ANTHOCYANIN IN GRAPE SKINS DURING MATURATION OF *VITIS VINIFERA* L. cv. CABERNET SAUVIGNON AND MERLOT NOIR FROM DIFFERENT BORDEAUX TERROIRS

LES ANTHOCYANES DES PELLICULES DE RAISIN *VITIS VINIFERA* L. cv. CABERNET SAUVIGNON ET MERLOT NOIR PENDANT LA MATURATION SUR DIFFÉRENTS TERROIRS BORDELAIS

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Abstract: Three varieties of red grapes have been analysed on the basis of their anthocyanin content to search a relation between this parameter and selected terroirs. For that, we compared their anthocyanin evolution during maturation. Then we analysed by HPLC the anthocyanin content of grapes at maturity and of their corrresponding wines. So, we established a comparison between potential anthocyanins in grapes and in corresponding wines. These observations permitted to occur some characteristics to these varieties and to evaluate the impact of terroir on grape skins anthocyanin composition.

Résumé : Trois cépages ont été étudiés. Les analyses ont concerné leur contenu anthocyanique afin de rechercher d'éventuelles relations entre ce paramètre et les terroirs retenus. Pour cela, nous avons comparé l'évolution des anthocyanes durant la maturation ; puis nous avons déterminé par HPLC la répartition des différentes anthocyanes des pellicules de raisins à maturité et de leurs vins correspondants. Ainsi, il a été possible d'établir une relation significative entre le potentiel anthocyanique des raisins et les anthocyanes des vins. Ces observations ont permis de définir les caractéristiques propres à ces cépages et d'évaluer l'impact du terroir sur la composition anthocyanique.

Keywords: anthocyanins, cultivars, maturation, terroir, HPLC

Mots clés : anthocyanes, cépages, maturation, terroir, CLHP

Abbreviations: A_1 total potential of anthocyanins; A_2 potential of extractive anthocyanins; Cf Cabernet Franc; Cs Cabernet Sauvignon; Mn Merlot noir; % diff diffusion percentage of anthocyanin from grapes to wines; EA index of cellular maturity; HPLC high performance liquid chromatography; LSIMS liquid secondary ions mass spectrometry; M/J ratio marc / juice; S/TA index of industrial maturity; TA titratable acidity; T-A Tannin-Anthocyanin combinations

INTRODUCTION

Anthocyanins are responsible of the colour of red wines (RIBÉREAU-GAYON, 1973). They are constitued by a phenyl-2-benzopyrilium skeleton. Differences of these compounds come from the substitution of the lateral ring, the number of glucoses moeity, the acylation of these glucoses and the nature of acylating compounds (BROUILLARD, 1982). Five monoglucosid (mG) anthocyanins have been identified in grape varieties (ROGGERO *et al.*, 1988): cyanidin-mG, delphinidin-mG, petunidin-mG, paeonidin-mG and malvidin-mG. Malvidin-mG beeing majority for the main *Vitis vinifera* L. (RIBÉREAU-GAYON, 1964 ; CHEYNIER *et al.*, 1999). Biosynthesis of anthocyanins is influenced by different factors such as synthesis of sugars, hydrous alimentation, UV irradations (climatic conditions), presence of some metals (chemical composition of soil) (DARNÉ, 1991; DARNÉ, 1993). These different factors participate to the « terroir » notion. So, we can understand the influence of

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J. Int. Sci. Vigne Vin, 2001, **35**, n°3, 149-156

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terroir on anthocyanin content of grape varieties (RIGAUD *et al.*, 1995). Anthocyanins can give some combinations with tannins, other phenolic compounds and can form chelates with some metals (i.e copigmentation) (BROUILLARD *et al.*, 1991; LIAO *et al.*, 1992; DANGLES *et al.*, 1994). These condensed forms participate to stabilisation of red wines colour. All anthocyanins identified in grapes are derived from skins (except for a few grape varieties « teinturiers »); they are localized exclusively in vacuoles of skin cells (AMRANI JOUTEI and GLORIES, 1996). For grapes coming from *Vitis vinifera* L., they are in monoglucosid form, esterified in part with phenolic acids or organic acids especially acetic acid (ROGGERO *et al.*, 1988).

