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Phenolic composition of white grapes (Var. Airen). Changes during ripening

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The presence of certain phenolic compounds in different parts (must, skins and seeds) of berries of *Vitis vinifera*, white variety Airen, during ripening were studied using HPLC and TLC, from veraison to technological maturity, over three consecutive years. Thirty-three different compounds were identified. Differences were chiefly quantitative, though some qualitative differences were also recorded, particularly between the seeds and the rest of parts of the berry. Program 5R of the BMDP-87 statistical package was used to obtain the plots of alterations in concentration in each of the identified components. The trends recorded were not linear but comprised patterns of alternating maxima and minima.

INTRODUCTION

The maturation of fruits presents several physiological and biochemical changes which modify their properties and so their final quality at maturity. With respect to grape, this is very important, since it is mostly used in wine-making, and the quality and composition of fruit at harvest has a great influence on the quality and composition of the resulting wine (Peynaud, 1989).

Knowledge of individualized phenolic compounds in the different parts of the berry will allow the contribution of these parts to be established in the final composition of wine, for they may become important with the development of skin contact techniques applied to white wines.

The presence of phenolic compounds in grapes has been reported by several workers, but most studies until now have focused on anthocyanin pigments (Glories, 1978; Piergiovanni & Volonteiro, 1983; Bakker & Timberlake, 1985; González *et al.*, 1986), hydroxycinnamic acids (Ong & Nagel, 1978; Singleton *et al.*, 1978; Okamura & Watanabe, 1979; Baranowski & Nagel, 1981*a*; Romeyer *et al.*, 1983; Boursiquot *et al.*, 1986; Singleton *et al.*, 1986; Lee & Jaworski, 1988) and catechins and procyanidins (Lea *et al.*, 1979; Baranowski & Nagel, 1981*b*; Romeyer *et al.*, 1986; Lee & Jaworski, 1989).

In contrast, low-molecular-weight phenols and flavonols have been scarcely studied. These compounds are located primarily in the skin (Ribéreau-Gayon & Milhé, 1970; Estrella *et al.*, 1984; Cheynier & Rigaud, 1986; Alonso *et al.*, 1987), in lower proportions than the anthocyanins. They increase in concentration during grape ripening particularly around maturity (Fernández de Simón *et al.*, 1992).

This paper considers the changes in benzoic acids and aldehydes, hydroxycinnamic acids and derivatives, monomers of flavan-3-ol and flavonol aglycones and glycosides, during grape ripening in the different parts of the berry, in a white variety, Airen, which is used in Spain for wine-making, particularly in 'La Mancha'.

MATERIALS AND METHODS

Sample collection and preparation

Samples were taken from Airen grapes grown in an experimental plot operated by the 'Escuela y Museo de la Vid y el Vino' (School and Museum of Grapes and Wine) in Madrid. Twenty-four Airen vines were sampled, according to a z-shaped pattern to avoid edge and centre effects. The cluster collected from each vine was randomly chosen each time. Care was taken to pick clusters both at different heights and distances from the trunk. Sampling was carried out at approximately 3-day intervals from 12 August to 4 October 1985 (12 samples), from 20 August to 24 September 1986 (14 samples) and from 18 August to 23 September 1987 (16 samples), in order to be able to detect any short-term changes taking place in berry composition during ripening. The sampling cycle was repeated each year with the same sampling pattern.

After collection, the grapes were stemmed. Two batches of 100 berries each were randomly selected from all the berries collected in each daily sample and were pressed to separate the must from the solids; the

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skins and the seeds were removed from the pulp. The skins were freeze-dried.

The freeze-dried skins and crushed seeds of each 100 berries were macerated overnight, three times with 100 ml of a synthetic wine solution (pH = 3·5) containing tartaric acid (0·7 g/litre), potassium bitartrate (1·11 g/litre) and 20% ethanol, so that extraction would resemble the extraction that takes place during fermentation of the solid portions of harvested grapes. Must (100 ml) and the three combined macerates were concentrated to one third, and then treated four times with 15 ml of diethyl ether. The four fractions were dried with sodium acetate and evaporated to dryness under vacuum. The residue was dissolved in 1 ml ethanol : water (50 : 50) and analysed by HPLC. By using diethyl ether as extractant, neither procyanidins nor anthocyanins, which would have interfered with subsequent analyses, were extracted. The extraction yield of hydroxycinnamic tartaric acids and gallic acid was also low (51%), in contrast to the results obtained when ethyl acetate was used as the extractant (91%). On the other hand, the extraction yield for the rest of the low-molecular-weight phenols was similar to that obtained with ethyl acetate, while reproducibility was greater when diethyl ether was used (standard deviation was 1–10% using diethyl ether and 3–17% using ethyl acetate) (Fernández de Simón *et al.*, 1990).

