6722	33.91	red
CS – Recas, Castle Rock	611	red	3.4193	3.5261	7.0164	0.1068	6.10	red
CS – Recas	613	red	3.2018	3.6012	6.803	0.3994	21.77	red
CS – Minis	596	Brawny	3.9156	3.4527	7.3683	-0.4629	-24.84	Brawny

Table 2. Chromatic properties of red wine determined by Glories method

Grape variety/Vineyard	A_{420}	A_{520}	A_{620}	I.C*	T	% yellow pigments	% Red pigments	% Blue pigments
CS – Murfatlar						38.02	51.36	10.61
CS – La Cetate, Oprisor, Mehedinti	3.5194	3.5767	1.1281	8.2242	0.98	42.79	43.48	13.71
CS – Dealu Mare, Valea Calugareasca	2.3271	3.3636	0.7898	6.4805	0.69	35.90	51.90	12.18
CS – Uricani, Iasi	2.7476	3.3497	0.7545	6.8518	0.80	40.10	48.88	11.01
CS – Prahova, Valley	1.9495	2.6217	0.5195	5.0907	0.74	38.29	51.49	10.20
CS – Recas, Castle Rock	3.4193	3.5261	0.8744	7.8198	0.97	43.73	45.09	11.18
CS – Recas	3.2018	3.6012	0.9416	7.7446	0.89	41.34	46.50	12.16
CS – Minis	3.9156	3.4527	1.3019	8.6702	1.13	45.16	39.82	15.02

The values of anthocyanins content are very different in rapport with origin place. It can be observed that the anthocyanins content is not correlated with the percent of red pigments. In these wines appears the co-pigmentation effect. The effect of co-pigmentation gives an increasing of wine absorption in visible spectrum. The most important co-pigments in wine are expected to be the flavan-3-ols and flavanols, hydroxycinnamic acids and in the case of self-association even the antocyanes molecules can react as co-pigments. The values of red wines intensity are given by co-pigments (Mazza, 1990).

Table 3. The values of polyphenols, total antioxidant capacity and monomeric anthocyanins for analyzed wines

Grape variety/Vineyard	Total poliphenols (mM acid gallic/L)	Monomeric anthocyanins (mg/L)
Cabernet Sauvignon – Murfatlar	18.09	163.32
Cabernet Sauvignon – La Cetate, Oprisor, Mehedinti	13.28	81.13
Cabernet Sauvignon – Dealu Mare, Valea Calugareasca	10.97	155.55
Cabernet Sauvignon – Uricani, Iasi	8.27	70.81
Cabernet Sauvignon – Prahova, Valley	18.19	177.46
Cabernet Sauvignon – Recas, Castle Rock	14.58	99.05
Cabernet Sauvignon – Recas	15.16	100.21
Cabernet Sauvignon – Minis	22.46	117.78

The best image of this effect it can be observe for wine from Oprisor -Mehedinti, where the hihg value of colorant intensity but the anthocyanidins content exists is low. For wine from vineyard Murfatlar, Valea Calugaresca and Prahova have the biggest anthocyanidins contents that are positive correlated with percent of red pigments. The anthocyanins is a little part from polyphenols compound from red wines, therefore not exist the correlations between total polyphenols content and anthocyanins content.

The polyphenols content are a measure of antioxidant power of red wines. It may tell that the polyphenols contribute to the definition of organoleptic quality, to the food-hygiene and to the

wines particularization. In grapes, juice and wine it can be find the followed phenolic compounds: phenolic acids, tannins and coloring substances. Quality and quantity of polyphenols are related to the variety vineyard, weather, soil and cultivation practices. The biggest values of polypheols content it was found in red wine from Minis, Valley - Prahova and Murfatlar. This finding is very important for particularization of wine from these vineyards.

Conclusions

The results obtained by standardized methods A and B and through Glories methods are in perfect accord, namely, the wine color identified by these methods is the same. The pigments structure reflects exactly the chromatic features of analyzed red wines. The pigments structure reflects exactly the chromatic features of analyzed red wines. In general case, for wine with red shade, the red pigment class participates in more measure (over 40%) to underline of wine color, for wine with brawny shade, the red pigments percent decrease (<40%) being accompanied of yellow-orange pigments percent increasing (over 45%). The values of total polyphenols and anthocyanins content are different in rapport with origin place. The study permits establishing the influence of origin place about chromatic properties of red wines and elaboration of methodology for estimation of red wines quality and authenticity.

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