Present study involves anthocyanin content of three different grape varieties (Merlot Noir, Cabernet Sauvignon and Cabernet Franc) grown on different terroirs in vineyard of Bordeaux (Gironde, France). First, a method to study the anthocyanin maturity of grapes the day of vintage is proposed. Then a quantitative determination of anthocyanin content was performed by HPLC. This study was undertaken to determine the difference of « anthocyanin maturity » between two different varieties (Mn, Cs) in different terroirs. These analysis permitted to visualize the reciprocal influence between the nature of variety and the terroir. With an improvement of method, a final result leads to a comparison between the anthocyanin content in grape skins and in corresponding red wines. The aim of this study is to anticipate the anthocyanin content of wine from grapes while taking terroir and variety into consideration.

MATERIALS AND METHODS

I - SELECTION OF GRAPES AND WINES

Terroirs have been selected because of their distribution on the whole of the Bordeaux region (Gironde, France): Entre-deux-Mers, Médoc, Graves, Pomerol. On these selected terroirs, the grape varieties were taken in the same vineyard. Parcells were choseen for the similitary of wine ages (35 years ± 5), the same density of plantation (5500 plants per ha), a comparable production (for Mn near 45 hl/ha and for Cs near 50 hl/ha) and a similar viticultural techniques (to limit the number of variation factors). Three selected varieties are *Vitis vinifera* L. cv Merlot Noir (Mn, n=6), Cabernet Sauvignon (Cs, n=5) and Cabernet Franc (Cf, n=1) for their typical characteristics from Bordeaux (the most representative of the Bordeaux region). Grapes have been picked up at maturity, the day of harvest which are fixed according S/TA (such as S/TA is maximum which is empirical known) and the latter stages of grape ripening. Like this, grape varieties are compared when their industrial maturity is attained.

	Soil	Terroir	Grape variety
T1	gravelly	Graves, Léognan	Mn, Cs
T2	gravelly	Graves, Pessac	Mn, Cs, Cf
T3	clayey-gravelly	Haut-Médoc, Pauillac	Mn, Cs
T4	alluvial-sandy	Bas-Médoc, Blanquefort	Mn, Cs
T5	clayey -sandy	Entre-deux-Mers	Mn, Cs

The selected parcells have been wine-making separately to have each corresponding wines. The wines of these different soils and of these three varieties were vinified in 50 hl stain stell tanks, with the same vinification conditions. Analysis were done 15 days after the end of malolactic fermentation.

All analysis have been repeated three times, on series of 4 sampling by parcell.

II - PREPARATION OF PLANT MATERIAL

400 berries have been picked up and distributed in two samples of 200 berries with equivalent weight.

1) Analyse of the first sample

200 berries have been pressed. Juice and marc have been separated:

- On juice: we determinated specific gravity, sugars, titratable acidity and pH.
- On marc: we dissolved residual sugars by rinsing with distilled water. Then, the marc has been filtered, dried (24 hours, 25 °C) and weighed.

So, we could calculate marc / juice ratio producted by 200 berries:

M/J = (marc weight [g] / juice volume [mL]) x 1000 (1)

2) Analyse of second sample

Second sample of 200 berries have been milled two minutes in a grinder;

2 x 50 g of this mixture have been taken; let V (mL) be a volume represented by this mass:

V (mL) = (50 x 1000) / density (2)

We added to first and second samples respectively V (mL) of aqueous solution (tartaric acid 5 g/L, pH 3,2 by NaOH N) and V (mL) of aqueous solution at pH 1 (HCl N / 10). These two samples have been homogenized and incubated 4 hours at 25°C. Then, they have been filtered through fibreglass. Anthocyanidin content of these two solutions has been evaluated by RIBÉREAU-GAYON and STONESTREET (1965) method.

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In these conditions:

ApH1 = A_1 (potential of total anthocyanins)
ApH3,2 = A_2 (potential of extractible anthocyanins).

3) Calculation and interpretations

Specific gravity and titratable acidity (TA) allow to obtain S/TA ratio, « industrial maturity ».

For A_1, the extraction is higher and independent of anthocyanin extractibility . This result represents the « total anthocyanin potential ». It depends of synthesis and accumulation of pigments. For A_2, it is a passive extraction near to the conditions of maceration in wine-making. It represents the « potential of extractible anthocyanins ». A_2 is always less than A_1 but it draw near to this latter in the last maturation when cells are alterated by the normal process of grape ripening.

Difference between these two values is conditional upon degree of degradation of cells, so it represents an indication of pigment extractibility and it could be considered like the « cellular maturity »:

$$EA = \frac{ApH1 - ApH3,2}{ApH1} \times 100 \quad (3)$$

When EA is low, anthocyanins are easily extractible from grapes.When it is high, anthocyanins are less able to solubilized in wine at maceration time.