Chromatographic analysis conditions

The analysis was accomplished using HPLC, employing a Waters Associates chromatograph equipped with two pumps M-6000A, a System Controller 720, an injector U6K, and a model 440 detector. Analysis of low-molecular-weight phenols was carried out according to the method described by Fernández de Simón *et al.* (1990).

Analysis of flavonol aglycones
A steel C_{18} NovaPak^R column (150 × 3·9 mm), and as mobile phase: water/methanol/acetic acid (57·5 : 37·5 : 5) (v/v). Flow rate: 0·7 ml/min. UV detection at 365 nm.

Analysis of flavonol glycosides
A steel C_{18} NovaPak^R column (150 × 3·9 mm), and as mobile phase acetic acid 2·5% and tetrahydrofuran/acetic acid/water 50 : 2·5 : 47·5 (v/v/v), in the proportion 65 : 35 (v/v). Flow rate: 0·7 ml/min. UV detection at 365 nm.

Identification of components was performed by comparing both retention times and absorbance ratios at different wavelengths with those of pure standards from Aldrich, Sigma and Carlo Erba (Hernández *et al.*, 1984; Banwart *et al.*, 1985). In addition, the components of the peaks collected from HPLC analysis were compared to solutions of pure substances using TLC (Diez *et al.*, 1980). For components for which no standards were available (hydroxycinnamic tartaric acids and flavan-3-ol gallates), identification was carried out by hydrolysis of the components of the peaks collected from the HPLC analysis, being the hydrolysis results analysed by both HPLC and TLC. Hydroxycinnamic tartaric acids were hydrolysed with a pectolytic enzyme (Rapidase CX^R), at a pH between 2 and 3, in darkness at room temperature for 5 days. This was then extracted with diethyl ether and ethyl acetate, as described above. The three cinnamic acids were identified in the organic phase, and the tartaric acid in the aqueous phase, by comparing with external standards. Flavan-3-ol gallates were hydrolysed with 5 N HCl, at 100°C, for 1 h. Gallic acid and (−)epicatechin were identified after hydrolysis of peak 23 and gallic acid and an unidentified peak after hydrolysis of peak 22, by comparing with external standards.

Statistical analysis

Program 5R of the BMDP-87 statistical package (Brown *et al.*, 1983) was used to obtain the plots of the alterations in concentration that took place over the sampling period in each of the components identified, calculating the polynomials of the lowest possible degree that fit the experimental data obtained. The degree of the polynomials was established by means of the goodness-of-fit test (F). This is a test of the inadequacy of the model at each degree, relative to the residual mean square from fitting the polynomial of highest degree (indicated by a tail probability greater than 0·05). The program reports polynomials of degrees 1 through a degree that the user specifies. A high value for F is an indicator of a poor fit, and that more terms or a higher degree are needed. Program 5R was run on a CYBER 155/855 computer (Control Data Corporation).

RESULTS AND DISCUSSION

Table 1 shows the determination coefficient (explained variance percentage) (R^2), residual mean square (RM^2) and the degree of polynomial + degree of freedom ($DP + DF$) values, for the degree of polynomial selected in each variable, in the year 1986. As explained before, 14 samples were taken this year and, from each, two batches of 100 berries were made. Each group was analysed in duplicate, so we have 56 data (four for each sampling day). As can be observed, the $DP + DF$ value was not constant nor equal to 56 for all the variables because there were outliers which were considered missing values. The final estimated regression coefficients were significantly different from zero with P greater than 0·05.

Differences between parts of the berry

Figure 1 shows typical chromatograms of low-molecular-weight phenols for each of the different parts of berry considered. Table 2 lists the phenolic compounds identified in each part of the berry. The order of presentation in Table 2 follows the order of the peaks in Fig. 1.

