JAP&T
TPA-Timişoara

Available online at http://journal-of-agroalimentary.ro

Journal of Agroalimentary Processes and Technologies 2013, 19(4), 378-382

Journal of Agroalimentary Processes and Technologies

Assessment the influence of maturation and aging on red wine color and their antioxidant properties

L.A Roman, Mariana-Atena Poiană*, Diana Veronica Dogaru, T.I Traşcă

Received: 11 September 2013; Accepted: 29 December 2013

**Banat's University of Agricultural Sciences and Veterinary Medicine, Faculty of Food Processing, Food Technology Department, Calea Aradului 119, 300645 Timişoara, Romania*

Abstract

Were investigated in relation to the antioxidant and chromatic properties the red wines processing in Minis vineyard from two grapes varieties: Cabernet Sauvignon and Cadarca harvested in 2011. It was determined the total antioxidant capacity, total polyphenols content and monomeric anthocyanins amount, as well as the main chromatic characteristics for young red wines bottled immediately after conditioning, red wines which immediately after conditioning were maturated in barrels for 6 months and then they were aged for 12 months bottled in glasses, as well as red wines after 6 months of maturation in barrels. Total antioxidant capacity it was determined by FRAP method (expressed as mM Fe2+/L). The polyphenols content it was determined by Folin-Ciocalteu method (expressed such as mM acid gallic/L). The monomeric anthocyanins it was evaluated by differential pH method and the chromatic properties by standardized method and by Glories method. The obtained results revealed that the chromatic and antioxidant characteristics of red wines present the distinctive values depending on the wine's evolution stage and grapes variety. By ageing, the antioxidant capacity decreased due to diminishing of total polyphenols content, especially monomeric forms of anthocyanins. The highest values for antioxidant capacity were found in young red wine (particularly from Cabernet Sauvignon grape's variety). The antioxidant capacity was highly correlated with the polyphenols amount.

Keywords: anthocyanins, chromatic parameters, polyphenols, red wine, antioxidant capacity

1. Introduction

Wine color is a main parameter in red wine analysis being the result of a complex mixture of several compounds, including free monomeric anthocyanins, the enhancement of their color due to copigmentation with other noncolored phenolics [2], and polymeric pigments [14,]. The color components of wine are the important parameters that contribute to the sensory characteristics (color and astringency) as well as the antioxidant properties of wine [10]. 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. 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. The anthocyanins composition in red wines depends not only on the original profile of anthocyanins in grapes, but also on the winemaking techniques [7]. The content of total monomeric anthocyanins plays a significant role to the red color only in very young red wines [11,15]. The monomeric anthocyanins in red wines are not particularly stable and decrease significantly during barrel maturation and bottle aging, with a significant

Corresponding author: *e-mail:* atenapoiana@yahoo.com.

increase in polymeric or condensed products [8,11]. Actually, during red wine evolution, most of these free anthocyanins will react with other phenolic compounds to form more complex and stable pigments, while a small part of them is destroyed through oxidation or precipitation. After several years of aging in bottle, although the wines' color is red, the monomeric anthocyanins are present in a very low amount. This fact is due to the polymerization or other reactions between monomeric anthocyanins and other compounds from red wines, as well as the breakdown reactions of a part of them [8]. Copigmented anthocyanins are the complexes that result by reaction between anthocyanins and copigments molecules or co-factors. In red wines can appear intramolecular copigmentation between anthocyanin molecules or between an anthocyanin and other colorless chemicals, named intermolecular copigmentation [2,3]. It can be argued that the copigmentation of anthocyanins in wines is a competitive equilibrium involving several anthocyanins and many cofactors. In young red wines, anthocyanins exist as weak complexes with themselves named self-associations, or with other compounds, named cofactors, resulting in the formation of copigmented anthocianins [2]. The main cofactors in young red wines are expected to be the flavan-3-ols and flavanols, hydroxycinnamic acids and hydroxycinnamoyl derivatives, oligomeric proanthocyanidins and in the case of self-association even the antocyanins molecules can react as copigments [2,4,5,9].

2. Materials and Methods

Wine samples. We analyzed 3 types of red wines from Minis vineyard (M), from the harvest of 2011 from two different kind of grapes: Cabernet Savignon and Cadarca, as follow:

- young red wines, bottled immediately after conditioning, marked 1-CS-M and 1-C-M;
- red wines which immediately after conditioning were maturated in oak barrels for 6 months, marked 2-CS-M and 2-C-R;
- aged wines bottled in glasses for 12 months, after a 6 months of maturation in barrels, marked 3-CS-M and 3-C-R.

The goal of this study was to analyze the color of wines (in terms the chromatic parameters, the content of monomer anthocyanins) and to evaluate the antioxidant characteristics (expressed by total antioxidant capacity and content of total polyphenols) in order to highlight the differences between specified parameters for Cadarca (red wines traditional specific for Minis region) and Cabernet Savignon, a red wine with international certified qualities.

