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CAFTARIC AND COUTARIC ACIDS IN FRUIT OF *VITIS*

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Key Word Index—*Vitis*; Vitaceae; grape; chemotaxonomy; hydroxycinnamates; caftaric acid; coutaric acid; phenols.

Abstract—The contents of *trans* and *cis* caftaric and coutaric acids were determined by HPLC under conditions fully protecting against oxidation in berry juices from five non-*Vitis* species, 28 *Vitis* species, 20 white and 17 red *Vitis vinifera* cultivars, six *Vitis labrusca* cultivars and 11 other varieties. These components appear to be genetically determined to a considerable degree. Replicate samples of the same variety from different sources generally gave similar composition. The compounds were absent from or present only in trace amounts in *Vitis rotundifolia* and four (of five) non-*Vitis* species. Other *Vitis* species all contained them but the content ranged from 5 mg/l to 1350 mg/l of caftaric and from a trace to 340 mg/l of coutaric acid. Cultivars of *Vitis vinifera* did not differ appreciably whether white or red berries were involved, but ranged from 16 to 430 mg/l of *trans*-caftaric acid, averaging 145 mg/l. *Vitis labrusca* and its cultivars averaged notably higher and hybrids were generally intermediate with their parent species. The *cis* percentage increased, particularly for coutaric with the varieties arranged in order of decreasing caftaric concentration, but appeared to reflect environmental rather than genetic influences. The proportion of coutaric acid, however, appeared quite variable (3–33% of the caftaric content in the vinifera cultivars) by variety and was apparently genetically controlled.

INTRODUCTION

Considering 'fruit' in the farmer-consumer sense of the word, grapes are the most economically important fruit worldwide. The major phenols present in the readily expressed juice, and white wine made from it, of nearly all grape cultivars are the hydroxycinnamates [1]. Caftaric [monocaffeoyl-L-(+)-tartaric] acid is generally present at roughly 100 mg/l with the analogous *p*-coumaric (coutaric) and ferulic (fertaric acid) derivatives present at about 20 and 5 mg/l, respectively [2]. These compounds in grapes replace the chlorogenic analogs present in most other plants [1, 2]. Various processing and storage reactions such as browning depend upon the kinds and amounts of different phenols naturally present. Therefore, it is important to know the content of these compounds in cultivars and the genetic variation among species of *Vitis*.

This study also has more general interest in that chlorogenic acid analogs have had little use as chemotaxonomic markers and presumably could function similarly. Tartaric acid is rare as the major acid in plants except for grapes, but caffeic esters of tartaric acid have been reported for chicory, endive, lettuce and spinach [3–5]. Discovery that an immediate major product of phenolase oxidation in grape juice is *S*-glutathionylcaftaric acid emphasized the lability of these compounds [6, 7]. It also provided a technique for measuring whether oxidation had been completely prevented and cast doubt on the few previous related studies that might have involved some oxidative losses.

This study was designed to determine the content of caftaric and coutaric acids and their glutathione thioether adduct, if any, under conditions designed to preclude oxidative changes during sampling. All commercial grape cultivars planted to the extent of 1500 or more acres in California, several cultivars such as Concord important elsewhere in the U.S., and as many *Vitis* species as possible were sampled. Objectives included estimation of the content of *trans*- and *cis*-forms and the ratios between caftaric and coutaric acids with respect to cultivar groups and species.

RESULTS AND DISCUSSION

The addition of sulphite to suppress polyphenolase action, ascorbic acid to reduce any quinone formed, and a CO_2-filled glove box to exclude oxygen as the berries were crushed were successful in all cases in preventing the formation of *S*-glutathionylcaftaric acid [7]. It was completely absent in most samples. Traces too low to quantify (< 0.5 mg/l) were found in the samples for *Vitis shuttleworthii*, *V. berlandieri*, *V. champini*, Black Corinth, one Pinot noir and Gewurztraminer. These traces are attributed to berry damage at the berry–pedicel junction during harvesting. These were generally soft or overripe samples with either very small berries or tight clusters.

An effort was made to harvest the berry samples near 20° Brix to minimize any effect from ripeness variation. This was not always possible because some samples either failed to reach the desired level or were already past it when sampled. However, studies separately reported [8] indicate that grapes tend to maintain a relatively constant content of hydroxycinnamates. The level characteristic for a variety only fell appreciably during ripening if berry enlargement was considerable and content high so that synthesis failed to keep up. It may rise as ripe berries shrivel. Therefore, it is believed that the relatively small ripeness differences near commerical ripeness are not a serious complication.

