Compositional Characterization of Prune Juice

Hendrik van Gorsel, Chingying Li, Eduardo L. Kerbel,† Mirjam Smits,‡ and Adel A. Kader*

Department of Pomology, University of California, Davis, California 95616

Processed juices from dried prunes with or without pulp, juice from prune concentrate, and the juices of fresh prune and nine other fruits were analyzed for anthocyanins, organic acids, sugars, phenolic compounds, and amino acids. Unique characteristics of processed prune juice were the predominance of α-aminobutyric acid, citrulline, taurine, O-phosphoethanolamine, and quinic acid and the absence of anthocyanins, (−)-epicatechin, phloridzin, and citric and tartaric acids. Comprehensive measurements of sugars, anthocyanins, nonvolatile acids, phenolic compounds, and amino acids made it possible to distinguish processed prune juices from fresh prune juice and the juices of plum, cherry, nectarine, peach, apple, pear, grape, kiwi fruit, and strawberry fruits.

INTRODUCTION

Prune juice is not a fruit juice in the usual sense but rather a water extract of dried prunes (Luh, 1980). It is a valued product that commands a high price on the market, and its production is expensive. Therefore, there is an economic incentive for adulteration of prune juice with less expensive fruit juices, fruit juice concentrates, and/or sugar syrups.

To determine the authenticity of processed prune juice, a comprehensive knowledge of its composition is required. Several authors (Fernandez-Florez et al., 1970; Fitelson, 1970; Flynn and Wendt, 1970; Henning and Herrmann, 1980; Ishii, 1983; Möller and Herrmann, 1983; Mosel and Herrmann, 1974; Wrolstad et al., 1981) have investigated some aspects of prune juice composition. However, little information is available on the composition and levels of organic acids, anthocyanins, and free amino acids in this juice. Furthermore, comparisons of fruit juice composition data among papers are often complicated by differences in the analytical methods used (Reyes et al., 1982).

We analyzed the juices from nine fruit species and from dried prunes for their contents of sugars, organic acids, free amino acids, phenolic compounds, and anthocyanins. With the same methods we compared the composition of fresh and processed prune juices. Those components that could be used as markers for establishing the authenticity of prune juice were identified.

MATERIALS AND METHODS

Sources of Fruits and Juices. Prune juices from dried prunes with pulp (prune DP) or without pulp (prune D) were purchased in local supermarkets in Davis, CA. These prune juices were water extracts of dried prunes. Processed prune juice reconstituted from concentrated water extracts of dried prunes (prune C) and frozen juice from fresh (i.e., not dried) prunes (prune FJ) were supplied by the California Prune Advisory Board. All of these juices were of the SunSweet brand. Fresh French prunes (prune UC) were obtained from the Pomology Teaching Orchard, University of California at Davis. The processed prune juices D, DP, and C were kept at 4 °C, while prune FJ was kept at −30 °C. Aliquots were drawn as needed. Three replicates were used for each juice.

* Author to whom correspondence should be addressed.

† Present address: Department of Horticulture, 1061 Horticulture Field Laboratory, University of Illinois, Urbana, IL 61801.

‡ Present address: Department of Horticulture, Agricultural University, Wageningen, The Netherlands.

Table I. Qualitative and Quantitative Differences in Organic Acids among Fruit Juices

	organic acid, mg/100 mL of juice				
juice	citric	ascorbic	malic	quinic	tartaric
prune DP	ND[a]	tr[b]	104 ± 14[c]	668 ± 25	ND
apple	ND	tr	518 ± 32	ND	ND
cherry	ND	tr	727 ± 20	ND	ND
grape	tr	tr	285 ± 58	ND	162 ± 24
kiwi fruit	730 ± 92	114 ± 6	501 ± 42	774 ± 57	tr
nectarine	140 ± 39	tr	383 ± 67	136 ± 28	ND
peach	109 ± 16	tr	358 ± 72	121 ± 11	tr
pear	ND	tr	371 ± 16	220 ± 2	ND
plum	ND	tr	294 ± 24	214 ± 68	ND
strawberry	207 ± 35	56 ± 4	199 ± 26	ND	ND

[a] ND, not detected. [b] Tr, trace (<10 mg/100 mL). [c] Mean ± standard deviation, $n = 3$.

Fresh Red Delicious apples, Bing cherries, black seedless grapes, Hayward kiwi fruits, Red Delight nectarines, Desert Gold peaches, d'Anjou pears, Roysum plums, and Douglas strawberries were bought from a wholesale market (General Produce, Sacramento, CA). Whenever possible, juices made from fresh fruits were used. Otherwise, the fruits were frozen at −30 °C for 1–3 months and then juices were made for the analyses. Unless otherwise indicated, for each species three replicates consisting of 10 fruits each were used.