III - PREPARATION OF WINES' SAMPLES

Wines' samples were collected after malolactic fermentation. Total anthocyanin content was evaluated by RIBÉREAU-GAYON and STONESTREET method (1965). Then, wines' anthocyanins have fractionnated: free anthocyanins (AL) and Tannins-Anthocyanins combinations (T-A). For that, 5 mL of wine were deposed on a pvpp column. Non-phenolic constituents were eliminated by H_2O (150 mL). Fraction of free anthocyanins were eluted by MeOH acidified by 5 p. cent of HCOOH (150 mL) and collected. Solvent was evaporated and the fraction was dissolved with 5mL of hydroalcoholic solution (ethanol 12 p. cent, pH 3,2). Level of free anthocyanins was evaluated by the method previously cited (RIBÉREAU-GAYON and STONESTREET, 1965). Then, T-A were deduced by difference between the concentration of total anthocyanins and those of free anthocyanins. This has permited to obtain a first coarse distribution of wines' anthocyanins. After, anthocyanin content of wines have been most finely analysed by HPLC.

IV - HIGH PERFORMANCE LIQUID CHROMATOGRAPHY ANALYSIS

1) Preparation of grapes and wines samples

100 berries supplementary have been picked up to quantify the anthocyanin content by High Performance Liquid Chromatography (HPLC). Skins have been separated from juice. They were weighed, freeze-dried, reduced to powder and then shaked for two minutes in a blender with 100 mL of hydroalcoholic solution (ethanol 12 p. cent and pH 3,2). The medium was agitated during 6 hours then centrifugated (20 min, 4000 g). The supernatant was filtered to eliminate insoluble fractions (millipore filter, 0,45 mm). Skin' extracts obtained were analysed by HPLC. The collected wines' samples were filtered through a 0,45 mm membrane before direct injection.

2) High performance liquid chromatography conditions

20 µL of sample were injected on a BECKMAN ultrasphere ODSTM C18 (250 x 46 mm; 5 µm) column at 20°C (± 1°C), and eluted with a flow rate of 1 $mL.min^{-1}$. Solvents, filtered through a 0,45 mm membrane were: Solvent A (acetic acid:water 5:95, v/v) and solvent B (acetic acid:methanol, 5:95, v/v)

Analytical method used was previously described by GUERRA *et al.* (1996). Gradient conditions were :

time (mn)	init.	0	62	65	79	80	114
A %	100	62	56	52	48	0	100
B %	0	38	44	48	52	100	0

Detection was monitored at 520 nm. Identification of anthocyanins was realized by co-injection of reference compounds (Extrasynthese ™) and confirmed by LC/MS LSIMS according to the method of VIVAS *et al.* (1996) used for ellagitannins. Levels of anthocyanins were quantified using standard curves developed from reference standards.

RESULTS AND DISCUSSION

I - INDUSTRIAL MATURITY OF GRAPES (table I)

This industrial maturity call out the wealth in sugars and in acidity of grapes. It is widely widespread like a quite usual because its realization is easy and its value permit to fix commonly the date of harvesting .

In using the descriptive statistics, we relate the following observations (table I):

As a general rule, we establish that weight of Cs berries is less than those Mn berries (average values: 275 for Cs and 300 for Mn). It's seems that weight of Cs berries depends less on terroir (low variance: 1195) than Mn which suffer some important fluctuations according to the considered terroir (high variance:

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Table I - Measurement berries weight, ratio sugar/titratable acidity (S/TA) and pomace/juice (M/J) of the different samples.

Mesure du poids des baies, des rapport sucres/acidité totale (S/AT) et marc/jus (M/J) des différents échantillons.

	Weight 200 berries (g)			S/TA			M/J		
	Mn	Cs	Cf	Mn	Cs	Cf	Mn	Cs	Cf
T1	275	290		70	41		220	255	
T2	377	316	303	69.5	58	43.5	159	286	257
T3	350	290		48	36		158	240	
T4	275	250		69	45		122	---	
T5	225	230		48	33		161	235	
mean	300.4	275.2		60.9	42.6		164	254	
variance	3825.8	1195.2		138.4	95.3		1242.5	527.3	
sd deviation	61.8	34.6		11.8	9.8		35.2	23.0	

3825). On the other hand, the ratio M/J is superior for Cs. As a matter of fact, for variety Mn, the size of berries is very variable according the terroir and so, the produce of must too (high variance: 1242). More, the ratio S/TA « index of industrial maturity » is also a good characterisation of considered variety (low variance). We observ that the ratio S/TA is more high for Mn than for Cs, that is explained by the characteristic of these grapes which are considered like a precocious variety. However, some variations depend on terroir getting in evidence some terroirs adapted to Cs and some other to Mn.