It is also believed that vineyard location and vintage year (weather) have relatively little influence compared to the genetic characteristics of the mother vine, but they do not appear to be without influence. Clonal differences within varieties may be factors especially in widely separated vineyards. A study [10] of White Riesling wines showed considerable variation among samples from different sources and vintages in their caftaric acid content yet averaging the same for California and Washington samples (123, mg/l). Alsatian samples averaged significantly lower, but again were fairly constant within their group over three vintages. Since these were wine samples, losses by conversion to glutathionylcaftaric undoubtedly occurred, but were not determined. A White Riesling wine prepared commercially had 66 mg/l of caftaric and, in contrast to wines from other varieties, no glutathionylcaftaric acid [7]. This will be considered further below, but it appears that the grape selection has the greatest influence on the juice content of hydroxycinnamates. The data of this report were all on 1984 vintage fruit harvested from two vineyards under the same management and about 60 km apart.

Most of the results are shown in Tables 1–4 arranged in decreasing order of caftaric acid content within each table. Not shown are the data obtained on fruit of *Ampelopsis brevipedunculata elegans*, *A. aconitifolia glabra*, *Zizyphus jujuba* (Rhamnaceae) and *Parthenocissus quinquifolia* (Vitaceae) all of which showed none or perhaps traces (in different chromatographic patterns) of *trans*-caftaric acid or its companions. *Parthenocissus tricuspidata* had 25.6 mg/l of *trans*-caftaric, 12.8 mg/l of *trans*-coutaric acid and traces of the respective *cis*-isomers. *Vitis rotundifolia* in three examples had none or traces of *trans*-caftaric acid. All other species and cultivars of *Vitis* (Tables 1–4) had at least 5 mg/l and up to 1337 mg/l of *trans*-caftaric acid. It seems significant that *V. rotundifolia* is considered, by some authorities, a separate genus or subgenus *Muscadinia* as opposed to *Euvitis*, the 'true' grapes. It appears that caftaric acid and its relatives are universal and characteristic within the genus *Vitis* with the exception of *V. rotundifolia.* As far as these data allow conclusions, caftaric acid appears of limited occurrence outside this genus. It is noteworthy that *V. rotundifolia* crossed with *V. vinifera* produced hybrids (two examples Table 4) with only low levels of *trans*-caftaric acid but an anomalously high apparent level of coutaric acid in one of them.

If the percentage of either acid that is *cis* is examined, in all four tables, it is seen to generally increase, particularly for coutaric acid, as the caftaric content decreases. For the data in Table 3, for example, the coefficient of linear correlation between *trans*-caftaric acid content and the percentage of the coutaric that was *cis* on a linear regression basis was -0.73, and for the *cis* percentage of caftaric was -0.62. The mean proportion of the caftaric acid that was *cis* was about 2% and of the coutaric was about 18%. These proportions of *cis*-forms seem more a function of environmental conditions than of genetic source and have low but about equal variability between replicates of the same variety as among varieties.

The percentage of *trans*-coutaric acid concentration relative to *trans*-caftaric acid concentration is evidently predominately influenced by genetics, but still has a linear correlation coefficient with *trans*-caftaric acid content of -0.42. Note in Tables 1–3 that replicate samples of the same variety or species from different vineyard sources were quite similar in the percent of *trans*-coutaric relative to *trans*-caftaric acid. *Vitis shuttleworthii*, St. Emillion, and Ribier seem notably low in the proportion of coutaric acid and *V. cordifolia*, *V. cinerea*, *V. solonis*, *V. aestivalis*, Emerald Riesling, Ruby Seedless, Emperor, Carignane, Ruby Cabernet, Rubired, and Salvador notably high. The one selection (but not the other) of a *V. vinifera* × *V. rotundifolia* cross was in a class by itself having four times as much apparent coutaric acid content as caftaric acid. Remembering that the identification and quantitation here depends on HPLC retention and peak area characteristics of known caftaric acid, it is possible that this result involves contamination of the identified peak with an unknown substance absorbing strongly at 320 nm. The chromatograms in this instance gave a large, symmetrical, well separated peak in the proper position, but it was not possible to study it further. An additional large, slower peak was unusual in this fruit indicating also an unusual amount of fertaric or another unidentified component. Note (Table 1) that one selection of *V. rotundifolia* anomalously appeared to have 4 ppm of *cis*-coutaric but no *trans*-coutaric acid, suggesting misidentification of that peak.

