Vitis 25, 107—117 (1986)

Department of Viticulture and Enology, University of California, Davis, CA, USA

Compositional changes in ripening grapes: Caftaric and coutaric acids

by

V. L. SINGLETON, J. ZAYA and E. TROUSDALE

Veränderungen in der Zusammensetzung reifender Trauben: Caftar- und Coutarsäure

Zusammenfassung: Beeren der *Vitis-vinifera*-Sorten Grenache, French Colombard und Ruby Cabernet (2 Herkünfte) wurden bei fortgeschrittener Reife geerntet und auf ihren Gehalt an Caftar- und Coutarsäure (Konzentration/ml Beerensaft, Gehalt/Beere, prozentualer Anteil der *cis*-Formen) untersucht; bei der Aufarbeitung war das Material vollkommen gegen Oxidation geschützt. Aufgrund ihres spezifischen Gewichtes konnten die Beeren einer Probe nach ihrem Reifegrad klassifiziert werden, wobei störende Einflüsse wie die Witterung eliminiert waren und innerhalb einer Reifeklasse nahezu identische °Brix-Werte vorlagen. Die beiden Herkünfte von Ruby Cabernet stimmten trotz beträchtlicher Unterschiede der Wachstumsbedingungen und Mostgewichte in ihrem Caftar- und Coutarsäuremuster untereinander viel enger überein als mit den anderen Sorten, woraus auf eine genetische Steuerung dieser Komponenten geschlossen werden kann. Das Verhältnis Coutarsäure : Caftarsäure sowie der prozentuale Anteil der *cis*-Formen zeigen gegen Ende der Beerenreife eine ansteigende Tendenz. Diese Inhaltsstoffe scheinen generell dann synthetisiert zu werden, wenn sich die reifenden Beeren vergrößern. Bei French Colombard und Ruby Cabernet, wo die Synthesegeschwindigkeit mit dem Beerenwachstum Schritt halten kann und mittlere Caftar- und Coutarsäuregehalte vorliegen, bleibt die Konzentration im Beerensaft nahezu konstant auf einem sortentypischen Niveau stehen. Bei der Sorte Grenache mit hohen Gehalten bleibt die Synthese hinter dem Beerenwachstum zurück, so daß die Konzentration/ml Beerensaft abfällt, obwohl der Gehalt/Beere noch ansteigt und eine relativ hohe Konzentration aufrechterhalten wird. Überreife, geschrumpfte Beeren zeigen einen Konzentrationsanstieg; wenn die Beerenhaut beschädigt ist, können sie jedoch durch Oxidation Caftarsäure verlieren.

Key words: berry, maturation, grape juice, sugar, phenol.

Introduction

Evaluation of compositional changes as grapes ripen is a recurring problem. The usual method has been to harvest at intervals during the ripening season and analyze later. Such procedures are subject to several potential sources of error, e. g., extraneous factors such as weather changes can confound the ripeness effects, stored samples may not remain comparable, and analyses performed at different times are likely to be more variable.

Segregation of intact grape berries by density is a procedure that can avoid these difficulties by providing a complete sugar content (ripeness) sequence from a single harvest. The first use of this technique with grapes was by NELSON *et al.* (1963) who applied it to segregate intact table grape berries for sensory testing. Wine grape berry populations were successfully characterized by SINGLETON *et al.* (1966) using density flotation. Further studies of the method and its application (SINGLETON *et al.* 1973) showed that there is essentially no air contained in the normal grape berry. Berries that just sank in a solution 1 °Brix lower than one in which they floated gave juice with slightly lower °Brix (of the order of 0.9 °Brix) than the mean °Brix of the two dipping solutions. The berry's density was slightly higher than that of its juice because of the

higher density of its skin and seed components. The proportions of skin and seeds in a berry vary by cultivar, berry size and other factors. Although the flotation bracket does not bear a constant relationship to juice °Brix, density segregation reliably provides a ripeness (sugar content) sequence and is a technique deserving of wider application. One objective of this study was to illustrate further the applicability of this technique.