In order to supress the « terroir effect », we have studied the behaviour of different varieties (Mn, Cs and Cf) on a same terroir. We have added a new variety (Cf) to the varieties already studied with the intention of to increase « variety effect » in relation to the « terroir effect ». Indeed, the selected terroir is T2 (Graves, Pessac) because, on this soil, the parcells of Cs, Cf, Mn are juxtaposed which limit to the full the « terroir effect ». These results check the preceding establishments: In the case of Mn, the weight of berries is higher to those of Cs berries, the ratio M/J is less than those of Cs, the ratio S/TA is highter. Cf has an intermediate behaviour. These results are confirmed by empirical observations realized in this vineyard many years ago.

We came to the conclusion that, as a general rule:

- Weight of berries and ratio M/J varies essentially in accordance with the terroirs. Therefore, we know that the « terroir notion » call out the chemical and physical characteristics of soil and the climatic conditions (GUILLOUX, 1981; MORLAT, 1989). Morever, the selected terroirs have been studied on pedology and climatic conditions (SEGUIN, 1970; COMPAGNON, 1970; DUTEAU, 1976). They are sufficiently distincts and distants to be much characteristic of their region. So, these results were fureseeable by reason of sensitiveness of weight of berries and ratio M/J with regard to climatic conditions. Indeed, we know that climatic conditions and especially precipitations are originally of some important dilutions of berry juice. Consequently, ratio M/J and berry weight are closely linked with the amount of available water. More, precipitations are very variable according to the terroir. Indeed, the capacity of soils to hold water (retention capacity) is different according their composition. In these conditions, the Mn seems to be the more sensitive to these dilutions what induce to weight of berries superior and to ratio M/J less that in the case of Cs.

- On the other hand, in all samples analysed, the ratio S/TA is superior for Mn, what is characterized like a precocious variety.

II - ANTHOCYANIN MATURITY OF GRAPES (figures 1 and 2)

This anthocyanin maturity is bounded with anthocyanin accumulation in skins (potential anthocyanins). However, we have recorded that grapes enclosing a high anthocyanin content don't always give the more coloured wines (AUGUSTIN, 1986; AMRANI-JOUTEI, 1993). Indeed, wine colour depend on anthocyanin concentration but also on the extractibility of these pigments. We know that wine colour is originate in an adequate « phenolic maturity » accompanied by a sufficient « cellular maturity » to permit a maximum extractibility of phenolic compounds: At maturity, the phenomenum of parietal degradation facilitate the solubilization of vacuolar anthocyanin content. So, we have considered the degree of degradation of skin cells, that is to say the extractibility of pigments. This « anthocyanin maturity » can be represented by the EA%.

Figure 1 shows the different behaviour of these two varities about the anthocyanin maturity: The potential of total anthocyanins (A_1) is very different according the considered terroirs. On the other hand, in the case of Cs, we note that extractible anthocyanins are relati-

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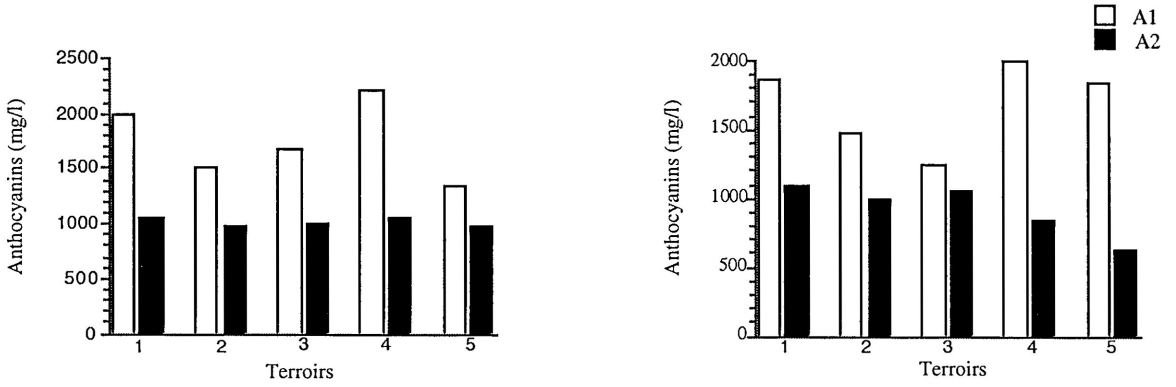