2. Method of analysis

Chromatic properties were established by standardized method A and B according to Pascu (2005) [12] and by Glories method (1984) [6]. By using standard method A were obtained the 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 from in colors spectral representation was obtained 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 585-598 nm. For red wines λd is between 599-650 nm, for red–scarlet λd is 540-585 nm.

Standard methods B permits color expression through intensity and hue. Color intensity, I.C, is based on the relation IC=A420+A520, where: A_{420}–absorption at 420 nm and A_{520}–absorption at 520 nm. The hue is expressed on angle α value (tgα= A520- A420) as follow: the wines with α between 0˚-51˚ are red wines, the wines with α between 52-80˚ is red-scarlet wines; the wines with negative angles are brawny wines.

Glories method [6] is much more exact, has in calculation the contribution of blue-mauve pigments to the total color of wines. 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. These parameters it calculated using the formulas:

$$I.C.^* = A_{420} + A_{520} + A_{620}$$

$$T = \frac{A_{420}}{A_{520}};\ 420\% = \frac{A_{420}}{I.C.^*} \times 100$$

$$520\% = \frac{A_{520}}{I.C.^*} \times 100;\ 620\% = \frac{A_{620}}{I.C.^*} \times 100$$

where: 420%, 520% and 620% represent the contribution of yellow, red and black color in the total wine color.

Chromatic properties were determined according to Glories method [6]. By this methods it was determined: the color intensity (IC, expressed in AU-absorbance units was given by the sum of the A_{420nm}, A_{520nm}, and A_{620nm}), the color tonality (T was expressed by the ratio of the A_{420nm} and A_{520nm}) and the wine chromatic structure expressed by the yellow, red and blue pigment contribution (%) to the red wine color.

Total monomeric anthocyanins content were quantified by the pH-differential method (Giusti&Wrolstad, 2001). Anthocyanins 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 anthocyanins content (mg/L) was calculated as cyanidin-3-glucoside.

Ferric Reducing Antioxidant Power (FRAP) assay [1]. The FRAP assay to base on antioxidant compounds capacity to reducing of Fe^{3+} ions to Fe^{2+} ions. The ferrous iones forms at acid pH a colored complex with TPTZ (2,4,6-tripyridyl-s-triazine) that has the maxime absorbance at 593 nm. Antioxidant capacity is direct proportional with ferrous ions amount and will be determinate on the base of calibration curve that use the etalon with knoun Fe^{2+} concentrations. The total antioxidant capacity was expressed in mM Fe^{2+}/L was calculated.

Total polyphenolic content was analyzed spectrophotometrically using an adapted Folin-Ciocalteu colorimetric method described by Singleton and Rossi (1965) [13]. Quantification of the data was calculated based on the calibration curve generated using gallic acid as the standard and the results was expressed as mM gallic acid/L.

3.Results and Discussion

In Table 1 is presented the data obtained by analyzing the chromatic structure elements using standard methods A and B, and in Table 2 is presented the contribution of red, blue and yellow pigment categories in the red wine color using Glories method [6]. Obtained results through applying B standard method and Glories method are consistent: through both methods we obtained the same tone of analyzed wines.

From Table 2, applying Glories method, we can observe that the pigments structure reveals wine chromatic qualities. For red wines red pigments are over 40% form wine total color. For all cases, the highest values for color intensity were obtained for Cabernet Savignon and the smallest for Cadarca, both for young wines and those in different stages of evolution. Blue compound slightly increase during wine ageing. Young wines strongly abrorb at λ=520 nm and aged wines absorb in a lesser extand at λ=520 nm and more at λ=420 nm.

Although all wines are from the same harvest and the same vineyard, chromatic structure of aged wines reflects the aging stage. For maturated wines, and maturated and aged wines we could observe a decreasing of red pigments contribution in red wine color specific for no bottled wines and a equilibrium through yellow and red pigments, that reveals an improvement of chromatic properties. For all analyzed cases we obtained the same direction of variation of IC and IC^*. The color tone presents values between 0.6 and 1.0 that is specific for red wines.

Figures 1 and 2 present the chromatic parameters of red wines in different stages of evolution.

