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RELATIONSHIP BETWEEN THE MAIN QUALITY PARAMETRES AND ANTOCYANIC CONTENT DURING GRAPES RIPENING IN DRĂNIC VITICULTURAL AREA

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ABSTRACT

The first link technological development of any type of wine and particularly red wine, is to determine the optimal timing of harvest. The parameters taken into account in determining this time, weight of 100 berries, glucides content and total acidity of the grapes, provide information on potential anthocyanin of the species, thus imposing a new criterion for assessing the maturity of red grapes and certain maturity phenolic. To do this for three years at the 3 varieties of red grapes studied in the area of wine shingle, and made determinations by the entry in the ripening until harvest of the main parameters that define the quality of red grapes weight of berries, the contents of glucides, acidity and anthocyans.

INTRODUCTION

From the economic point of view, the grapevine is the most important fruit in the world. The genus *Vitis* L. involves more than 50 species. Of them, the most widespread and cultivated is the European grapevine, *Vitis vinifera* L. Approximately70% of the total harvests of grapes are used for making wine, 27% for direct consumption as table grapes, 2% for drying to raisins, and less than 1% for making musts and/or distillates.

The quality of grapes is determined by the contents of the primary metabolites (i.e. sugars and organic acids) and of the secondary ones (i.e. phenolic compounds and aromatic substances). The contents and proportions of primary metabolites are decisive for the quality of grapes (Rusjan *etal*. 2008; Ali *et al*. 2009).

Photosynthesis is a fundamental physiological process that determines the contents of sugars in grapes. Photosynthetic processes take place in leaves and also in green berries. The sugars synthesized are transported to berries via phloem. In the grapevine (*Vitis vinifera* L.) cultivars, the major transported sugar is saccharose which is enzymatically hydrolyzed to glucose and fructose in berries (Shiraishi 2000).

Glucose, fructose, malic acid, and tartaric acid are primarily stored in the vacuoles of mesocarp cells; however, some glucose and fructose may be found also in the exocarp (Lund & Bohlmann 2006).

A sufficient and harmonic content of acids in grapes plays a critical role as far as the suitability of grapes for wine making is concerned (De Bolt *et al*. 2007). Acids also help to maintain the colour of wine and influence esterification and wine aroma (Fowles 1992, Stoica F., et al. 2015).

Although the wine acidity is generally expressed in equivalents of tartaric acid or sulphur acid, there are several free organic acids and their saltsin grapes. Of them, tartaric acid and malic acid are the most important. In general, tartaric acid and malic acid represent 69% to 82% of all organic acids present in berries and leaves of grapevine (Kliewer 1966).

The contents and compositions of sugars and organic acids present in grapevine berries were evaluated in several studies (Lamikanra*et al*. 1995, Baduca C. et al., 2016). These two substance groups are important also in the breeding and selection of new cultivars (Liu *et al*. 2007, Cichi D.,et al., 2016).

Anthocyanins, the pigments responsible for the red colour of grapes, are widely used to carry out classification and chemotaxonomic studies in flavonoid metabolism.

Anthocyanins are contained in the grape skin, exceptin the case of a few cultivars whose pulp is also pigmented. Thus, a close relationship can be expectedbetween anthocyanin composition and visual appearance (Fernandez-Lopez J.A. et al.,1998).The International Office of the Vine plants (OIV) has adescriptor list for grape vine varieties and Vitis species which classifies the grape varieties in seven groupsaccording to their external colour: 1 (green-yellow), 2(pink), 3 (red), 4 (red-grey), 5 (red-dark violet), 6 (blue-black) and 7 (red-black) (OIV, 1988).

Anthocyanins are gradually accumulated in berry skins fromveraison through grape ripening, (Gomez-Plaza, E.2006, Fournand,D. et al., 2006) malvidin-3-glucoside beingthe most abundant anthocyanin in almost all red grape varieties.

However, the anthocyanin concentration may decline just beforeharvest and/or during over-ripening (Rolle L. et al., 2011)

MATERIAL AND METHODE

Grape sample

This study was carried out with grapes of the three cultivars Vitis viniferacv. Cabernet Sauvignon, Merlot and Feteasca neagra from the wine-growing center Dranic-Dolj.

Grape samples of three red cultivars (V. viniferaL.) were collected at harvest maturity at different calendar date. Determination of sugar content, total acidity, weight of 100 grains, gluco-acidic index and anthocyanins was done by sampling from 5 to 5 days until the harvest maturity for each individual variety.