Apparatus. A Bio-Rad high-performance liquid chromatography (HPLC) system, equipped with refractive index (RI) and ultraviolet (UV) detectors, was used for the analysis of organic acids, sugars, and phenolics. Mobile phases were continuously degassed with helium. Anthocyanins were analyzed using a Hewlett-Packard HPLC system with a diode array detector. Amino acids were analyzed with a Beckman Model 7300 amino acid analyzer with a dual-channel spectrophotometric detector. In all cases tentative identification of constituents was based on comparison of retention times with those of known standards.

Determinations of Sugars and Organic Acids. Fruit juices were prepared by squeezing wedges of 5 or 10 fresh or frozen fruits through two layers of cheesecloth using a Hamilton Beach Model 932 extractor (Waterbury, CT). Juices were centrifuged at 25000*g* for 25 min at 4 °C. The supernatant was adjusted to a pH between 8 and 9 with 58% NH_4OH, and 2 mL of sample was passed through a column with 2 g of anion-exchange resin (Bio-Rex 5 analytical grade, 100–200 mesh, chloride form). The column was then rinsed with 2 × 4 mL double-deionized water, and the eluate was collected for sugar analysis. Next, 2 mL of 10% H_2SO_4 was added to the column, followed by rinsing of the column with 2 × 4 mL of double-deionized water. The eluate was collected for organic acid analysis.

Individual sugars were separated with a 25 × 0.4 cm HPX-87C column at 85 °C and detected with a RI monitor. Double-deionized water was used as the mobile phase at a flow rate of 0.6 mL/min. Sucrose, glucose, fructose, and sorbitol (Sigma Chemical

0021-8561/92/1440-0784$03.00/0

Table II. Qualitative and Quantitative Differences in Sugar Composition of Processed Prune and Fresh Fruit Juices

	sugar, g/100 mL of juice			
	sucrose	glucose	fructose	sorbitol
juices				
prune DP[a]	0.11 ± 0.03[b]	7.00 ± 0.31	4.63 ± 0.29	4.35 ± 0.24
prune D	ND[c]	11.60 ± 1.10	7.40 ± 0.50	7.35 ± 0.95
prune C	ND	10.20 ± 0.80	6.55 ± 0.45	6.45 ± 0.55
prune FJ	4.35 ± 0.45	10.10 ± 0.85	5.10 ± 0.60	6.35 ± 0.70
prune UC	6.10 ± 0.70	4.35 ± 2.00	2.90 ± 2.60	8.00 ± 0.60
apple	0.82 ± 0.13	2.14 ± 0.43	5.31 ± 0.94	0.20 ± 0.04
cherry	0.08 ± 0.02	7.50 ± 0.81	6.83 ± 0.74	2.95 ± 0.33
grape	0.29 ± 0.08	9.59 ± 1.03	10.53 ± 1.04	ND
nectarine	8.38 ± 0.73	0.85 ± 0.04	0.59 ± 0.02	0.27 ± 0.04
peach	5.68 ± 0.52	0.67 ± 0.06	0.49 ± 0.01	0.09 ± 0.02
pear	0.55 ± 0.12	1.68 ± 0.36	8.12 ± 1.56	4.08 ± 0.79
plum	0.51 ± 0.36	4.28 ± 1.18	4.86 ± 1.30	6.29 ± 1.97
kiwi fruit	1.81 ± 0.72	6.94 ± 2.85	8.24 ± 3.43	ND
strawberry	0.17 ± 0.06	1.80 ± 0.16	2.18 ± 0.19	ND
syrups				
beet sugar	61.80 ± 3.60	ND	ND	ND
corn syrup	35.00 ± 4.24[d]	28.90 ± 3.18	ND	ND
high-fructose corn syrup	3.37 ± 0.06[d]	32.60 ± 0.56	32.30 ± 0.25	ND

[a] Types of prune juices: extracted from dried prunes with pulp (DP) or without pulp (D); made from concentrate (C); extracted from fresh prunes (UC); frozen juice from fresh prunes (FJ). [b] Mean ± standard deviation, $n = 3$. [c] ND, not detected (less than 0.05 g/100 mL). [d] It is likely that what was determined in these samples was maltose, not sucrose.

Table III. Concentrations (Milligrams per 100 mL of Juice) of Hydroxymethylfuraldehyde (HMF) and Individual Phenolic Compounds in Tested Prune Juices

juice type[a]	HMF	(+)-catechin	chlorogenic acid	caffeic acid	phloridzin
prune DP	93.4 ± 4.6[b]	16.9 ± 1.6	33.5 ± 5.3	4.5 ± 1.8	ND[c]
prune D	85.8 ± 1.4	12.6 ± 1.5	32.6 ± 5.4	3.6 ± 2.5	ND
prune C	92.0 ± 10.1	17.9 ± 4.9	36.4 ± 9.3	5.1 ± 2.1	ND
prune FJ	0.8 ± 0.4	41.0 ± 4.1	37.9 ± 10.2	ND	10.0 ± 2.1
prune UC	ND	8.4 ± 1.2	2.8 ± 1.4	ND	1.7 ± 0.5

[a] For description of prune juices, see footnote for Table II. [b] Mean ± standard deviation, $n = 3$. [c] ND, not detected (less than 1.5 mg/100 mL).