The caftaric acid contents reported are means of duplicate analyses of separate berry samples. For the 26 examples where 40 berries were used for each duplicate, the average deviation of *trans*-caftaric acid was $\pm 1.5\%$ from the mean of the two, i.e. quite close agreement combining both the berry and analytical variation. Three separate Grenache sources (Table 3) had a relatively high and constant *trans*-caftaric acid content, 261–290 mg/l. Literature values for this variety for different years and widely separated vineyards invariably indicate this variety to be high relative to others and fairly close to these values [2, 6, 9]. Other comparisons with the literature could be made and agree roughly, but owing to uncertainty about oxidative change in the literature data, they were not considered useful. Note that in Tables 1–3 the nine examples of more than one set of samples representing different vines from the same species or cultivar agree well for *V. monticola*, Chardonnay, Grenache, Pinot noir, Cabernet Sauvignon and Ruby Cabernet not only in *trans*-caftaric content, but also in *trans*-coutaric acid content and other details. The sets for Semillon and French Colombard did not agree well but there was a large ripeness difference, and Carignane also did not but there was a large berry size difference and the amounts per berry were relatively close. Further comparisons among the eight varieties for which values were available from 1982 and 1983 vintages [6] gave an average variation from the mean of $\pm 20\%$ for single varieties and more than double that among varieties. These data indicate the juice content of these compounds is primarily determined by the genetic make-up of the particular species or cultivar.

Several points of interest become apparent in close study of the data. Palomino is highest in caftaric acid content especially on a per berry basis and is noted for making quality sherry wines. White grapes noted for consumption as table grapes (Malaga, Perlette, Thompson Seedless, Calmeria) are generally low in caftaric acid content (Table 2). With the notable exception of Ribier which had a very high juice concentration and the most caftaric acid per berry of any species or variety, the red table varieties tended to follow the same pattern (Flame Tokay, Ruby Seeless, Emperor; Table 3), although Cardinal was intermediate.

The red vinifera cultivars (Table 3) averaged slightly higher in both caftaric and coutaric acid content than did the white ones (Table 2), but they overlapped for all but the extreme examples of Carnelian and Calmeria. With

Table 1. Caftaric and coutaric acid contents of juice of berries of *Vitis* species

Vitis species	Juice Brix	Berry wt (g)	Caftaric (Ca) acid *trans* (mg/l)	Caftaric (Ca) acid *cis* (mg/l)	Caftaric (Ca) acid % *cis*	Coutaric (Cu) acid *trans* (mg/l)	Coutaric (Cu) acid *cis* (mg/l)	Coutaric (Cu) acid % *cis*	% *t*-Cu/*t*-Ca	μg/berry *t*-Ca	μg/berry *t*-Ca
aestivalis	25.2	0.55	1337	16	1.2	326	16	4.5	24	618	151
monticola	19.8	0.57	1155	4	0.3	59	3	5.2	5	563	29
monticola	21.8	0.57	1010	6	0.6	43	2	4.1	4	496	21
rufotomentosa	15.1	0.21	772	2	0.2	30	2	6.0	4	127	5
simpsonii (pixiala)	23.3	0.34	664	6	1.0	21	tr	—	3	184	6
arizonica	27.4	0.20	484	0.2	0.1	34	5	15.9	7	67	5
labrusca	19.1	2.18	462	6	1.3	43	3	7.0	9	918	85
smalliana	7.2	0.42	443	2	0.4	24	2	7.5	5	163	9
treleasei	15.8	0.61	405	2	0.4	36	6	17.3	9	217	19
candicans	23.2	0.41	403	4	1.1	66	19	28.1	16	136	22
lincecumii	16.6	1.60	246	4	1.8	35	3	9.4	14	362	52
Afganistan source	21.6	0.44	220	3	1.2	14	tr	—	6	82	5
girdiana	16.1	0.34	207	1	0.4	30	5	17.6	14	57	8
shuttleworthii	20.1	1.17	185	2	1.1	3	tr	—	2	193	3
amurensis	17.8	0.57	128	2	1.7	22	5	20.8	17	61	11
californica	22.5	1.46	122	3	2.8	11	1	12.8	9	159	4
berlandieri	14.8	0.35	89	1	1.1	13	tr	—	14	26	4
novae-angliae	24.7	1.38	71	4	5.0	13	2	15.8	18	87	16
doaniana	18.6	1.42	57	0.5	0.8	7	1	16.9	12	73	9
cinerea	16.6	0.27	53	tr	—	23	3	11.7	43	12	5
slavinii	22.8	0.57	48	tr	—	5	2	33.3	10	24	2
longii	21.4	0.69	43	tr	—	8	2	29.6	19	26	5
champini	20.4	0.74	43	tr	—	6	7	112.9	14	28	4
riparia	18.9	0.29	41	2	3.9	6	tr	—	15	10	1
rupestris	16.3	0.29	40	tr	—	8	1	14.3	19	10	2
solonis	19.6	0.79	17	tr	—	6	tr	—	32	12	4
cordifolia	22.6	0.20	5	tr	—	6	2	20.7	135	1	1
rotundifolia (Thomas)	15.1	4.47	0	0	0	0	0	0	0	0	0
rotundifolia (Creek)	16.1	3.18	tr	0	0	0	0	0	0	tr	0
rotundifolia	18.1	0.95	1.5	tr	—	0	4	—	0	1.3	0
Mean	19.3	0.91	292	—	1.3	—	—	17.8	16.6	—	—