Table 1. Red wines chromatic properties determined through A and B method

Wine /grapes		Method A		Method B					
		λd	Wine color	A_{420}	A_{520}	I.C	tgα	α	Wine color
Minis¹	1-CS-M	611	Red	3.319	3.926	7.245	0.607	31.25	Red
	1-C-M	612	Red	2.879	3.422	6.300	0.543	28.51	Red
Minis²	2-CS-M	631	Red	3.250	3.353	6.604	0.103	5.88	Red
	2-C-M	622	Red	2.931	3.014	5.945	0.083	4.74	Red
Minis³	3-CS-M	617	Red	3.095	3.149	6.244	0.054	3.10	Red
	3-C-M	613	Red	2.532	2.545	5.077	0.013	0.78	Red

¹-young red wines; ²-red wines maturated in barrels for 6 months; ³- red wines aged for 12 months in bottles, after 6 months of maturation in barrels

Table 2. Red wines chromatic properties determined through Glories method

Wine /grapes		A_{420}	A_{520}	A_{620}	I.C*	T	Chromatic structure % Yellow pigments	Chromatic structure % Red pigments	Chromatic structure % Blue pigments
Minis[1]	1-CS-M	3.319	3.926	0.824	8.07	0.85	41.13	48.65	10.22
	1-C-M	2.879	3.422	0.611	6.91	0.84	41.65	49.51	8.84
Minis[2]	2-CS-M	3.250	3.353	0.786	7.39	0.97	43.99	45.38	10.63
	2-C-M	2.931	3.014	0.659	6.60	0.97	44.38	45.64	9.98
Minis[3]	3-CS-M	3.095	3.149	0.788	7.03	0.98	44.01	44.78	11.21
	3-C-M	2.532	2.545	0.601	5.68	0.99	44.59	44.83	10.58

[1]–young red wines; [2] -red wines maturated in barrels for 6 months; [3]–red wines aged for 12 months in bottles, after 6 months of maturation in barrels

Table 3. Total polyphenoles content, monomer anthocyanins and total antioxidant capacity of analyzed wines

Sample		Polyphenoles (mM gallic acid /L)	FRAP (mM Fe^{2+}/L)	Total monomeric anthocyanins (mg/L)
Miniş[1]	1-CS-M	19.06	32.28	175.10
	1-C-M	13.81	25.30	140.22
Miniş[2]	2-CS-M	14.58	27.48	99.05
	2-C-M	11.21	20.46	78.21
Miniş[3]	3-CS-M	12.79	23.56	88.12
	3-C-M	10.71	19.42	70.12

[1]-young red wines; [2] -red wines maturated in barrels for 6 months; [3]– red wines aged for 12 months in bottles, after 6 months of maturation in barrels

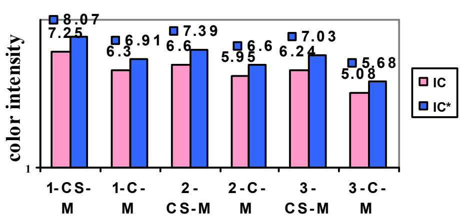

Figure 1. Graphical representation of color intensity of analyzed red wines

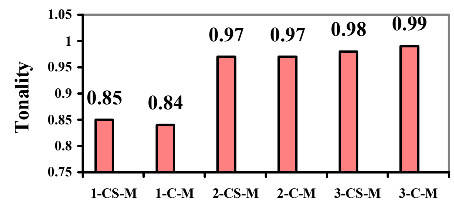

Figure 2. Graphical representation of analyzed tone wines

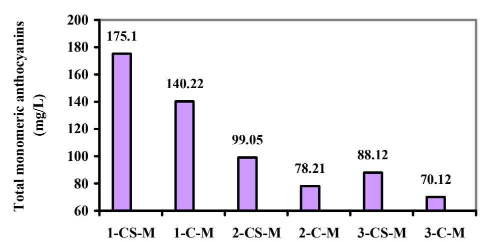

Figure 3. The values of total monomer anthocyanins content for analyzed wines

Figures 3-5 show the changes in the monomer anthocyanins content, polyphenols content and total antioxidant capacity in response to aging period. In Table 3 are presented values for total antioxidant capacity, polyphenols content and monomer anthocyanins from analyzed red wines.

For each case, monomer anthocyanins content was correlated with color intensity IC and IC^* (high anthocyanins content reveal also a intense color density). The highest values of monomeric anthocyanins were in Cabernet Savignon wines, followed by Cadarca wines. Anthocyanins content differ depending on type of grapes for wine, or, in case of the same type of grapes differ depending on wine obtaining technology.

For wine samples which followed specific processes of maturation and ageing phases were observed smaller values for anthocyanins content in comparison with young wines.

The obtained results reveal that the grapes variety and evolution stage have an important role to define the red wines color. In the same time it was observed a decreasing in the values of total phenols and total antioxidant capacity depending on the technology followed for wine obtaining, as it can be seen in Figures 4 and 5. This fact proves that the antioxidant properties of investigated wines were significantly affected by maturation and aging processes.