These analyzes were conducted in 3 consecutive viticultural years, 2015, 2016 and 2017.

Anthocyanin extraction

Grape anthocyanins determined by the method of Poissant Leon. For this use an average of 50 grain samples, weighed and carefully detach from the husks. In order to remove excess moisture, the skins were buffered with filter paper and dried in a hot air source.

Dry skins are powdered quartz fine sand after which they are passed into a flask with ground glass stopper by repeated washing with 1% HCl solution (approx. 10 ml concentrated HCl / liter).

In order to extract anthocyanins first wash fraction (50 ml) to be in contact with the skins to about 12 hours. Thereafter, the filtered or centrifuged extraction liquid is brought to a constant volume of 200 ml by mixing and the fractions resulting from repeated acid addition and kept in contact with the extract for at least one hour.

After obtaining the skin sample and the anthocyanin extract, the filtered extract is read on a 1 cm cuvette spectrophotometer at the optical density of 520 nm.

The amount of anthocyanins is determined on the basis of the formula:

mg/kg grapes = [Do 520 x 22,76 x 0,4/G 100 berries] x 1000

RESULTS AND DISCUSSIONS

The Dranic plantation is one of the youngest in Dolj county and was founded in 2007 through the process of reconversion and restructuring of the wine sector in our country.In the absence of clear data from the literature showing the direct relationship between natural factors and the evolution of the red wine grape ripening process, this detailed study was needed.This study may be the start for the suitability of this area for obtaining high-quality red wines.

The grade of maturation of grapes has an essential role in defining the organoleptic characteristics of quality red wines; therefore setting the optimum harvest time has become an indispensable technological link.In obtaining red wines knowledge of the evolution of fermentable sugar content and acidity is not sufficient, so it is necessary to establish the phenolic maturity by following the evolution of the anthocyanins in the grape skin (Fernadez Lopez at al., 1998).

Analyzing the data obtained during the three years studied, it is first of all noted that at all three varieties studied the firstfruitsstarted around August 5, not spread on varieties due to the high temperatures recorded in recent years. From the point of view of achieving full maturity, at the latest, the Cabernet Sauvignon variety (Table 1) proved to be present in the ecoclimatic conditions, which made the highest berries weight on 15.09 in the first two years of study, and the highest absolute content in carbohydrates.

In the exceptional climatic conditions recorded in 2017 with excessively high temperatures, the full maturity of the Cabernet Sauvignon variety was achieved at 10.09 owing to the climate change that led to a forced maturation of the grapes.

The grapes were harvested on 19.09, 16 days earlier than in the previous years, at a concentration in carbohydrates 242 g / l, which is unusual even for the southern area of the country.

In 2016 after reaching full maturity, on the background of precipitation for 4 days between 18 and 21.09 by 8 l / m^2, at the next determination on 20.09, there was a slight increase in berries weight and a decrease in the carbohydrate and anthocyanin content, after which the process proceeded normally until the harvest took place on 4.10, when the grapes had a carbohydrate content of 228 g / l.

The total acidity had a balanced evolution in the first two years of study, recording values at 5.15 g / l H_2SO_4 at 2.10 2015, 5.32 g / l H_2SO_4 at 4.10.2016 and was slightly deficient in 2017 by 4, 60 g / l of H_2SO_4 at 19.09.

The glucoacidimetric index given by the ratio of carbohydrates to acidity is between 35 and 50. It highlights the very good quality of the harvest, which records all years and all varieties of values that make it possible to obtain high quality wines.

Analyzing the behavior of the Merlot variety (Table 2) in the studied area, it is found that it is the earliest variety, achieving full maturity at 30.08 in the first two years when it recorded over 200 g / l and at 25.08 in 2017. Grapes were harvested at 9.09 in 2015, 5.09 in 2016 and 30.08 in 2017, when grapes provided alcoholic strengths in future 14 vol% wines.

The Fetească Neagră variety (Table 3) had an intermediate behavior regarding the ripening dynamics between Cabernet Sauvignon and Merlot. Thus, full maturity was conducted on 5.09 in 2015 and 2016 and 30.08 in 2017, and harvesting was done at technological maturity, 20.09 in 2015, 7.09 in 2016 and 6.09 in 2017, when the grapes have achieved content of carbohydrates and acidity for the types of wine to be obtained.

