Vitis 37 (2), 93–94 (1998)

Research Note

Evolution of anthocyanins during grape maturation of two varieties (*Vitis vinifera* L.), Castelão Francês and Touriga Francesa

A. M. Jordão, J. M. Ricardo da Silva and Olga Laureano

Introduction: In red varieties the anthocyanin content of berries increases distinctly at veraison. Darné (1988) showed that in Cabernet-Sauvignon two or three weeks before the onset of colour change, anthocyanins were already present in berry skins. The anthocyanin evolution during berry maturation can be separated in three phases (Somers 1976; Pirie and Mullins 1977; Ribéreau-Gayon 1982; Budin 1983; Hrazdina *et al.* 1984; Darné 1988; Gonzalez-San José *et al.* 1990). Anthocyanins show a slow increase, followed by a rapid increase, and then a stabilisation is observed. Somers (1976) observed maximum anthocyanin concentration occurring 20-30 d after veraison. After prolonging the maturation period, a decrease of the anthocyanin level associated with shrinkage of the berries was observed (Somers 1976; Pirie and Mullins 1980). Using polynomial regression models Gonzalez-San José *et al.* (1990) showed that in Tempranillo the anthocyanin concentration increased nonlinearly during maturation. Considering the importance of anthocyanins for red wine quality, the purpose of the present work was to study the evolution of these pigments during grape maturation of two important cultivars in Portugal. This work is part of a larger study in which the evolution of flavanols during grape maturation is investigated.

Material and methods: Grapes: 200 berries of Castelão Francês and Touriga Francesa grapes were sampled in 1995 in a vineyard located in the region of Palmela (south of Lisbon). For Touriga Francesa the sampling started when the grapes began to change colour (veraison, July 5) and for Castelão Francês grapes 7 d later at the same developmental stage.

Anthocyanin extraction: Each sample was prepared as described by Carbonneau and Champagnol (1993). The resulting slurry (maceration for 24 h at 25 °C) was centrifuged for 10 min (3500 rpm) and filtered through a 0.45 µm filter.

HPLC analysis: The equipment used for analytical HPLC was a Perkin-Elmer system with a 410-LC pump and a solvent programmer (model 420). The analyses followed the procedure described by Roggero *et al.* (1986).

Statistical analysis: In order to analyse the differences in the results obtained, a variance analysis was performed and, when necessary, also the Duncan's multiple range test to separate the means. All statistical calculations

Table

Distribution (% w/w) of anthocyanins of Castelão Francês and Touriga Francesa grape varieties during maturation

Anthocyanin	Sampling date							
	July, 5		July, 26		August, 16		September, 6	
	Castelão Francês	Touriga Francesa	Castelão Francês	Touriga Francesa	Castelão Francês	Touriga Francesa	Castelão Francês	Touriga Francesa
Delp-3-gluc	ND	4.4	4.5	2.5	4.1	1.5	6.2	0.9
Cyan-3-gluc	ND	2.6	2.2	0.2	1.6	0.1	2.6	0.1
Petun-3-gluc	5.8	7.0	7.3	4.6	7.3	2.9	8.5	2.5
Peon-3-gluc	5.8	6.1	15.2	3.5	16.0	3.2	11.7	3.6
Malv-3-gluc	58.8	53.5	61.0	67.0	64.6	52.6	59.2	46.3
Delp-3-acetylgluc	ND	0.6	ND	0.2	ND	0.1	0.2	0.1
Cyan-3-acetylgluc	ND	ND	ND	0.3	ND	0.1	0.1	0.3
Petun-3-acetylgluc	ND	0.7	ND	0.7	ND	0.3	0.4	2.5
Peon-3-acetylgluc	ND	0.9	ND	0.5	ND	0.5	0.5	3.6
Malv-3-acetylgluc	11.7	8.8	3.4	1.2	1.6	12.9	4.0	12.9
Delp-3-coumarylgluc	ND	ND	ND	0.3	ND	0.2	0.2	0.5
Cyan-3-coumarylgluc	ND	ND	ND	ND	ND	0.1	0.1	0.1
Petun-3-coumarylgluc	ND	0.9	0.6	2.5	0.8	2.3	0.9	1.9
Peon-3-coumarylgluc	ND	0.9	0.6	1.2	0.5	1.3	0.9	1.2
Malv-3-coumarylgluc	17.6	14.9	5.1	20.5	3.2	21.8	4.6	23.4
Total anthocyanins (Malv-3-gluc, mg. g^{-1} berry)	0.003^{A}	0.112^{B}	0.177^{A}	0.566^{B}	0.369^{A}	0.854^{B}	1.092^{A}	0.645^{B}

