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Journal of Agroalimentary Processes and Technologies 2009, *15*(3), 408-413

Journal of Agroalimentary Processes and Technologies

The analysis of chromatic and antioxidant properties of some romanian red wines

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Abstract

The goal of this study was to investigate the antioxidant and chromatic properties of red wines processed in famous Romanian vineyards. Were analyzed bottled red wines, from 2003 harvesting year in the vineyards: Recas, Minis, Murfatlar and Calugareasca Valley. From Recas, Minis and Murfatlar were analyzed Cabernet Sauvignon, Merlot and Pinot Noir red wines; from Calugareasca Valley: Cabernet Sauvignon, Merlot, Black Peak and red wines from varieties mixtures: Merlot&Black Peak and Cabernet Sauvignon&Merlot. Antioxidant profile of red wines was evaluated through total antioxidant capacity. The chromatic properties were analyzed in terms of color composition, chromatic parameters, total anthocyanins and polyphenols content. It was established correlations between chromatic and antioxidant characteristics. The highest values of color intensity were obtained for Cabernet Sauvignon wine and the smallest for Pinot Noir. The values of color tint were situated in the range of 0.6-1.0 for red shade wines and higher than 1.0 in case of bricky colored wines. The highest values for total antioxidant capacity, polyphenols and monomeric anthocyanins were found in Cabernet Sauvignon wine, followed by Merlot and Pinot Noir. Between antioxidant capacity and polyphenols content it was established a linear dependence. The color composition of analyzed red wines is influenced by the grape variety and viticultural region

Keywords: anthocyanins, chromatic parameters, polyphenols, red wines, total antioxidant capacity

1. Introduction

The establishment of chromatic and antioxidant characteristics is extremely important because these properties have a decisive role in red wines quality inoculation. Polyphenols compounds from the red wines, even in small concentrations, had a significant antioxidant capacity, due to their special adapted chemical structure (Fernandez-Pachon et al., 2004). Polyphenols quantity and quality from the red wines depend on vineyard, grapes varieties and winemaking process (Mazza et al., 1999). Polyphenolic compounds structure change with the evolution of a red wine due to the polymerization, condensation and oxidation reactions. Anthocyanins pigments, especially monomeric forms, responsible for wine antioxidant properties pass as polymers with different molecular masses (Liao et al., 1992). The color components of wine are the important parameters that contribute to the sensory characteristics and the antioxidant properties of wine (Fernandez-Pachon et al., 2004; Villano et al., 2006). Objective measurement of the components of wine color is an essential part of the modern concept of winemaking called "*red wine color management*", in relation to their antioxidant characteristics. Chromatic changes perceptible during a red wine evolution are accompanying antioxidant properties. Chromatic parameters have a definitely role in a wine's evolution, but are insufficient for its antioxidant properties specification. In order to have a complete

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view, the obtained results through red wines color analysis, must be correlated with the obtained results in case of antioxidant capacity determination and polyphenols content modifications. On world's plan there are studies which confirm the existence of a strong correlation between polyphenols content and wine antioxidant capacity, also the dependence between antioxidant capacity and different forms of anthocyanins: monomeric, polymeric, copigmented (Mazza et al., 1999; Burn et al., 2000; Monagas et al., 2006;). In this paper are presented the results obtained in the case of chromatic parameters and antioxidant power determinations for some red wines assortments obtained in famous vineyards from Romania. We are evaluating different red wine types regarding the chromatic and antioxidant characteristics. On the base of obtained results were established the correlations between polyphenols compounds, total antioxidant capacity and chromatic features which helps to appreciate the red wines quality.

2. Materials and Method

Wine samples. Were analyzed bottled red wines, which's acquisition was made in 2007 on Romanian market. From the acquisition moment and till the analysis moment (2 weeks) bottles were kept at constant temperature conditions (10-15°C).

Analyzed red wines were obtained in 2003 harvesting year in the following vineyards. From Recas were analyzed red wines Cabernet Sauvignon (CS), Merlot (M) and Pinot Noir (PN) from two assortments, respectively Schwabenn Wein (SW) and Castle Rock (CR). From Minis and Murfatlar were analyzed red wines Cabernet Sauvignon (CS), Merlot (M) and Pinot Noir (PN). From Calugareasca Valley were analyzed red wines Cabernet Sauvignon (CS), Merlot (M), Black Peak (BP) and red wines from grapes varieties mixture: Merlot&Black Peak (M&BP) and Cabernet Sauvignon&Merlot (CS&M).