Caftaric and coutaric acids (mono caffeoyl and mono *p*-coumaroyl L(+)-tartaric acids) are the major phenolic substances of unmodified fresh grape juice. Their variation during ripening of grapes has been the subject of only a few studies. DUMAZERT *et al.* (1973) reported the concentration of caftaric acid more than doubled during ripening of one variety from mid July to mid August and then declined to about the original level by the end of September. ONG and NAGEL (1978) reported caftaric acid in White Riesling dropped in 1976 from near 400 ppm in a sample at 7 °Brix to less than 200 ppm in a later sample at 11 °Brix and rose only slightly in riper samplings. In 1977 the content dropped less severely over a similar period. ROMEYER *et al.* (1983), with HPLC after seed removal and freeze drying followed by solvent extraction, found caftaric acid decreased in concentration during ripening in Grenache (highest) and three other varieties, precipitously at first and slowly after about 20 Aug. reaching about 60 µg/g of berry. On the basis of µg/berry, values ranged between about 60 and 180. ONG and NAGEL (1978) and ROMEYER *et al.* (1983) agreed that coutaric and fertaric paralleled the ripening changes in caftaric acid.

In view of the few and somewhat conflicting data and especially considering the discovery of S-glutathionyl caftaric acid as an indicator of enzymic oxidation in grape juice (SINGLETON *et al.* 1984, 1985), further study of changes in caftaric and coutaric acids during grape ripening was needed. The purpose of this work was to determine the variation in these two main hydroxycinnamates of grapes in relation to ripeness under conditions with proven protection from oxidation and extraneous variations such as weather. Fertaric acid was not included because the amount present has been shown to be considerably lower (ONG and NAGEL 1978; ROMEYER *et al.* 1983), no suitable standard was available, it should be resistant to oxidative loss, and is reported to parallel changes in caftaric and coutaric acids.

Density segregation was particularly suitable to investigate the true ripeness changes in grapes of caftaric and coutaric acids because determination of these hydroxycinnamates requires extreme precautions to prevent enzymic oxidation. Furthermore, their determination was more difficult if the samples were not analyzed at nearly the same time under identical conditions (SINGLETON *et al.* 1984, 1985).

Materials and methods

Grapes were obtained from University plots as follows: Ruby Cabernet, Davis, 1 Aug. 1984; French Colombard, Davis, 9 Aug. 1984; Grenache, Davis, 14 Aug. 1984; and Ruby Cabernet, Oakville (Napa Co.), 12. Sept. 1984. Random clusters were collected so as to represent the entire plot and brought to the laboratory in 20 kg wooden boxes to avoid bruising. Sufficient individual berries were randomly cut from each cluster so that a sufficient pool of single berries for the whole distribution of any one harvest was available. The berries were individually snipped so as to remove the pedicel with the torus without breaking the berry skin. Accidentally damaged berries were discarded. The group of berries representing any one variety-location sample were gently mixed by pouring back and forth from cotton towels before segregation by density.

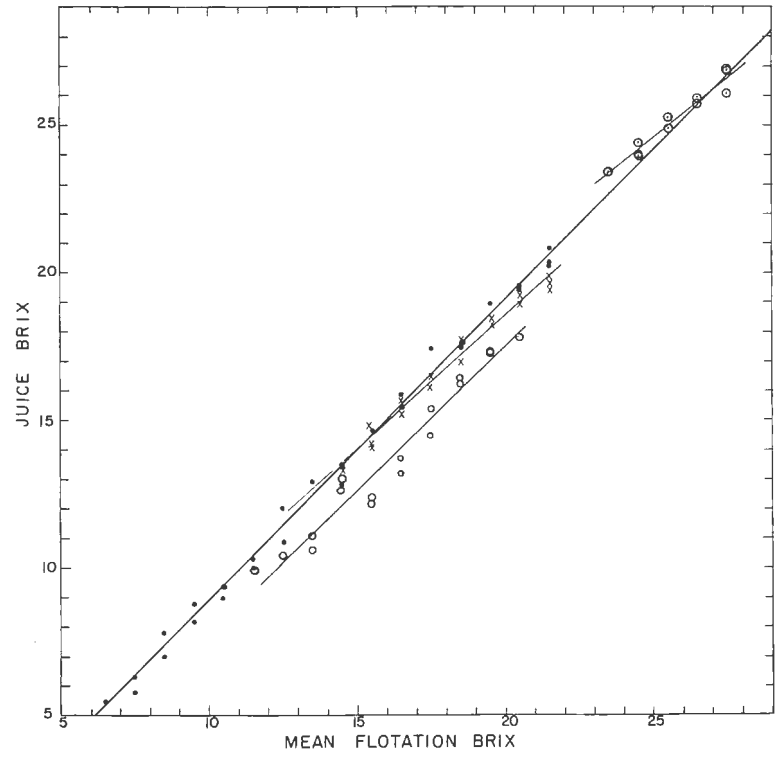
The segregation solutions were prepared by weighing sucrose and distilled water so as to prepare portions of adequate volume, 1 % sucrose (1 °Brix) apart, covering the ripeness range expected 6—28 °Brix in total. Each solution was rechecked by refractometry (taking care to apply the appropriate temperature corrections) initially, periodically during, and again for the final redip at the end. Appropriate adjustment to the intended °Brix was made when necessary. The berries were dipped from high °Brix to low, transferring those floating to the next lower °Brix dipping solution, and removing those sinking to the appropriate flotation bracket sample. This direction of transfer facilitates adjustment of the dipping solution by adding water instead of sucrose. The dipping was finished for each small group of berries as quickly as possible so that no one berry spent more than perhaps 1 min in a solution of appreciably higher or lower °Brix than its juice. This minimized water loss or gain by osmosis from the berries and the mean berry weight calculated from proportions of the segregated berries agreed with that before segregation. After sufficient berries had been segregated, each fraction was revalidated with the carefully readjusted sucrose solutions defining its flotation bracket, e. g., 20.0—21.0 °Brix. Barring human error, the only source of disagreement in this redipping appeared to be from an occasional entrained air bubble in the first dipping. Although not deemed necessary here, this type of density segregation seems applicable to finer divisions than 1 °Brix since almost all berries in one fraction floated, for example, in 21.0 °Brix and sank completely in 20.0 °Brix with only a few hovering.