Table 2. Caftaric and coutaric acid contents of juice of commercially important white varieties of *Vitis vinifera*

Cultivar	Juice Brix	Berry wt (g)	Caftaric (Ca) acid *trans* (mg/l)	Caftaric (Ca) acid *cis* (mg/l)	Caftaric (Ca) acid % *cis*	Coutaric (Cu) acid *trans* (mg/l)	Coutaric (Cu) acid *cis* (mg/l)	Coutaric (Cu) acid % *cis*	% *t*-Cu / *t*-Ca	μg/berry *t*-Ca	μg/berry *t*-Ca
Palomino	20.2	2.42	295	4	1.5	42	5	9.9	14.2	648	92
Pinot blanc	20.8	1.44	266	3	1.2	18	1	6.8	6.7	255	17
Semillon (D)*	11.3	1.13	197	2	1.0	11	tr	—	5.5	206	11
Semillon (N)*	21.2	2.17	98	1	1.3	4	tr	—	4.1	193	8
Rkatsiteli	20.8	2.05	181	4	2.4	19	5	20.2	10.3	337	35
St. Emilion	20.6	1.79	179	5	2.9	6	1	18.8	3.1	290	9
Emerald Riesling	21.3	1.84	154	2	1.5	47	6	11.8	30.7	255	78
Muscat blanc	22.4	2.11	143	4	2.6	24	6	19.3	16.6	272	45
Muscat Alexandria	17.0	3.57	141	3	1.9	6	2	20.5	4.4	468	21
French Colombard	8.7	1.15	142	1	0.7	18	3	15.0	12.8	153	20
French Colombard	19.8	1.79	97	2	2.5	15	4	21.5	15.5	157	24
Chardonnay (D)	22.1	1.14	135	1	0.4	15	4	18.7	11.3	136	15
Chardonnay (N)	21.0	1.55	122	3	2.6	12	3	19.4	9.5	170	16
Burger	19.5	2.68	119	2	1.6	4	tr	—	3.6	291	11
Chenin blanc	20.6	1.94	110	2	2.2	11	3	20.6	9.8	193	19
White Riesling	20.7	1.91	109	3	2.5	8	3	25.2	7.6	188	14
Sauvignon blanc	22.4	1.63	97	2	2.0	12	3	18.7	12.6	140	18
Grey Riesling	23.9	1.59	81	2	1.9	15	4	20.7	17.9	115	21
Malaga	19.0	3.89	61	2	4.0	11	2	19.1	17.5	217	38
Perlette	19.0	2.65	59	3	4.5	6	2	29.3	9.8	144	14
Thompson Seedless	21.5	1.34	56	2	3.3	3	1	18.8	4.6	52	3
Gewurztraminer	20.1	1.27	54	1	1.8	3	1	23.8	5.9	62	4
Calmeria	18.8	4.64	16	0	—	tr	tr	—	—	68	tr
Mean	19.7	2.07	127	2.4	2.1	14	3.0	18.8	10.6	218	24

*D = Davis vineyard (warmer, earlier), if not designated this was the source; N = Napa Valley vineyard (cooler, later).