Table 1. Determination coefficient (R^2), residual mean square (RM^2) and degree of polynomial + degree of freedom ($DP + DF$), for the degree of polynomial selected in each variable, in year 1986

Phenolic compounds	Skin			Must			Seed		
	R^2 (%)	RM^2	$DP + DF$	R^2 (%)	RM^2	$DP + DF$	R^2 (%)	RM^2	$DP + DF$
Gallic ac.	99·90	0·0031	55	99·92	0·0591	55	97·14	1745·4	55
Protocatechuic ac.	98·38	0·6059	53	94·23	0·2698	52	—	—	—
p-Hydroxybenzoic ac.	99·96	0·0199	55	97·68	0·0591	52	—	—	—
Vanillic ac.	99·92	0·0014	55	99·85	0·0021	55	—	—	—
p-Coumaric ac.	93·33	0·0444	53	93·40	0·0296	52	—	—	—
Ferulic ac.	95·06	0·0846	53	97·78	0·0591	52	—	—	—
p-Hydroxybenzoic ald.	94·06	0·2052	53	92·99	0·0085	52	—	—	—
Vanillic ald.	89·96	0·0068	52	99·87	0·0019	55	—	—	—
Syringic ald.	97·28	0·0733	53	92·71	0·3269	52	—	—	—
Aesculetin	94·79	0·0286	54	95·87	0·0575	52	—	—	—
(+) Catechin	—	—	—	—	—	—	85·07	146235	55
(−) Epicatechin	—	—	—	—	—	—	88·78	198869	55
Caffeoyltartaric ac.	—	—	—	94·99	0·5263	53	—	—	—
p-Coumaroyltartaric ac.	—	—	—	96·38	0·2777	53	—	—	—
Feruloyltartaric ac.	96·99	0·7219	52	99·04	0·4731	53	—	—	—
Myricetin	99·95	0·1065	55	99·98	0·0068	55	—	—	—
Quercetin	99·95	0·0012	55	94·22	0·1321	52	—	—	—
Kaempferol	99·49	0·0017	55	—	—	—	—	—	—
Q-3-rutinoside	93·79	0·3373	53	94·34	0·1293	52	—	—	—
Q-3-galactoside + Q-3-glucoside	95·81	4·5402	53	96·68	2·4464	52	—	—	—
Q-3-rhamnoside	96·58	0·3402	53	—	—	—	—	—	—
K-3-rhamnoglucoside	96·27	162·70	53	97·46	5·0661	52	—	—	—
M-3-rhamnoside	96·32	2·0279	53	97·62	0·0418	52	—	—	—

ac, acid; ald, aldehyde; Q, quercetin; K, kaempferol; M, myricetin.

The largest differences in composition were recorded between the seeds and the other parts of the berry. Thus, the components identified in the seeds included flavan-3-ols ((+)catechin, (−)epicatechin, (−)epicatechin-gallate and other gallates), along with gallic acid, while benzoic and cinnamic acids and aldehydes and flavonols were not detected. Monomers of flavan-3-ols made up the largest share of the components identified, the concentration of (+)catechin being the higher. Furthermore, these components are present in the seeds in much higher concentrations than the rest of the components identified in the other parts of the berry. This suggests that the components present in the seeds will exert a major influence on the total phenol composition of the berry, even though the seeds make up only about 5% of its total weight.

The concentrations of benzoic and cinnamic acids and benzoic aldehydes which, with the exception of gallic acid, were not present in appreciable quantities in the seeds, were similar in the skin and must. The low-