The segregated fractions were blotted free of dipping solution by gently rolling in cotton towels and duplicates of 40 berries each counted out for analysis. The average deviation of duplicate analyses for *trans*-caftaric acid content was ±2.6 % from the mean of two. Note that this would include any analytical as well as berry sample variation.

The berries were weighed and transferred to a glove box where they were processed to juice in a carbon dioxide atmosphere using a small, levered hand press as uniformly as possible. Solid ascorbic acid and potassium metabisulfite in excess were added to the berries just before the crush-press operation. These details and the analyses by reversed phase HPLC were essentially the same as described previously (SINGLETON *et al.* 1984, 1985). The peak areas were converted to amounts by using the response factor (peak area per unit mass) determined under the same conditions with pure *trans*-caftaric acid isolated from grapes.

Results and discussion

The efficacy of density segregation in the fruit studied is illustrated in the accompanying figure. The linear regression intercepts, slopes, and correlation coefficients are given in Table 1. Note that although there was very high correlation in all cases between juice °Brix and berry density as shown by the flotation bracket, it was slightly lower for the combined data than for each of the four individual harvests. The values in Table 1 compare very closely with similar values obtained on six other white varieties in South Africa (SINGLETON *et al.* 1973). These data and the specific °Brix values shown in Tables 2, 3, 4, and 5 for the four harvests illustrate that ripeness sequences as determined by sugar content were established by the density segregation method. Since each harvest was on a single date, weather variables were eliminated within sets. A further advantage is that all berries at each ripeness level are nearly identical in juice °Brix and not just a population average as would be true in periodic sampling for ripeness sequence.



Juice °Brix compared to the mean of the 1 °Brix flotation bracket of segregated grape berries. ● = Grenache, × = French Colombard, ○ = Ruby Cabernet (Davis), ⊙ = Ruby Cabernet (Napa).

Vergleich der °Brix-Werte des Beerensaftes mit den Mittelwerten von Beeren, die mit Hilfe des Schwimmverfahrens (Intervalle von 1 °Brix) klassifiziert wurden. ● = Grenache, × = French Colombard, ○ = Ruby Cabernet (Davis), ⊙ = Ruby Cabernet (Napa).

Table 1

Linear Regressions (Y = AX + B) and correlation coefficients (R)

Lineare Regressionen (Y = AX + B) und Korrelationskoeffizienten (R)

Variety	X	Y	A	B	R
Colombard	Flotation °Brix	Juice °Brix	+0.902	+0.445	+0.994
Grenache	Flotation °Brix	Juice °Brix	+1.025	−1.432	+0.996
Ruby Cabernet (Davis)	Flotation °Brix	Juice °Brix	+0.986	−2.161	+0.977
Ruby Cabernet (Napa)	Flotation °Brix	Juice °Brix	+0.811	+4.300	+0.977
Combined	Flotation °Brix	Juice °Brix	+1.049	−2.427	+0.948
Grenache	Juice °Brix	μg/ml *t*-caftaric acid	−4.207	+356.55	−0.806
Grenache	Juice °Brix	μg/berry *t*-caftaric acid	+5.564	+181.99	+0.880