Table 3. Caftaric and coutaric acid contents of juice of commercially important red varieties of *Vitis vinifera*

Cultivar	Juice Brix	Berry wt (g)	Caftaric (Ca) acid *trans* (mg/l)	Caftaric (Ca) acid *cis* (mg/l)	Caftaric (Ca) acid % *cis*	Coutaric (Cu) acid *trans* (mg/l)	Coutaric (Cu) acid *cis* (mg/l)	Coutaric (Cu) acid % *cis*	% *t*-Cu/*t*-Ca	μg/berry *t*-Ca	μg/berry *t*-Ca
Carnelian	20.7	1.63	430	5	1.1	39	3	6.7	9.0	630	57
Ribier	19.7	5.63	294	4	1.3	9	tr	—	3.2	1523	49
Grenache (D)*	18.9	1.26	290	4	1.3	20	1	6.5	7.0	327	23
Grenache (D)	20.2	1.22	267	2	0.7	21	2	9.6	7.8	291	23
Grenache (N)*	21.0	1.62	261	3	1.2	17	1	7.0	6.7	379	25
Black Corinth	23.4	0.22	221	2	0.9	31	4	10.2	14.0	45	7
Mission	20.1	2.23	216	3	1.5	35	4	9.4	16.1	365	59
Petite Sirah	21.8	1.62	188	3	1.4	35	5	13.4	18.5	274	51
Zinfandel	21.4	2.13	171	4	2.0	11	2	12.7	6.4	328	21
Pinot noir (D)	21.7	0.66	160	2	1.3	9	3	26.2	5.6	92	5
Pinot noir (N)	19.3	1.20	139	2	1.2	8	1	6.9	5.7	150	9
Cabernet Sauvignon (N)	23.2	1.05	140	6	3.9	10	4	26.8	7.4	129	10
Cabernet Sauvignon (D)	22.0	1.12	110	1	1.2	9	2	17.8	8.0	110	9
Cardinal	17.6	6.12	140	4	2.8	10	tr	—	6.9	795	55
Carignane (D)	20.6	1.54	109	2	1.7	29	5	15.3	26.4	152	40
Carignane (N)	19.6	2.16	56	1	2.4	14	3	18.2	25.8	112	29
Ruby Cabernet (D)	16.6	1.44	108	2	2.0	25	8	23.3	23.1	142	33
Ruby Cabernet (N)	24.2	1.45	103	2	2.3	24	6	19.3	23.2	132	31
Flame Tokay	20.2	4.77	93	4	4.5	6	2	27.9	6.6	408	27
Merlot	22.4	1.02	79	2	2.1	8	2	20.2	9.5	71	7
Ruby Seedless	21.4	2.35	61	2	3.0	20	8	28.4	33.3	132	44
Gamay (Napa)	19.5	2.31	57	2	2.9	5	2	27.5	8.8	107	9
Emperor	17.4	3.44	48	2	4.2	10	4	20.4	29.0	153	31
Mean	20.6	2.10	163	2.8	2.0	18	3.4	16.8	13.4	298	28

*D = Davis vineyard (warmer, earlier), if not designated this was the source; N = Napa Valley vineyard (cooler, later).

Table 4. Caftaric and coutaric acid contents of red juice or non-*vinifera* cultivars

Cultivar	Juice Brix	Berry wt (g)	Caftaric (Ca) acid trans (mg/l)	Caftaric (Ca) acid cis (mg/l)	Caftaric (Ca) acid % cis	Coutaric (Cu) acid trans (mg/l)	Coutaric (Cu) acid cis (mg/l)	Coutaric (Cu) acid % cis	% t-Cu/t-Ca	μg/berry t-Ca	μg/berry t-Ca
Red Juice varieties											
Alicante Bouschet	16.6	2.21	238	2	1.0	30	4	12.6	12.5	484	61
Salvador	20.0	1.15	171	2	1.4	44	5	9.7	25.8	175	45
Saperavi	21.8	1.52	168	3	1.6	28	5	14.2	16.9	229	39
Rubired	22.2	1.40	87	2	1.1	31	7	18.5	35.2	109	39
Labrusca varieties											
Catawba	17.6	2.10	322	4	1.2	36	4	9.5	11.3	620	70
Niagara	15.1	3.08	280	5	1.8	41	4	9.5	14.6	807	118
Concord	17.0	2.62	223	2	1.1	12	tr	—	5.6	539	30
Isabella	16.0	2.36	155	1	0.9	21	2	9.2	13.4	338	45
Niabell	14.9	5.30	131	2	1.8	10	tr	—	7.3	653	48
Delaware	20.0	1.61	104	2	2.0	17	1	4.4	16.6	151	25
Hybrid varieties											
Vidal 256	19.0	1.22	107	1	0.6	12	2	12.7	11.0	117	13
DeChaunac (Seibel 9549)	18.9	1.36	94	2	1.9	15	2	13.6	16.1	115	19
Foch	22.1	1.10	62	2	2.7	4	tr	—	7.1	61	4
Aurore (Seibel 5279)	17.6	1.56	56	2	4.3	8	2	23.1	14.8	80	12
Baco noir (No. 1)	20.6	1.02	47	tr	—	3	tr	—	7.3	42	3
vinifera × *rotundifolia*	24.0	0.43	14	tr	—	2	1	26.7	16.3	5	1
vinifera × *rotundifolia*	25.4	0.36	16	tr	—	66	10	13.2	422.3	5	20