Fig. 1 - Anthocyanin maturity of one variety on different terroirs (A1: potential anthocyanins mg/L; A2: extractive anthocyanins mg/L) A: Cabernet Sauvignon (SD A1: 357.4 mg/L; SD A2 : 32.8 mg/L); B: Merlot noir (SD A1: 309.6 mg/L; SD A2 : 193.3 mg/L)

Maturité anthocyanique d'un cépage sur différents terroirs (A1: anthocyanes potentielles mg/L ; A2: anthocyanes extractibles mg/L) A: Cabernet Sauvignon (SD A1 : 357,4 mg/L ; SD A2 : 32,8 mg/L) ; B : Merlot noir (SD A1 : 309,6 mg/L ; SD A2 : 193,3 mg/L)

vely constant on different terroirs. This variety seems to be characterize by a constant degree of degradation of skin cells. Mn have a different behaviour, the skin anthocyanins are more or less extractible according to terroirs.

So, we can suggest that:

- The accumulation of anthocyanins is independent on variety but is more bounded with terroir (climatic conditions, nature of soil: presence of metals...) which is directly involved in the biosynthesis of these pigments.

- The degradation of skin cells and so the extractibility of anthocyanins are proper characteristics of the considered varieties.

Furthermore, the comparison between these two varieties (figure 2) shows that the extractibility of Cs

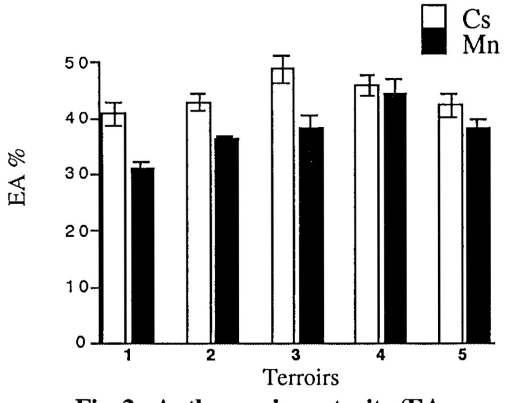


Fig. 2 - Anthocyanin maturity (EA p. cent)
(for Cabernet Sauvignon: SD EA = 3,2 p. cent; for Merlot noir: SD EA = 4,9 p. cent)

Maturité anthocyanique (EA p. cent)
(Pour le Cabernet Sauvignon : SD EA = 3,2 p. cent ; pour le Merlot noir : SD EA = 4,9 p. cent)

anthoyanins is more homogeneous but also less good than those of Mn.

III - ANTHOCYANIN CONTENT OF GRAPES (figure 3)

Anthocyanin content of these two grape varieties have been analysed by HPLC in reverse phase. We obtained, for each samples, the nature of monoglucosid anthocyanins and their distribution. The results have shown that terroir have an important effect on this anthocyanin distribution (percentage of delphinidin-mG over malvidin-mG varied between terroirs from 23 to 35 p. cent in Mn and from 21 to 35 p. cent in Cs), since the accumulating of these compounds is under the direct influence of terroir (climate, soil...). But, on the other hand, two characteristics seem to differentiate Cs from Mn: for every studied terroirs, the levels of delphinidine-mG and malvidine-mG are more important for Cs than for Mn. So, the level of total anthocyanins-mG is superior for Cs (figure 3). This tendency was become general on every terroirs.

With the same experimental conditions and for the same making up of samples, we don't note some significant differences in oligomeric procyanidin distribution (SAINT-CRICQ de GAULEJAC *et al.*, 1998). As the matter of fact, procyanidin distribution seems to be essentially due to the terroir and not to the grape variety. So, we came to conclusion that anthocyanin content is more suited to characterize the grape variety than procyanidin content.