Red wine color analysis was done in accordance with Boulton's spectrophotometric method (Boulton, 1996). For each wine the following parameters were measured by spectrophotometric assay: fraction of color due to monomeric anthocyanins (MA), co-pigmented anthocyanins (CA) and polymeric anthocyanins (PA).

Chromatic properties were determined according to Glories method (Glories, 1984). 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.

Ferric Reducing Antioxidant Power (FRAP) assay **(**Benzie&Strain, 1996**).** 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 (TAC) in mM $Fe^{2+} \cdot L^{-1}$ was calculated.

Total polyphenolic content was analyzed spectrophotometrically using an adapted Folin-Ciocalteu colorimetric method described by Singleton and Rossi (1965). 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 $\cdot L^{-1}$.

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 ($mg \cdot L^{-1}$) was calculated as cyanidin-3-glucoside.

3. Results and Discussion

The chromatic properties of red wines obtained by applied of Glories method are reported in the Table 1. By obtained results it is observed in case of red shade wines that red pigments participate with over 40% to the wines total color. In case of the bricky colored wines, the percent of red pigments class decrease under 40%, being accompanied by increases of color percent due to yellow pigments.Despite the fact that all the wines came from the same yield, it is observed a different color evolution: CS and M wines from Minis vineyard have bricky colored shade and the other analyzed wines have red shade. This fact is due to different color stabilization by aging. Color stabilization on red, in case of the majority of the wines, can be explained given anthocyanins content diminution and tannin-anthocyanins combinations appearance, and also of the polymers compounds and intermolecular associations, having the red color (Pascu, 2005). Color tonality presents values between 0.6 and 1.0, in case of red shade wines and higher than 1.0, in case of bricky colored wines. In case of all vineyards, the highest values of coloring intensity were obtained in case of CS wines and the smallest in case of PN, which is in accord with their potential to synthesize anthocyanins (Villano et al., 2006). Blue pigments participate in different proportions to wine color (the highest values were obtained in case of Minis and Murfatlar wines). The color structure, expressed by the percentage due to monomeric, co-pigmented and polymeric anthocyanins is reported in Table 2. From these data can be observed that the polymeric pigments fraction takes part mostly in the defining the red color from 2003 harvest years. Polymeric pigments participate over 65% to the red wine color while monomeric and copigmented anthocyanins have a relatively reduced contribution share to the color of the wine.

The polymeric pigments are the stable compounds responsible of the chromatic properties of red wine. These compounds are formed during the wine making process and in the time of ageing through reactions which the place between free anthocyanins and tannin.

Table 1. Chromatic parameter of red wines estimated by Glories method

Wine	IC	T	Chromatic structure		
			Yellow pigments (%)	Red Pigments (%)	Blue pigments (%)
Calugareasca Valley					
C S	4.841	0.62	34.91	56.04	9.04
M	4.396	0.60	34.46	57.03	8.5
BP	4.613	0.65	35.85	54.86	9.29
M&BP	4.734	0.62	35.01	56.09	8.89
CS&M	4.669	0.62	35.02	56.05	8.93
Minis					
CS	9.560	1.10	41.06	37.29	21.65
M	9.411	1.12	42.32	37.88	19.80
PN	6.941	0.78	38.63	49.47	11.90
Recas					
SW-CS	5.781	0.69	36.46	53.15	10.39
SW-M	5.106	0.80	40.50	50.48	9.01
SW-PN	4.941	0.79	40.22	50.64	9.13
CR-CS	7.902	0.98	43.89	44.90	11.21
CR-M	7.435	0.96	43.80	45.84	10.36
CR-PN	6.312	0.89	42.62	47.83	9.55
Murfatlar					
CS	6.994	0.68	32.75	48.36	18.89
M	6.133	0.64	30.91	48.57	20.52
PN	5.038	0.75	36.00	47.85	16.15

Table 2. Impact of origin vineyard and grape variety on the red wine color composition

Wine	MA (%)	CA (%)	PA (%)
Calugareasca Valley			
C S	14.79	7.86	77.33
M	15.26	6.67	78.07
BP	17.03	6.3	76.67
M&BP	16.54	7.14	76.32
CS&M	14.85	7.42	77.73
Minis			
CS	21.16	13.05	65.79
M	19.61	12.46	67.93
PN	14.27	9.44	76.29
Recas			
SW-CS	15.16	9.31	75.53
SW-M	13.11	9.05	77.84
SW-PN	10.35	7.18	82.47
CR-CS	17.75	8.42	73.83
CR-M	18.05	9.12	72.83
CR-PN	9.16	7.79	83.05
Murfatlar			
CS	17.35	8.03	74.62
M	14.28	8.43	77.29
PN	9.23	6.91	83.86