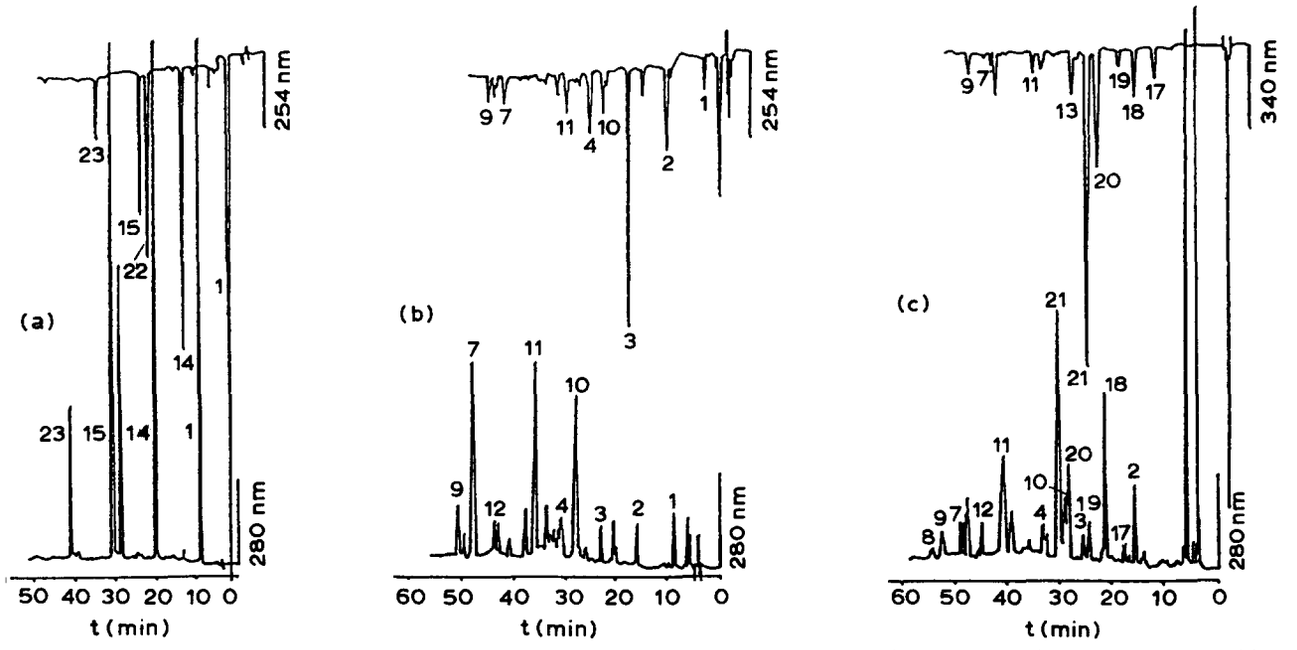

Fig. 1. Chromatograms of seeds (a), skins (b) and must (c). Peak numbers correspond to compound names listed in Table 2.

Table 2. Distribution of phenolic compounds in different parts of the berry

Phenolic compounds	Skin	Must	Seed
1. Gallic ac.	+	+	+
2. Protocatechuic ac.	+	+	−
3. *p*-Hydroxybenzoic ac.	+	+	−
4. Vanillic ac.	+	+	−
5. Caffeic ac.	+	+	−
6. *cis-p*-Coumaric ac.	+	+	−
7. *trans-p*-Coumaric ac.	+	+	−
8. *cis*-Ferulic ac.	+	+	−
9. *trans*-Ferulic ac.	+	+	−
10. *p*-Hydroxybenzoic ald.	+	+	−
11. Vanillic ald.	+	+	−
12. Syringic ald.	+	+	−
13. Aesculetin	+	+	−
14. (+)Catechin	−	−	+
15. (−)Epicatechin	−	−	+
16. *cis*-Caffeoyltartaric ac.	−	+	−
17. *trans*-Caffeoyltartaric ac.	−	+	−
18. *cis-p*-Coumaroyltartaric ac.	−	+	−
19. *trans-p*-Coumaroyltartaric ac.	−	+	−
20. *cis*-Feruloyltartaric ac.	+	+	−
21. *trans*-Feruloyltartaric ac.	+	+	−
22. Gallate	−	−	+
23. Epicatechingallate	−	−	+
24. Myricetin	+	+	−
25. Quercetin	+	+	−
26. Kaempferol	+	−	−
27. Isorhamnetin	+	−	−
28. Q-3-rutinoside	+	+	−
29. Q-3-galactoside	+	+	−
30. Q-3-glucoside	+	+	−
31. Q-3-rhamnoside	+	−	−
32. K-3-rhamnoglucoside	+	+	−
33. M-3-rhamnoside	+	+	−

ac, acid; ald, aldehyde; Q, quercetin; K, kaempferol; M, myricetin.

molecular-weight phenolic composition was extremely varied, and the concentrations of all the phenol components were much higher in the skin than in the must. Hydroxycinnamic acids were in both cases the major components.