IV - ANTHOCYANIN CONTENT OF CORRESPONDING WINES (table II)

On wines corresponding to previously analysed grapes, we have determinated the anthocyanin content

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by HPLC too. The results show an anthocyanin distribution less characteristic of variety than in the case of grapes. The case of wine is peculiar that there is a certain complexity of anthocyanin content compared with grapes. This is due to the presence of combinations Tannin-Anthocyanin (T-A) in wines (DOURNEL, 1985). However, according to the table II, we can establish that the Cs wines contain a rate of total anthocyanin generally superior to Mn' wines. In the same case, Cs wines seems to favour T-A (percentage of T-A most important than percentage of free anthocyanins). But these results explain themselves partly by a rate of tannins generally superior in these wines than in the Mn' wines (AUGUSTIN, 1986). So, anthocyanin distribution in wines depend closely on the presence of tannins. We must take the procyanidin content of wines into account because it have directly an influence on the anthocyanin content.

V - COMPARISON BETWEEN ANTHOCYANIN CONTENT IN GRAPES AND CORRESPONDING WINES (table II)

We have compared the anthocyanin content in grapes (mg/L of juice) with those of their corresponding wines (mg/L of wine) (table II). From the results obtained by RIBÉREAU-GAYON and STONESTREET method, we can note that the total anthocyanins of wine are in all cases inferior to the extractible anthocyanins of grape (A_2). It can be explain by two hypothesis:

- First, a partial anthocyanin extraction depending to the maceration techniques (bumping-over, intensity and frequence).

- Second, a possible reaction of anthocyanins with various compounds contributing to the formation of non-SO_2 discolored combinations. So, these combinations can not be evalueted in wine by the method of RIBÉREAU-GAYON and STONESTREET and the quantity determination of total anthocyanin of wine are realized at fault.

On the other hand, the results obtained by HPLC have permitted to establish the diffusion percentage of anthocyanin from grapes to wines (% diff). This experimentation has shown that this diffusion percentage

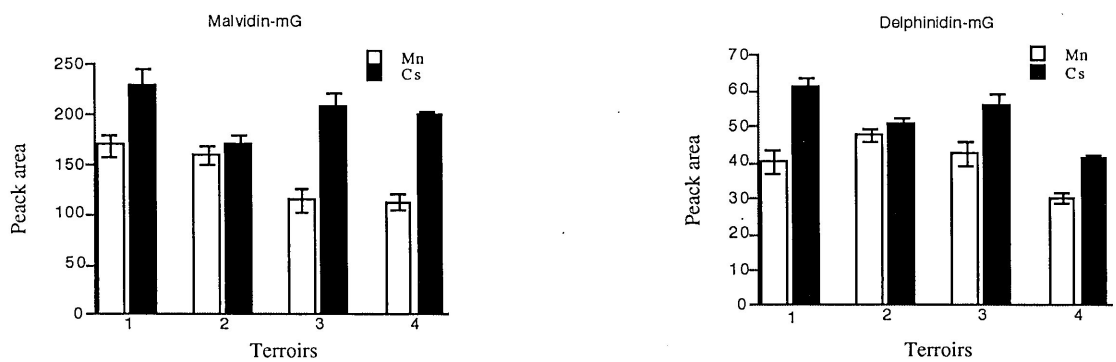


Fig. 3 - Different behaviour of Cabernet Sauvignon and Merlot noir facing the anthocyanin distribution.

Comparaison de la distribution en anthocyanes du Cabernet sauvignon et du Merlot noir.

Table II - Anthocyanin concentration (mg/L) in grapes and in their corresponding wines.

Concentration en anthocyanes (mg/L) des raisins et des vins correspondants.

	Merlot noir			Cabernet Franc			Cabernet Sauvignon			Mean
	grape	wine	% diff	grape	wine	% diff	grape	wine	% diff	% diff
Quantity determination by HPLC										
Delphinidin	30,4	16,7	55,0	43,0	21,9	50,9	61,9	30,1	48,6	51,5
Cyanidin	6,5	trace	≈0	9,7	trace	≈0	10,4	trace	≈0	0,0
Petunidin	42,7	28,8	67,4	51,1	32,5	63,6	61,1	32,7	53,5	61,5
Paeonidin	31,1	11,7	37,7	48,2	13,0	27,0	43,0	12,9	30,0	31,6
Malvidin	326,3	301,2	92,3	359,2	342,0	95,2	403,9	329,0	81,4	89,6
Total	437,0	358,4		511,3	409,5		580,4	404,6		
Quantity determination by RIBÉREAU-GAYON and STONESTREET method										
Anthocyanins[a]	984	736		852	665		993	718		

[a]Anthocyanins: extractible anthocyanins (A_2) for grapes; total anthocyanins for wines

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varies a little according to the varieties (variation coefficient < 8 p. cent) but varies a lot according to the considered anthocyanin-mG. For example, % diff is pratically non-existent for cyanidin-mG even thoug almost all of malvidin-mG are rediscovered in wine (% diff = 0,89).