Table 3. Antioxidant capacity, polyphenols and anthocyanins content of analyzed wines

Wine	P (mM gallic acid • L^{-1})	TAC (mM Fe^{2+} • L^{-1})	MA (mg • L^{-1})
Calugareasca Valley			
C S	10.38	17.59	151.19
M	7.41	15.45	135.02
BP	9.27	16.96	140.25
M&BP	9.06	16.71	138.90
CS&M	8.94	16.64	141.89
Minis			
CS	21.93	31.86	99.04
M	21.06	31.2	92.25
PN	12.00	21.9	84.04
Recas			
SW-CS	12.45	22.44	86.24
SW-M	11.64	20.94	67.41
SW-PN	10.52	18.84	60.42
CR-CS	13.67	25.44	93.19
CR-M	11.66	21.64	79.71
CR-PN	8.64	16.46	77.16
Murfatlar			
CS	17.14	29.17	129.08
M	16.04	28.02	119.45
PN	12.87	23.19	111.18

During winemaking and aging, anthocyanins are thought to react with tannins to give rise to polymeric pigments, the stable color compounds in wine When it comes to the rate of wine color participation due to co-pigmentation of anthocyanins, one can notice that in the case of Minis wine these take part in the range 9-13% comparativelly with other vineyard when their participation was situated in the range 6-9%. This difference of almost 3-4% in Minis favor explains partially the more intense color of the Minis red wines. Here the co-pigmentation phenomenon comes

along explained by color enhancement. The co-pigmentation is due to molecular associations between pigments and other, usually noncolored, organic molecules in solution (Boulton, 1996; Liao et al., 1992).

The red wines antioxidant power, polyphenols and monomeric anthocyanins amounts, are reported in Table 3.

From these data results that the highest values for TAC, P and MA were found in Cabernet Sauvignon wine, followed by Merlot wine and Pinot Noir. This finding is maintained for all investigated vineyards. MA differs depending on grapes variety and origin place. In case of Calugareasca Valley wines, the AM obtained values are situated between 135-150 mg/L, for Minis wines between 84-99 mg/L, for Recas wines we have lower values, 60-93 mg/L and for Murfatlar wines 111-129 mg/L. In the case of CS wines were obtained high differences between anthocyanins amount: from 86.54 to 151.19 mg/L.

Simple regression models were applied using the Origin 4.1 software program. As a result of mathematical processing of the obtained results can be reported that total antioxidant capacity is strongly correlated with polyphenols content. In parallel to the decreasing of the polyphenols content we can notice that total antioxidant capacity for all investigated red wine is decreased. The linear correlations FRAP=f (P) are showed in Fig.1. The coefficient of correlation r^2=0.9758. The results obtained in this paper must be interpreted depending on origin vineyard and grapes variety, which are decisive factors for red wines color definition.

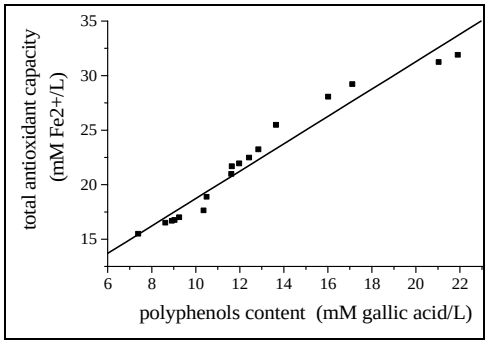

Figure 1. Linear correlation between total antioxidant capacity and polyphenols content

4. Conclusions

The chromatic and antioxidant properties of red wines present the distinctive values in rapport with origin vineyard and grapes variety. These parameters contribute to the particularization of red wines from these vineyards. There are significantly differences between total antioxidant capacity, polyphenols and monomeric anthocyanins content from the red wines given the origin place and grapes variety. For all analyzed wines, the highest values for polyphenols, monomeric anthocyanins and total antioxidant capacity were finding in Cabernet Sauvignon wine, followed by Merlot and Pinot Noir. Was also emphasized linear dependence between TAC=f(P). For all analyzed wines, color intensity modification is due to monomeric anthocyanins and these are accompanied by TAC decreasing. The copigmentation phenomenon participates to the color structure of analyzed wines. The magnitude of this effect is influenced by the grape variety and viticultural region. The availability of selective UV-VIS methods for the measurement of cromatic and antioxidant characteristics represents a valuable opportunity for winemakers.

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