Furthermore, in the must, hydroxycinnamic tartaric acids were detected in high concentrations, particularly in the early samples, when grapes were less mature. These compounds were not identified in other parts of the berry, with the exception of feruloyltartaric acid in the skins, probably because they undergo a sharp decrease during veraison (Romeyer *et al.*, 1983), in conjunction with the low extraction yield for these components using diethyl ether, as referred to previously.

With respect to the flavonols, four aglycones (myricetin, quercetin, kaempferol and isorhamnetin) were detected in the skin, but the isorhamnetin was only recorded in grape samples collected around maturity. However, only myricetin and quercetin were detected in the must, and in much smaller quantities than in the skin. Similarly, flavonol glycosides were detected in much greater numbers and quantities in the skin than in the must.

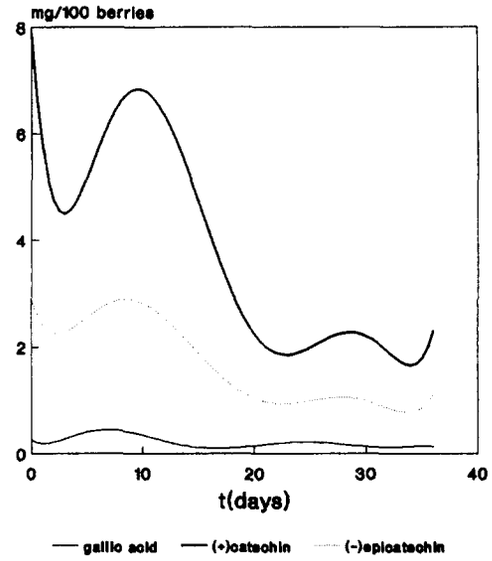

Fig. 2. Evolution of concentration of gallic acid, (+) catechin and (−) epicatechin in seeds during ripening (year 1987).

Evolution during ripening

Plotting the polynomial regression equations of the concentration values for each of the components over the grape ripening period yielded a series of curves. The concentration curves were distinctly non-linear, instead presenting a series of maxima and minima. The evolution of the compounds in each part of the berry was similar over the 3 years, so the curves may apply to all of them, no comparison being needed. The only difference from one year to another was some shift in the maxima, due to climatological differences among years.

Variations in the concentrations of components present in the seeds (Fig. 2), follow declining trends, with substantial decreases in concentration during a first stage, after which the decline continued at a slower rate, levelling off at a minimum, with few variations during a second stage.

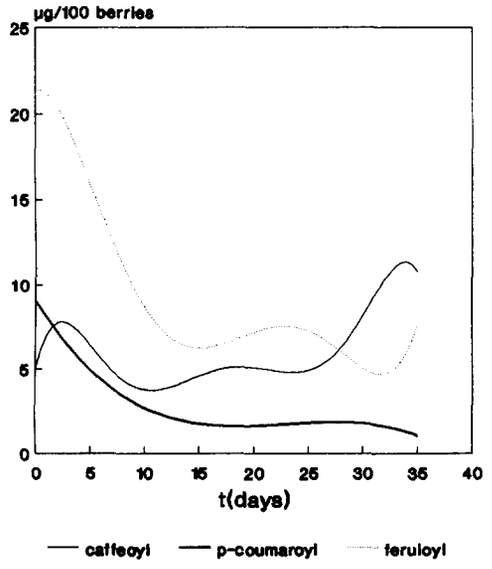

Fig. 3. Evolution of concentration of hydroxycinnamic esters in must during ripening (year 1986).

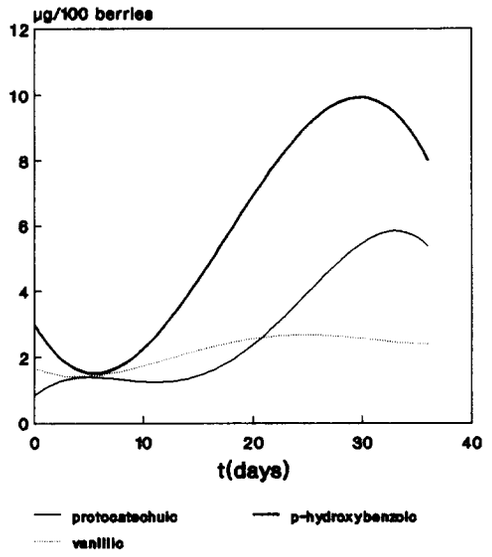

Fig. 4. Evolution of concentration of benzoic acids in the skin during ripening (year 1987).