Each value represents the mean from duplicate samples; ND = not detected; Delp = delphinidin, Cyan = cyanidin, Petun = petunidin, Peon = peonidin, Malv = malvidin, Gluc = glucoside. Means separated by LSD multiple range test at the 5 % level. Means followed by the same letter are not significantly different ($p<0.05$).

Correspondence to: Dr. J. M. Ricardo da Silva, Universidade Técnica de Lisboa, Instituto Superior de Agronomia, Secção de Ciência e Tecnologia de Alimentos (Sector de Enologia), 1399 Lisboa Codex, Portugal. Fax: +351-1-3635031 and +351-1-3602036.

were performed using the Statgraphics Statistical Computer Package.

Results and Discussion: The Table shows the distribution (%) of different monomeric anthocyanins detected in both cultivars during ripening. The principal anthocyanin was malvidin-3-glucoside. The concentration varied between 58.8 and 64.8 % of the total anthocyanin content in Castelão Francês grapes. For Touriga Francesa, this pigment varied between 46.4 and 67.0 %. The second most abundant component was the peonidin-3-glucoside in Castelão Francês (between 5.8 and 16.0 %), while in Touriga Francesa, the second most abundant was the petunidin-3-glucoside in the first 40 d of the sampling period. Among the acetyl anthocyanins the results indicate the same order for Touriga Francesa concerning the anthocyanidin form, while for Castelão Francês only at the last sampling date all acetyl anthocyanins were detected. Thus the principal acetyl anthocyanin was malvidin-3-acetylglucoside, which varied between 4.0 and 11.7 % in Castelão Francês and between 8.8 and 12.9 % in Touriga Francesa grapes. The second most abundant pigment was the peonidin-3-acetyl-glucoside while (and) the acetylated anthocyanins constituted the smallest group in both grape varieties. The results indicate that in the coumarylglucoside group, malvidin-3-coumarylglucoside was the principal individual pigment in both varieties.

For both grape varieties, cyanidin and delphinidin derivatives, which are the primary pigments in the biosynthetically pathway (ROGGERO *et al.* 1986), constituted the smallest group during maturation while malvidin derivatives were the most abundant, confirming the results of BAKKER and TIMBERLAKE (1985). On the other hand, the group of anthocyanin-3-glucoside-derived pigments were the most abundant, followed by the 3-coumaryl-glucoside-derived, during grape maturation. The concentration of the anthocyanin-3-glucoside increased gradually and finally more rapidly in Castelão Francês grapes. In Touriga Francesa, the increase of these pigments was followed by a decrease 60 d after veraison. ROGGERO *et al.* (1986) stated that malvidin-3-glucoside represents the ultimate form in chains of biosynthesis transformation. For Castelão Francês (Figure), we observed a gradually increase during ripening, in particular for malvidin-3-glucoside which increased from 0.23 to 0.59 $mg \cdot g^{-1}$ berry in the last 20 d of maturation. For Touriga Francesa a decrease was observed for malvidin-3-glucoside (from 0.44 to 0.29 $mg \cdot g^{-1}$ berry) in the last 20 d of maturation.

The authors thank the company JOSÉ MARIA DA FONSECA, Vinhos S.A., for the supply of grapes and for all support.