Table 1

Evolution of Cabernet Sauvignon grapes maturing in 2015-2017

Year	Parameter analized	CALENDARISTIC DATA												
		5.08	**10.08**	**15.08**	**20.08**	**25.08**	**30.08**	**5.09**	**10.09**	**15.09**	**20.09**	**25.09**	**30.09**	**2.10**
2015	Glucides, g/l	85	94	115	126	149	178	182	191	199,5	210	219	235	240
	Total acidity g/l H_2SO_4	13.8	13.2	12.5	11.20	10.35	9.20	8.40	7.85	6.80	6.20	5.85	5.40	5.15
	Weight of 100 berries g	69	75	89	95	99	101.2	112	113.5	**115.5**	115	114.3	113.6	112
	Index z/a	6.15	7.12	9.20	11.25	14.39	19.34	21.6	24.33	29.33	33.87	37.43	43.51	46.60
	Anthocyans, mg/kg berries	183	475	730	950	1140	1198	1210	1247	1274	1305	1300	1295	1294
2016	Glucides g/l	90.4	95.4	121	143.2	158.4	168	188	195	215	214	220.4	226.2	228
	Total acidity g/l H_2SO_4	14.66	13.25	12.78	11.57	10.12	9.40	8.13	7.98	7.01	6.80	5.95	5.45	5.36
	Weight of 100 berries g	67	74	85	91	96	100.2	106	109.5	**111.2**	111.4	109.8	107.8	106.5
	Index z/a	5,4	7,2	9,46	12,37	15.65	17.87	23.1	24.43	29.24	32.05	37.37	41.50	42.53
	Anthocyans mg/kg berries	190	450	710	980	1160	1292	1350	1390	1410	1433	1430	1427	1426
2017	Glucides, g/l	90.4	95.4	114.5	148.2	169	195	206	231	237	242.4	245		
	Total acidity g/l H_2SO_4	12.49	11.46	10.68	10.02	9.35	8.85	7.13	6.50	5.10	4.60	4.10		
	Weight of 100 berries, g	60	71	83	89	95	100.2	101.5	**104.8**	103.7	102.5	101.2		
	Index z/a	7.23	8.32	10.72	14.5	18.07	22.02	28.8	35.53	41.57	47.34	49.29		
	Anthocyans, mg/kg berries	210	465	810	995	1180	1292	1312	1420	1498	1496	1493		

Table 2.

Evolution of Merlot grapes maturing in 2015-2017

Year	Parameter analized	CALENDARISTIC DATA								
		5.08	**10.08**	**15.08**	**20.08**	**25.08**	**30.08**	**5.09**	**10.09**	**15.09**
2015	Glucides, g/l	102.7	125.5	165	190	209	219	235	242	245
	Total acidity g/l H_2SO_4	9.85	8.50	7.45	6.75	5.50	5.10	4.75	4.35	4.20
	Weight of 100 berries, g	75	82	98	110.5	114	**119.5**	118	117.5	117
	Index z/a	10.42	14.76	22.14	28.14	38.0	42.94	49.47	55.63	58.33
	Anthocyans, mg/kg berries	210	525	802	978	1104	1211	1225	1218	1217.7
2016	Glucides, g	112.7	135.5	166	195	215	222.4	239	243	
	Total acidity, g/l H_2SO_4	9.2	8.3	7.10	6.45	5.70	4.95	4.85	4.10	
	Weight of 100 berries, g	75	82	98	101.5	112	**120**	117	116	
	Index z/a	12.25	16.93	23.38	30.23	42.15	44.92	49.27	59.26	
	Anthocyans, mg/kg berries	250	595	810	989	1110	1250	1275	1273	
2017	Glucides, g/l	126.12	168	180.5	202	217	235	247		
	Total acidity, g/l H_2SO_4	7.5	6.8	5.67	5.45	4.89	4.58	4.02		
	Weight of 100 berries, g	68	82	98	108.5	**112**	110.3	109		
	Index z/a	16.81	24.70	31.83	37.06	44.37	51.31	61.44		
	Anthocyans, mg/kg berries	301	615	830	1020	1085	1170	1205		

Establishing the best harvest date was achieved by analyzing the evolution of anthocyanins content during grapes maturation. Analyzing the evolution of anthocyanins accumulation in the three studied varieties, it is found that each variety has its own potential for the accumulation of anthocyanins, which is different depending on the variety and the climatic conditions of the year.

Of the three varieties studied, Cabernet Sauvignon has the highest accumulation potential of anthocyanins in all 3 years (1305 mg / berries - 1498 mg / berries). It should be noted that the maximum of the anthocyanins accumulation after reaching full maturity takes place after the harvest year around their slight decrease is recorded. 2017 year very warm, phenolic maturity achieved on 15.09 coincides with a high unmet index glucoacidimetric situation in previous years.