Table 2

Grenache grapes, caftaric and coutaric acid content as affected by ripeness

Rebsorte Grenache – Caftar- und Coutarsäuregehalt der Beeren in Abhängigkeit von der Reife

Flotation bracket °Brix	Juice °Brix	Berry weight g	Caftaric acid				Coutaric acid				% *t*-coutaric/ *t*-caftaric
			µg/ml		%	µg/berry	µg/ml		%	µg/berry	
			trans	*cis*	*cis*	*trans*	*trans*	*cis*	*cis*	*trans*	
6.0 – 7.0	5.5	0.72	324	1.4	0.4	217	22	Trace	—	15	6.9
7.0 – 8.0	6.0	0.76	310	0.3	0.1	217	21	Trace	—	15	6.7
8.0 – 9.0	7.4	0.71	328	0.5	0.2	213	21	Trace	—	14	6.5
9.0 – 10.0	8.5	0.82	337	Trace	—	255	22	Trace	—	17	6.5
10.0 – 11.0	9.2	0.77	322	Trace	—	228	21	Trace	—	15	6.6
11.0 – 12.0	10.2	0.80	315	Trace	—	229	17	Trace	—	13	5.5
12.0 – 13.0	11.4	0.84	324	0.3	0.1	247	19	Trace	—	14	5.7
13.0 – 14.0[1])	12.9	0.92	301	0.5	0.2	254	20	Trace	—	17	6.6
14.0 – 15.0	13.4	0.93	297	0.6	0.2	250	18	Trace	—	15	6.0
15.0 – 16.0[1])	14.6	0.98	295	2.5	0.8	261	20	1.6	7.4	18	6.8
16.0 – 17.0	15.6	0.96	293	Trace	—	256	17	Trace	—	15	5.9
17.0 – 18.0[1])	17.4	1.06	295	2.2	0.7	282	18	Trace	—	17	6.5
18.0 – 19.0	17.4	1.06	271	0.9	0.3	257	17	0.6	3.4	16	6.2
19.0 – 20.0[1])	18.9	1.26	290	3.8	1.3	327	20	1.4	6.5	23	7.0
20.0 – 21.0	19.4	1.14	279	1.9	0.7	284	21	2.1	9.2	21	7.5
21.0 – 22.0	20.2	1.22	267	1.9	0.7	292	21	2.2	9.6	23	7.8

[1]) These samples after segregation were held at 12 °C for 2 weeks before pressing.

S-glutathionyl caftaric acid was completely absent (no suggestion of a peak in HPLC) in all samples, except traces (a feeble unmeasurable peak) were found in the 25.8 and 26.8 °Brix samples and 5.0 mg/l in the 28.9 °Brix sample of the late harvested Ruby Cabernet from Napa. This shows not only that the glove box-ascorbic-sulfite system was completely effective in preventing phenolase oxidation, but also that some oxidation can occur in the field as berries are overripe. These high-°Brix berries were shriveled (diminished berry weight, Table 5) and showed tissue breakdown and juice exposure at the pedicel link as harvested.

The most extended series of ripeness levels, especially in the early stages, was provided by the Grenache harvest (Table 2). Grenache is also particularly suitable because, as has already been reported, it is notably high in caftaric acid content. The expected increase in berry weight as juice °Brix (ripeness) increases is shown. Four berry samples held at 12 °C for 2 weeks after segregation showed no appreciable differences from the samples processed immediately and are included. This indicates that intact berries can be stored for a short time, if cool and humid, without appreciable change in the parameters measured. Furthermore, it shows that the handling incidental to °Brix segregation did not initiate tissue breakdown.

The highest *trans*-caftaric acid content in the juice (Table 2) was at 8.5 °Brix and then trended downward. There was a maximum range of 337—267 mg/l or a difference of 70 mg/l or 20.7 % decline over the ripeness range of 8.5—20.2 °Brix. All the data are best fitted by a simple linear regression (Table 1) and the correlation is a fairly high negative value. Using that regression line, the range 5.0—22.0 °Brix for these Grenache berries was characterized by 335—264 mg/l = 71 mg/l drop or −21.2 %.