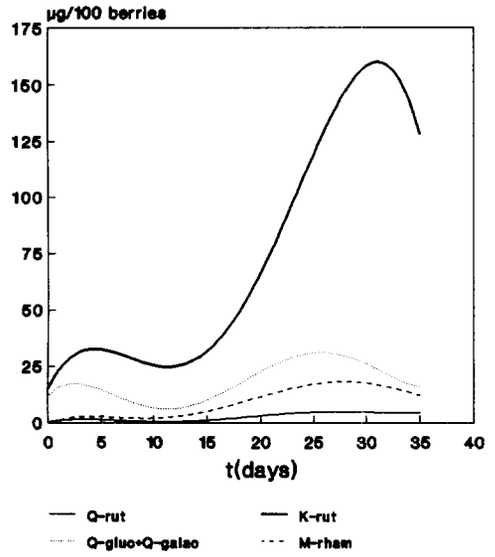

Fig. 6. Evolution of concentration of flavonol glycosides in the skin during ripening (year 1986).

The concentrations of hydroxycinnamic tartaric acids in the must followed a similar trend (Fig. 3), their concentrations declining until maturity. Conversely, the remaining low-molecular-weight phenols (benzoic acids, Fig. 4 and aldehydes, Fig. 5, and cinnamic acids) follow a rising trend, with few variations in concentration during the first stage but with a large increase during the second stage, peaking at a high maximum.

Flavonol aglycones and glycosides undergo a slight increase in concentration around the time of veraison, and a higher increase at maturity, reaching a maximum (Fig. 6). In the must, glycosides were detected in low concentration and they declined during ripening. This can be explained by the accumulation of these compounds in the skin.

The results obtained show that the phenol composition underwent an alteration in the grapes during maturation, changing from one composition rich in hydroxycinnamic tartaric acids, gallic acid and flavan-3-ols around the time of veraison to another at maturity in which the concentration of these components was lower. Moreover, a variety of benzoic and cinnamic acids and aldehydes and flavonol aglycones and glycosides, with differing concentration levels, were present at maturity.

The maximum concentrations of benzoic and cinnamic acids and aldehydes and flavonol aglycones and glycosides at the end of the ripening period did not coincide with the minimum concentrations of the flavan-3-ols and hydroxycinnamic tartaric esters. Provided that these compounds are suitable substrates in browning phenomena, this should be considered when determining the date of harvest in order to avoid browning in white varieties, such as Airen. This, together with data on acidity and sugars, would provide a sounder scientific basis for determining the ideal harvest conditions for the grapes according to the final intended use and should therefore be taken into account when choosing optimum harvest time.

This work will be complemented with an ANOVA study to compare the results of the different years.

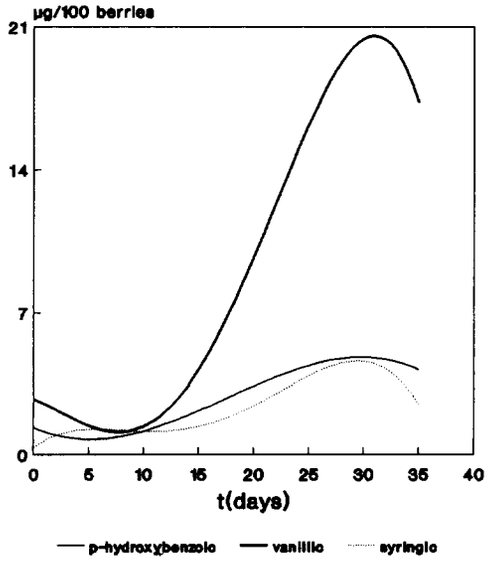

Fig. 5. Evolution of concentration of benzoic aldehydes in the skin during ripening (year 1986).

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