Although there are qualitative similarities between theclasses of compounds produced by the three cultivars asoutlined earlier, some quantitative differences were notedfor glucides and anthocyans content at the same variety in different years. Thedominance of the anthocyans in Cabernet Sauvignon was also observedin all three years studied.

The same evolution of anthocyans contents was observed also at Merlot and Feteasca neagra varieties but the accumulation are smallar.

At Merlot and Fetească neagră which also have the potential anthocyanins high, but is not the Cabernet Sauvignon, maturity phenolic is made earlier, or around 5 September, however the loss of anthocyanins in over-ripening are faster especially Fetească neagră, so harvesting must be done quickly, unlike Cabernet Sauvignon that can be harvested in a longer period of time.

From the analysis of the data obtained during the 3 years studied, the phenolic maturity was 15-20.09 for the Cabernet Sauvignon variety, 30.08 - 5.09 for Merlot and 10.09 - 15.09 for the Fetească neagră variety.

Following the evolution of the accumulation of anthocyans during maturation to the three varieties, it is observed that from the firstfruits, their accumulation is very intense for 20-25 days. Then it becomes slower and finally the content starts to diminish, this phase corresponding to the beginning of over-maturity of berries.

A distinct difference between Cabernet Sauvignon, Merlot and Feteasca neagra grapes was achieving the full maturity materialized through different harvest dates in 2017 compared to the other two years.

Table 3.

Evolution of Fetească neagră grapes maturing in 2015-2017

Year	Parameter analized	CALENDARISTIC DATA								
		5.08	**10.08**	**15.08**	**20.08**	**25.08**	**30.08**	**5.09**	**10.09**	**15.09**
2015	Glucides, g/l	99.5	112	129	180.2	189	198	206.7	219	228
	Total acidity g/l H_2SO_4	9.80	9.45	7.65	7.50	6.90	6.45	6.25	5.25	4.50
	Weight of 100 berries g	83	96	104	113	121	125	**128.3**	127.5	126
	Index z/a	10.15	11.85	16.86	24.02	27.39	30.69	33.07	41.71	50.66
	Anthocyans mg/kg berries	195	447	635	870	1005	1027	1121	1132	1140
2016	Glucides g/l	91.8	102.5	138	192.7	207	212	225	231	237
	Total acidity g/l H_2SO_4	10.33	9.65	7.79	7.49	6.95	6.46	6.10	5.65	5.10
	Weight of 100 berries g	85	95	102.5	111	118	122	**127**	125.5	123
	Index z/a	8.8	10.62	17.71	25.72	29.78	32.81	36.88	40.88	46.47
	Anthocyans mg/kg berries	180	425	680	880	1010	1065	1115	1135	1129
2017	Glucides g/l	105.56	136.5	152.4	171.3	196	219.6	230	239	243
	Total acidity g/l H_2SO_4	9.12	8.67	8.20	7.65	6.89	6.12	5.60	5.05	4.92
	Weight of 100 berries g	73	87	95	103	112	**119**	116	114,5	114
	Index z/a	11.57	15.74	18.58	22.39	28.44	35.88	41.07	47.32	49.39
	Anthocyans mg/kg berries	210	407	705	895	1012	1045	1098	1104	1099

In the studied area, red grapes were harvested after full maturity, at different dates, depending on the type of wine Blanc de Rouje, Rose or Red, especially taking into account the anthocyans content.

CONCLUSIONS

Drănic vineyard is one of the youngest vineyards in Dolj County, enjoying a high degree of favorability ecopedoclimatic. Wine production in this area is oriented entirely toward achieving white, rose and red wines of high quality.

Although the Dranic wine-growing area is quite new on the country's wine map, the first recognitions of the quality of the wines obtained from this plantation began to appear.

The medals obtained so far by Dranic wines at the big competitions are the best proof of the vocation of this area for quality viticulture, Establishing the momentum of full maturity is not enough to appreciate the quality of the black grapes, so it is necessary to establish the moment of realization of the phenolic maturity.

In climatic conditions in the studied area, the differences between full and phenolic maturity is lower for the Melot and Fetească neagră varieties and higher for Cabernet Sauvignon. The Cabernet Sauvignon variety is more easily over-ripening, with lower losses in anthocyanins and can therefore be harvested over a longer period of time.

In the wine year 2017 due to the high temperatures due to the lack of rainfall, full and phenolic maturity was achieved in all three varieties studied earlier than in previous years.

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