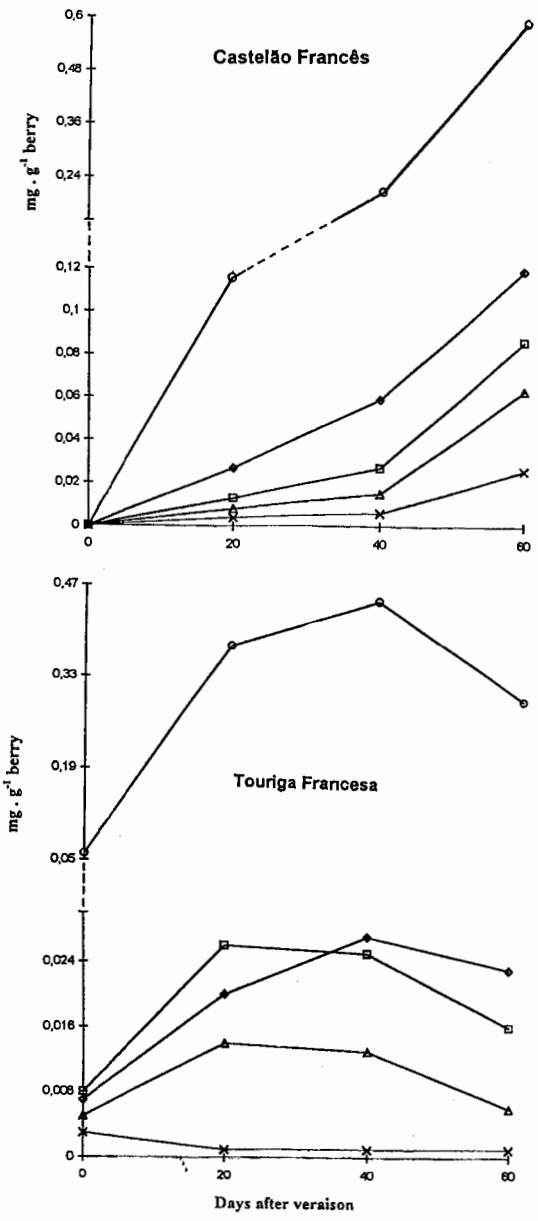

Figure: Evolution of anthocyanin-3-glucosides in Castelão Francês and Touriga Francesa during maturation. ◊ = peonidin-3-glucoside, □ = petunidin-3-glucoside, Δ = delphinidin-3-glucoside, x = cyanidin-3-glucoside, o = malvidin-3-glucoside.

BAKKER, J.; TIMBERLAKE, C. F.; 1985: The distribution of anthocyanins in grape skin extracts of Port wine cultivars as determined by high performance liquid chromatography. J. Sci. Food Agricult. **36**, 1315.

BUDIN, R.; 1983: Accumulation of anthocyanins, sugars and organic acids during the phenophase of ripening of Sylvaner and Loran berries. Vinohrad **21**, 111-113.

CARBONNEAU, A.; CHAMPAGNOL, F.; 1993: Nouveaux systèmes de culture integré du vignoble. Programme AIR-3-CT 93.

DARNE, G.; 1988: Évolution des differentes anthocyanes des pellicules de Cabernet Sauvignon au cours du développement des baies. Conn. Vigne Vin **22**, 225-231.

GONZALEZ, M. L.; BARRON, L. J. R.; DIEZ, C.; 1990: Evolution of anthocyanins during maturation of Tempranillo grape variety (*Vitis vinifera*) using polynomial regression models. J. Sci. Food Agricult. **51**, 337-343.

HARZDINA, G.; PARSONS, G. F.; MATTICK, L. R.; 1984: Physiological and biochemical events during development and maturation of grape berries. Amer. J. Enol. Viticult. **35**, 220-227.

PIRIE, A., MULLINS, M. G.; 1977: Interrelationships of sugars, anthocyanins, total phenols and dry weight in the skin of grape berries during ripening. Amer. J. Enol. Viticult. **28**, 204-209.

- -; - -; 1980: Concentration of phenolics in the skin of grape berries during fruit development and ripening. Amer. J. Enol. Viticult. **31**, 34-36.

RIBEREAU-GAYON, P.; 1982: The anthocyanins of grapes and wines. In: P. MARKAKIS (Ed.): Anthocyanins as Food Colors, 209. Academic Press, New York.

ROGGERO, J. P.; COEN, S.; RAGONNET, B.; 1986: High performance liquid chromatography survey on changes in pigment content in ripening grapes of Syrah. An approach to anthocyanin metabolism. Amer. J. Enol. Viticult. **37**, 77-83.

SOMERS, T. C.; 1976: Pigment development during ripening of the grape. Vitis **14**, 269-277.