Two hypothesis can explain these variations:

- either anthocyanins with a low % diff (paeonidin-mG and cyanidin-mG) are a little extractible and so a little susceptlible to be solubilized in wines.

- either these anthocyanins are as much extractible as the other but they are very reactive in wine and their concentration decreases rapidly.

This lastest hypothesis seems to be confirmed by the study of DALLAS *et al.* (1996). According to these authors, these anthocyanins (paeonidin-mG and cyanidin-mG) react very slowly and with the same reaction rate when the medium do not contain some procyanidins. And, in grapes, several research groups (AMRANI JOUTEI, 1993; MERLIN *et al.*, 1985; PECKET and SMALL, 1980) have already demonstrated that anthocyanins are localized exclusively in vacuoles of skin cells and are not in contact with tannins. This explain the presence of cyanidin-mG in grapes for every analysed samples. On the other hand, DALLAS *et al.* (1996) have also shown that, in presence of procyanidins and acetaldehyde (wine conditions), these anthocyanins and especially cyanidin-mG are more reactives (K the more higher for the cyanidin-mG). So, they can rapidely form some combinations such as « Procyanidin-Acetaldehyde-Anthocyanin -mG ». This can justify the disappearance of cyanidin in wines which is susceptible to react with other phenolic compounds.

CONCLUSION

Industrial and anthocyanin maturity of grapes shows some characteristics proper to Mn and to Cs, though the biosynthesis and so the accumulation of anthocyanidins in skin cells of grapes are essentially influenced by the terroir (climatic conditions...). However, the anthocyanin distribution analysed by HPLC remains largely a characteristic of varieties and seems to be a little influenced by the terroir (contrary to the procyanidin distribution). On the other hand, in red wines the medium is too complex by the presence of other phenolic compounds and so anthocyanins become very reactive.

So, anthocyanin typicity of varieties find itself on a level of the industrial and anthocyanin maturity of grapes and of the anthocyanin distribution in skins. But this typicity disappears in wines because of the complexity of the medium. Only the wines resulting from different species possess some markers characteristic of these species such as: diglucosid anthocyanins for hybrid varieties, a level of malvidine very high for the Gamay...

ROGGERO *et al.* (1988) have equally classified varieties according to anthocyanin content of skins. Even if these authors justify that anthocyanin distribution is largely a characteristic of species, however the analytical results show that it is only possible to differenciate and to classify some very different varieties. Mn, Cs and Cf beeing classified in the same group. More, their characteristics vary so hard year by year that is the sign of an important sensitiveness to seasonal influences or to problems of maturation. It is a question of vintage which is worth studing at some future date.

REFERENCES

AMRANI JOUTEI K., 1993. Recherches sur la localisation des anthocyanes et des tanins dans le raisin. Les conditions de leurs extractions. *Thèse*, Université de Bordeaux II, 150p.

AMRANI JOUTEI K. and GLORIES Y., 1996. Isolement des protoplastes de pellicules de raisin et optimisation de leur rendement. *J. Int. Sci. Vigne Vin*, **30**, 41-45.

AUGUSTIN M., 1986. Étude de l'influence de certains facteurs sur les composés phénoliques du raisin et du vin. *Thèse*, Université de Bordeaux II, 100p.

BROUILLARD R., 1982. Chemical structure of anthocyanins. *In Anthocyanins as food colors*, Markakis P., (Ed.), Academic Press, New York.

BROUILLARD R., WIGAND M-C., DANGLES O., and CHEMINAT A., 1991. pH and solvent effects on the copigmentation reaction of malvin with polyphenols, purine, and pyrimidine derivatives. *J. Chemical Society, Perkin Transaction 2*, 1235-1241.

CHEYNIER V., ES-SAFFI N.E. and FULCRAND H., 1999. Structure and colour properties of anthocyanins and related compounds. *In Pigments in food technology*. Minguez Mosquera M.J., Galan M.J., Mendes D.H., (Eds.), Sevilla, 23-35.

COMPAGNON J., 1970. Contribution à l'étude des sols de vignobles des Graves et de l'alimentation en eau de la vigne. *Thèse*, Université de Bordeaux II, 130 p.