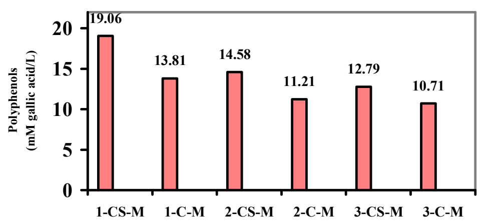

Figure 4. Graphical representation of total polyphenols content for analyzed wines

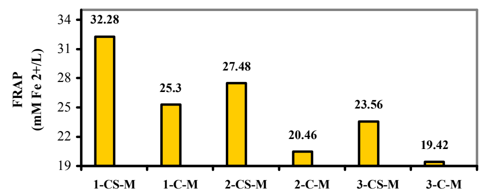

Figure 5. The values of total antioxidant capacity for analyzed wines

4.Conclusion

The results obtained by standard method A, B as well as Glories method [6] are consistent: through all methods used in the investigation process we obtained the same tonality of analyzed wines. Pigments structure reflects the chromatic properties of wines: for red wines, the red pigments category represents the highest contribution in the red wine total color. For all analyzed cases were obtained the same direction of variation of both parameters (IC and IC*). For young red wines it was observed a decreasing in the percent of yellow pigments, this evolution being accompanied by increasing of red pigments contribution in wine color. The polyphenols content and antioxidant capacity presents distinct values according to grapes variety and wine `s stage of evolution. Young red wines present the highest values for antioxidant capacity, polyphenols content and monomeric anthocyanins. The highest value of antioxidant capacity and the biggest content of total polyphenols were found in Cabernet Savignon wine, followed by Cadarca wine. Color intensity modification is due to the decreasing of total polyphenols content, especially monomeric anthocyanins content, and this is followed by decreasing of the total antioxidant capacity.

Compliance with Ethics Requirements: Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human and/or animal subjects (if exists) respect the specific regulations and standards.

References

1. Benzie I.F.F.; Strain L**.** Ferric reducing ability of plasma (FRAP) as a measure of antioxidant power: The FRAP assay. *Analytical Biochemistry*. **1996**, *239*(1):70–76.
2. Boulton R.. The copigmentation of anthocyanins and its role in the color of red wine: a critical review. *Am. J. Enol. Vitic*. **2001,** *52*(2): 67-87.
3. Boulton. R.. A method for the assessment of copigmentation in red wines. *Am. J. Enol. Vitic*. **1996**, *47*: 346.
4. Gauche C.; Da Silva Malagoli E.; Luiz M.T.B**.** Effect of pH on the copigmentation of anthocyanins from Cabernet Sauvignon grape extracts with organic acids. *Scientia Agricola.*,**2010,** *67*(1):41–46.
5. Giusti M.M.; Wrolstad R.E. Unit F1.2: Anthocyanins. Characterization and measurement with UV-visible spectroscopy. *Current Protocols in Food Analytical Chemistry. New York: John Wiley & Sons*. **2001,** p 1-13.
6. Glories Y. La couleur des vins rouges. *Conn. Vigne Vin.***,** **1984**, *18*(4):253-271.
7. Gonzalez-San Jose M.L., Santa-Maria G., Diez C. Anthocyanins as parameters for differentiating wines by grape variety, wine-growing region, and wine-making methods. *Journal of Food Composition and Analysis*, **1990**, *3*(1): 54–66.
8. He, F.; Liang N.N.; Mu, L.; Pan, Q.H.; Wang, J.; Reeves, M.J.; Duan, C.Q. Anthocyanins and their variation in red wines I. Monomeric anthocyanins and their color expression. *Molecules*. **2012**, *17*(2):1571–1601.
9. Mirabel, M. and Saucier, C. Copigmentation in model wine solutions: Occurrence and relation to wine aging. *Am. J. Enol. Vitic*. **1999,** *50*: 211-218.
10. Monagas M.; Martín-Álvarez P.J.; Bartolomé B. and Gómez-Cordovés C. Statistical interpretation of the color parameters of red wines in function of their phenolic composition during ageing in bottle. *Eur. Food Res. Tech***. 2006,** *222*(5-6): 702-710.
11. Monagas, M.; Bartolomé, B.; Gómez-Cordovés, C. Evolution of polyphenols in red wines from *Vitis vinifera L.* during aging in the bottle. *European Food Research and Technology*. **2005**, *220*(3–4):331–340.
12. Pascu L. Red wine quality establishing on the basis of chromatic properties. *Revista de Chimie.* **2005**, *56*(7):703–707.
13. Singleton, V.L.; Orthofer, R.; Lamuela-Raventos, R.M. Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin-Ciocalteu reagent. *Methods* in *Enzymology*., **1999,** 299(Part A):152–178.
14. Somers, T.C. and Evans, M.E. Wine quality: Correlations with colour density and anthocyanin equilibria in a group of young red wines. *J. Sci. Food. Agric*. **1974**. *25*:1369-1379.
15. Wrolstad, R.E.; Durst, R.W.; Lee, J. Tracking color and pigment changes in anthocyanin products. *Trends in Food Science and Techology*. **2005**, *16*(9):423–428.