Content per berry was calculated after subtracting the weight of one typical seed (40 mg) from the berry weight. The result was divided by the density of the juice (from °Brix tables at 20 °C) and multiplying by the µg of caftaric or coutaric acid per ml. As the berry ripened the content per berry increased (Table 2) and from the best fit (linear) regression (Table 1) the increase was from about 210 µg/berry at 5.0 °Brix to 304 µg/berry at 22.0 °Brix (46 %) with a fairly high positive correlation. All seeded grape varieties average over one seed per berry and no normal berry has more than four seeds. If there were more than one seed per berry it would, by our method of calculation lower the amount of caftaric or coutaric acids per berry, but increase the difference between high and low °Brix berries. The assumption is implicit that the fluid of the skin has the same content of caftaric acid as the juice. This may not be true although evidence is good that it is not greater. For these reasons the content per berry may be overestimated, but should be proportional.

Together the data for Grenache indicate there is a decline in the concentration of caftaric acid in the juice as the berry ripens, but a greater increase in the amount per berry. Thus, it appears there was considerable net synthesis of caftaric acid as the berry ripened, but the berry enlargement was greater.

The *trans*-coutaric acid content (Table 2) averaged 6.5 % of that of *trans*-caftaric acid rising slightly in the higher ripeness stages. The concentration of *trans*-coutaric acid was nearly constant averaging 19.7 mg/l of juice but increased from about 15 to about 23 µg/berry as °Brix increased from 5.5 to 20.2.

The content of the *cis* isomers of caftaric and coutaric acids as shown in Table 2 is the analytical value multiplied by 1.58 since the HPLC response factor was based upon *trans*-caftaric and the *trans* forms have an absorbance about 1.58 times that of the *cis* (SINGLETON *et al.* 1978). The *cis* in each case was calculated as a percent of the sum of both forms of the respective acids. They both appeared to rise in the higher °Brix samples and the percentage *cis* averaged about 0.5 % for caftaric and 7 % for coutaric acids.

Table 3

Colombard grapes, caftaric and coutaric acid content as affected by ripeness

Rebsorte Colombard – Caftar- und Coutarsäuregehalt der Beeren in Abhängigkeit von der Reife

Flotation bracket °Brix	Juice °Brix	Berry weight g	Caftaric acid				Coutaric acid				% *t*-coutaric/ *t*-caftaric
			µg/ml		%	µg/berry	µg/ml		%	µg/berry	
			trans	*cis*	*cis*	*trans*	*trans*	*cis*	*cis*	*trans*	
13.0 – 14.0	12.8	1.60	95	Trace	—	141	13	2.8	17.7	19	13.7
14.0 – 15.0	13.4	1.57	98	Trace	—	143	12	2.4	16.6	18	12.4
15.0 – 16.0	14.2	1.64	94	1.1	1.2	142	11	2.2	16.4	17	11.9
16.0 – 17.0	15.4	1.68	96	1.4	1.4	148	13	2.7	16.9	21	13.8
17.0 – 18.0	16.2	1.64	94	0.9	0.9	141	12	2.4	16.2	19	13.2
18.0 – 19.0	17.2	1.63	95	1.3	1.3	142	13	2.5	16.6	19	13.2
19.0 – 20.0	18.3	1.79	93	1.6	1.7	152	13	3.5	21.1	21	14.1
20.0 – 21.0	19.0	1.77	97	2.2	2.2	156	14	4.3	23.0	23	14.8
21.0 – 22.0	19.8	1.79	97	2.5	2.5	157	15	4.1	21.5	24	15.5

Table 4

Ruby Cabernet Davis grapes, caftaric and coutaric acid content as affected by ripeness

Rebsorte Ruby Cabernet (Davis) – Caftar- und Coutarsäuregehalt der Beeren in Abhängigkeit von der Reife