DALLAS C., RICARDO DA SILVA J.M. and LAUREANO O., 1996. Products formed in model wine solutions involving anthocyanins, procyanidins B2 and acetaldehyde. *J. Agric. Food Chem.*, **44**, 2402-2407.

DANGLES O., ELHABIRI M. and BROUILLARD R., 1994. Kinetic and thermodynamic investigation of the aluminium-anthocyanin complexation in aqueous

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solution. *J. Chemical Society, Perkin Transaction 2*, 2587-2596.

DARNÉ G., 1991. Recherches sur la composition en anthocyanes des grappes et des feuilles de vigne. *Thèse ès sciences*, Université de Bordeaux II, 210 p.

DARNÉ G., 1993. Nouvelles hypothèses sur la synthèse des anthocyanes dans les baies et dans les feuilles de vigne. *Vitis*, **32**, 77-85.

DOURNEL J-M., 1985. Recherches sur les combinaisons anthocyanes-flavanols. Influence de ces réactions sur la couleur du vin rouge. *Thèse*, Université de Bordeaux II, 120 p.

DUTEAU J., 1976. Le vignoble des Côtes du Bourg, les sols et le climat. Influence sur la croissance des sarments et sur la maturation du raisin. *Thèse*, Université de Bordeaux II, 160 p.

GUERRA C. and GLORIES Y., 1996. Influences des conditions de formation de combinaisons anthocyane / flavane-3 / Ethanal sur leur couleur. *Polyphénols communication 96*, P122, 289-290.

GUILLOUX M., 1981. Évolution des composés phénoliques de la grappe pendant la maturation du raisin. Influence des facteurs naturels. *Thèse*, Université de Bordeaux II, 140 p.

LIAO H., CAI Y. and HASLAM E., 1992. Polyphenol interactions. Anthocyanins: Co-pigmentation and colour changes in red wines. *J. Sci. Food Agric.*, **59**, 299-305.

MERLIN J., STATOUA A. and BROUILLARD R., 1985. Investigation of the in vivo organisation of anthocyanins using resonance raman microspectrometry. *Phytochemistry*, **24**, n°7, 1575-1581.

MORLAT R., 1989. Le terroir viticole : contribution à l'étude de sa caractérisation et de son influence sur la vigne. Application aux vignobles de moyenne vallée de la Loire. *Thèse*, Université de Bordeaux II, 2 tomes, 350 p.

PECKET R.C. and SMALL C.-J., 1980. Occurrence, location and development of anthocyanoplasts. *Phytochemistry*, **19**, 2571-2576.

RIBÉREAU-GAYON P., 1973. Interprétation chimique de la couleur des vins rouges. *Vitis*, **12**, 119-142.

RIBÉREAU-GAYON P. et STONESTREET E., 1965. Le dosage des anthocyanes dans les vins rouges. *Bull. Soc. Chim. France*, **9**, 2649-2652.

RIGAUD J., CHEYNIER V., ASSELIN C., BROSSAUD F. and MOUTOUNET M., 1995. Caractérisation des flavonoïdes de la baies de raisin : Application à l'étude de terroir. *In Œnologie 95*, Lonvaud-Funel A., Lavoisier Tec et Doc (éd.), Paris, 137-140.

ROGGERO J.P., LARICE J.L., ROCHEVILLE-DIVORNE C., ARCHIER P. and COEN S., 1988. Composition anthocyanique des cépages. I- Essai de classification par analyse factorielle discriminante. *Rev. Fr. Œnol. (cahier scientifique)*, **112**, 41-48.

SAINT-CRICQ de GAULEJAC N., FREITAS V., GLORIES Y., BOURGEOIS G. and VIVAS N. 1998. Fractionnement et dosage des procyanidines oligomères des raisins et des vins : Relation avec la qualité des vins. *Sci. Aliments*, **18**, 59-76.

SEGUIN G., 1970. Les sols viticoles du Haut-Médoc, influence sur l'alimentation en eau de la vigne et sur la maturation du raisin. *Thèse ès sciences*, Université de Bordeaux, 150 p.

VIVAS N., GLORIES Y., BOURGEOIS G. and VITRY C., 1996. Les ellagitanins de bois de cœur de différentes espèces de chênes (*Quercus* sp.) et de chataîgnier (*Castanea sativa* Mill.). Dosage dans les vins rouges élevés en barriques. *J. Sci. Tech. Tonnellerie*, **2**, 24-49.

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