respect to relative coutaric acid content in these varieties, Emerald Riesling, Ruby Seedless, Emperor, Carignane, and Ruby Cabernet are high and St. Emilion and Ribier low. The wild grape species tend to be higher in caftaric and coutaric acid concentration (Table 1) compared to the European wine grape (Tables 2 and 3), but 18 of the 27 species had less than 300 mg/l of caftaric acid. Because the wild species mostly have small berries, the amounts per berry are generally smaller than the cultivars. *V. aestivalis* was outstandingly high in both caftaric and coutaric acids with *V. monticola* very high in caftaric concentration. *V. labrusca* was highest among those North American species most used in developing fruited varieties and this is reflected in varieties derived from it, notably Catawba, Niagara and Concord (Table 4).

The other varieties most used in breeding work and rootstocks *V. riparia* and *V. rupestris* (Table 1) are low as are the direct producer hybrids (Table 4). Relatively high proportions (but not concentration) of *trans*-coutaric acid occurred in *V. cinerea* and *V. cordifolia* (Table 1), and one of the *vinifera* × *rotundifolia* crosses (Table 4) as already mentioned. The red-juice grapes covered the range noted in other varieties (Table 4) and do not seem as a group to be unusual in their hydroxycinnamate content even though they are in anthocyanin content.

The chromatograms for the vinifera varieties were relatively similar, whereas those from non-vinifera varieties and species often produced unusual patterns and large unknown peaks. For example, Isabella and *V. monticola* gave two sizeable long-retained peaks not noted in others. *V. solonis* and Baco noir appeared to have other substances with similar retentions including apparently relatively high fertaric acid content. Oxidation of Aurore juice gave in addition to glutathionylcaftaric acid considerable of what appears to be cysteinylcaftaric acid.

EXPERIMENTAL

Fruit sources. The designations carried in the records and vine markings of the variety and species collections of the University of California, Davis, were used. After a field estimation of Brix, the chosen vines were sampled (usually 7–8 AM) so as to represent the total fruit present (either all available clusters or ones selected randomly over the vine) with clusters or cluster parts sufficient to yield at least 30 berries or 40 g. The individual berries were snipped with small scissors so as to remove the pedicel with the torus without breaking the berry skin. Any berries seen to be damaged were discarded.

The berries were counted, weighed and placed in a glove box under a flowing CO_2 atmosphere. There they were mixed with solid ascorbic acid and potassium metabisulphite (*ca* 200 mg each) and then wrapped in cheesecloth and pressed in a small, levered hand-press as uniformly as possible. The juice was filtered (prefilter with Celite followed by 0.45 μm membrane) and chromatographed on a C_{18} reversed phase column with pH 2.6 16% aq. MeOH essentially as described before [6, 7]. Peak areas were converted to amounts by using the peak area per unit mass determined under the same conditions with pure *trans*-caftaric acid isolated from grapes. The *trans*-coutaric acid content was estimated from the same response factor. The amounts determined by the same method for the *cis*-forms were multiplied by 1.58 which is the relative absorbance difference, thus providing a better estimate of the true content.

Juice Brix was determined by refractometry on a separate sample. The percentage *cis* was calculated as the proportion of the sum of the two forms determined for either caftaric or for coutaric acids. The weight of each substance per berry was calculated from the berry weight minus an estimated standard weight of 40 mg for seeds in each seeded berry, divided by the density equivalent to the juice Brix, times the concn of each substance. The seed number increased to near four per berry for the small wild berries, but the average seed size dropped, so a standard estimate of seed amount per berry was deemed adequate for the present purposes. The amounts per berry were probably overestimated especially on smaller berries since no correction was made for the berry skin, which has a lower concentration per unit weight of hydroxycinnamates.

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