Flotation bracket Brix	Juice Brix	Berry weight g	Caftaric acid				Coutaric acid				% *t*-coutaric/ *t*-caftaric
			μg/ml		%	μg/berry	μg/ml		%	μg/berry	
			trans	*cis*	*cis*	*trans*	*trans*	*cis*	*cis*	*trans*	
11.0 – 12.0	10.0	1.10	123	2.7	1.4	126	30	8.1	16.7	31	24.8
12.0 – 13.0	10.4	1.11	104	2.7	1.6	107	26	7.3	17.8	27	25.0
13.0 – 14.0	11.1	1.34	125	3.3	1.7	156	34	10.0	18.8	42	26.8
14.0 – 15.0	12.8	1.49	116	2.8	1.5	161	30	9.0	19.0	41	25.8
15.0 – 16.0	12.3	1.53	120	2.8	1.5	170	31	9.5	19.2	44	26.0
16.0 – 17.0	13.4	1.32	113	2.5	1.4	137	27	8.5	19.9	33	24.2
17.0 – 18.0	15.0	1.46	106	2.5	1.5	141	26	8.4	20.4	35	24.6
18.0 – 19.0	16.3	1.43	101	2.5	1.6	132	22	7.0	19.8	29	22.1
19.0 – 20.0	17.4	1.62	94	2.5	1.7	139	20	6.3	19.8	30	21.4
20.0 – 21.0	18.8	1.50	100	2.7	1.7	137	21	7.4	22.1	29	21.2
21.0 +	19.5	1.25	107	2.5	1.5	120	23	7.3	20.0	26	21.6

Table 5

Ruby Cabernet Napa grapes, caftaric and coutaric acid content as affected by ripeness

Rebsorte Ruby Cabernet (Napa) — Caftar- und Coutarsäuregehalt der Beeren in Abhängigkeit von der Reife

Flotation bracket °Brix	Juice °Brix	Berry weight g	Caftaric acid				Coutaric acid				% *t*-coutaric/ *t*-caftaric
			µg/ml		%	µg/berry	µg/ml		%	µg/berry	
			trans	*cis*	*cis*	*trans*	*trans*	*cis*	*cis*	*trans*	
22.0 – 23.0	23.4	1.53	105	2.2	2.1	142	22	7.4	25.2	30	21.0
23.0 – 24.0	23.4	1.37	101	3.0	2.9	124	22	5.2	18.8	27	22.1
24.0 – 25.0	24.2	1.45	103	2.4	2.3	132	24	5.7	19.3	31	23.2
25.0 – 26.0	25.1	1.39	113	2.8	2.4	103	28	5.8	17.4	25	24.3
26.0 – 27.0	25.8	1.33	110	2.8	2.5	99	25	6.2	19.6	30	23.1
27.0 – 28.0	26.8	1.30	119	2.3	1.9	135	29	6.6	18.4	33	24.6
28.0+	28.9	1.09	116	1.9	1.6	108	28	6.6	19.0	26	24.4

Table 3 shows similarly derived data for the variety French Colombard. The content of *trans*-caftaric acid was lower by about 2/3, the *trans*-coutaric was about 1/2 and the % coutaric/caftaric about double compared to Grenache. The % *cis* was considerably higher for caftaric and for coutaric acid than in Grenache.

The content in Colombard of caftaric acid was nearly constant as was coutaric acid with a small increase in the ripest samples, particularly if the *cis* increase was added to the *trans*. The µg per berry increased with ripening for both cinnamates but only about 10 %. In this set it appeared that net biosynthesis was in proportion to or very slightly greater than berry enlargement.

Tables 4 and 5 show data from two harvests of Ruby Cabernet vineyards separated by about 60 km, considerable average climate difference and 42 d between samplings. Note that despite these differences and large differences in the °Brix levels the values generally are much more similar between these two harvests of the same variety than among the three different varieties, suggesting genetic control as a primary factor compared to ripeness or weather. Alone these data may not be very convincing, but combined with our other observations and the literature, genetic (varietal) control is seen to be primary.

The concentration of *trans*-caftaric acid in the juice fell with increased °Brix in the low °Brix (Davis) set and rose slightly in the high°Brix (Napa) set. This is attributed to berry shriveling in the overripe set. Note that berry weight dropped nearly 30 % whereas caftaric only rose perhaps 15 %. Some loss to S-glutathionyl caftaric acid, as much as 5 mg/l at 28.9 °Brix, helps explain the discrepancy. Content per berry appeared to rise to a point and then to fall off in the highest °Brix berries.

Conclusions

Advantages provided by berry density segregation enabled a more detailed study of ripeness relationships with the contents of *trans*- and *cis*-forms of caftaric and coutaric acids. In so far as these results with four harvests of three *Vitis vinifera* varieties can be extrapolated, it appears that the concentration of these compounds, their ratio to each other, and the relative proportion of the *cis* forms is largely varietally (genetically) set. For example, the relatively high content in Grenache agrees with all previous reports.

It appears that there is biosynthesis to maintain the concentration of caftaric and related acids relatively constant as the berry ripens. If the content is high, the concentration may fall but the amount per berry rises as the berry size increases during ripening. This was found here with Grenache and appears to fit the results of ONG and NAGEL (1978) with White Riesling. It is important to note that if oxidation is not completely prevented during sample preparation the loss of caftaric acid will give both greater lowering of concentration (as pH rises) and lowered per berry content as the berry ripens. This might explain the lower content and somewhat different trends reported for Grenache by ROMEYER *et al.* (1983).

Cold storage, at least for 2 weeks, did not appreciably alter the hydroxycinnamate picture. Highly ripe, even shriveled berries, also seem to maintain their content of caftaric acid unless cracking and oxidation occur, but the proportion of coutaric acid and the proportion of *cis* isomers tends to rise slightly.

Summary

Caftaric and coutaric acid contents (juice concentration, amounts per berry, percent of the *cis* forms) were investigated in samples fully protected from oxidation as ripeness increased in harvests from Grenache, French Colombard and two harvests from different vineyards of Ruby Cabernet *Vitis vinifera* grapes. Segregation by berry density gave sugar content (ripeness) sequences free of other variables such as weather and provided berries of nearly identical °Brix at each ripeness level. The two Ruby Cabernet harvests, even though differing considerably in growing conditions and average °Brix level, were much closer in the details of caftaric and coutaric acid compositions to each other than to the other varieties indicating close genetic (varietal) control of these components. The proportion of coutaric to caftaric and the percentage of *cis* forms tend to rise toward the end of ripening. The overall ripening pattern appears to be that these components are synthesized as the berry enlarges during ripening. If the rate of synthesis is able to keep up with the berry enlargement and the content moderate (French Colombard, Ruby Cabernet), the concentration in juice stays nearly constant at a level typical for the variety. If the content is high (Grenache) and the synthesis does not keep up with berry enlargement, the concentration in juice falls as the berry content rises during ripening, but a relatively high concentration is maintained. Overripe, shriveling berries rise in concentration, but may lose caftaric acid by oxidation if tissue breakdown occurs.

Acknowledgements

We thank the American Vineyard Foundation for funds that helped make this research possible.

Literature cited

DUMAZERT, G.; MARGULIS, H.; MONTREAU, F. R.; 1973: Evolution des composés phénoliques au cours de la maturation d'un *Vitis vinifera* blanc: Le Mauzac. Ann. Technol. Agric. **22**, 137—151.

NELSON, K. E.; BAKER, G. A.; WINKLER, A. J.; AMERINE, M. A.; 1963: Chemical and sensory variability in table grapes. Hilgardia **34**. 1—42.

ONG, B. Y.; NAGEL, C. W.; 1978: Hydroxycinnamic acid-tartaric acid ester content in mature grapes and during maturation of White Riesling grapes. Amer. J. Enol. Viticult. **29**, 272—281.

ROMEYER, F. M.; MACHEIX, J. J.; GOIFFON, J. J.; REMINIAC, C. C.; SAPIS, J. C.; 1983: Browning capacity of grapes. 3. Changes and importance of hydroxycinnamic acid-tartaric acid esters during development and maturation of the fruit. J. Agricult. Food Chem. **31**, 346—349.

SINGLETON, V. L.; DE WET, P.; DU PLESSIS, S.; 1973: Characterization of populations of grapes harvested for wine and compensation for population differences. Agroplantae **5**, 1—12.

— — ; OUGH, C. S.; NELSON, K. E.; 1966: Density separations of wine grape berries and ripeness distribution. Amer. J. Enol. Viticult. **17**, 95—105.

— — ; SALGUES, M.; ZAYA, J.; TROUSDALE, E.; 1985: Caftaric acid disappearance and conversion to products of enzymic oxidation in grape must and wine. Amer. J. Enol. Viticult. **36**, 50—56.

— — ; TIMBERLAKE, C. F.; LEA, A. G. H.; 1978: The phenolic cinnamates of white grapes and wine. J. Sci. Food Agricult. **29**, 403—410.

— — ; ZAYA, J.; TROUSDALE, E.; SALGUES, M.; 1984: Caftaric acid in grapes and conversion to a reaction product during processing. Vitis **23**, 113—120.

Eingegangen am 21. 10. 1985

Dr. V. L. SINGLETON
Viticulture and Enology Department
University of California
Davis, CA 95616
USA