Co.) were used as standards. Commercial beet sugar, corn syrup, and high-fructose corn syrup (HFCS) were used in the analysis for comparison.

Individual organic acids were separated with a 25 × 0.4 cm HPX-87H column at 65 °C for citric, malic, and quinic acids and at 24 °C for tartaric and ascorbic acids. A refractive index (RI) monitor was used for determining citric, malic, quinic, and tartaric acids. Ascorbic acid was determined with a UV monitor at 245 nm. Mobile phases were 0.05 N H_2SO_4 at 0.8 mL/min for citric, malic, and quinic acids; 0.002 N H_2SO_4 at 0.6 mL/min for tartaric acid; and 0.01 N H_2SO_4 at 0.5 mL/min for ascorbic acid. Citric, malic, quinic, tartaric, and ascorbic acids (Sigma) were used as standards.

Determination of Phenolics. Ten grams of flesh with skin from 5 or 10 fresh or frozen fruits was homogenized with 20 mL of 100% methanol in a Polytron homogenizer (Brinkmann Instruments, Westbury, NY). The homogenate was cleared by filtration through Whatman No. 4 filter paper or centrifugation for 20 min at 18000*g*, and the filtrate or supernatant was evaporated to dryness in 10–11 h with a Speed Vac concentrator (Savant Model SVC100H, Hicksville, NY). The residue was dissolved in 7 mL of 100% methanol. For samples of prune DP, prune D, prune C, and prune FJ, 10 mL of juice was centrifuged for 20 min at 18000*g* and the supernatant was evaporated to dryness in 5.5 h with a Speed Vac concentrator. The residue was dissolved in 3 mL of methanol to extract the phenols. All samples were kept at −10 °C overnight.

The next day, an aliquot of the extract was diluted with 4 parts of 0.1 M $NH_4H_2PO_4$ buffer (pH 2.8). Phenolic compounds were separated with a 25 × 0.4 cm reversed-phase C_{18} column (Bio-Sil ODS-5S) and detected with a UV monitor at 280 nm; 0.1 M $NH_4H_2PO_4$ buffer (A) and 80% methanol (B) were used as mobile phases. The gradient profile was modified from the method reported by Wulf and Nagel (1978). After an initial 2 min at 20% B, the gradient was increased from 20 to 80% B in 12 min, kept at 80% B for 10 min, and returned to 20% B in 5 min. The flow rate was 0.6 mL/min. Commercial (+)-catechin, chlorogenic acid, (−)-epicatechin, caffeic acid, ferulic acid, and phloridzin were used as standards. Chlorogenic acid isomers were kindly provided by Prof. S. F. Yang. The standards were prepared in 100% methanol and then diluted with 0.1 M $NH_4H_2PO_4$ buffer (1:5 v/v).

Determination of Anthocyanins. Ten grams of fruit tissue was homogenized with 15 mL of 100% methanol (HPLC grade) in a Polytron homogenizer at intermediate speed. The homogenate was centrifuged at 25000*g* for 25 min at 4 °C, and the supernatant was made up to 25 mL with 100% methanol. For samples of prune DP, prune D, prune C, and prune FJ, 10 mL juice was centrifuged and the supernatant was made up to 25 mL with 100% methanol. Individual anthocyanins were separated with a 25 × 0.4 cm Hibar LiChrosorb RP-18 (5 μm) reversed-phase column. The eluent was monitored at 326 and 520 nm. At each 326-nm elution peak an absorbane spectrum (250–600 nm) was acquired. The solvent method of Wulf and Nagel (1978) was used with slight modifications. In 1988, mobile phase A was 10% formic acid and mobile phase B was 10% formic acid in 50% acetonitrile; the gradient was from 0 to 25% B in 20 min followed by an increase from 25 to 75% B in 10 min. This condition was kept for 5 min before a return to the initial condition. The flow rate was constant at 1.0 mL/min. In 1989, mobile phase A was 0.1 M phosphoric acid and mobile phase B was 20% 0.1 M phosphoric acid plus 80% acetonitrile. After an initial 5 min at 0% B, a gradient from 0 to 15% B in 20 min was used, followed by an increase from 15 to 22.5% B in 15 min and to 62.5% B in 10 min. The column was then flushed at 100% B for 10 min before a return to the initial condition. The flow rate was constant at 1.0 mL/min. The tentative identification of anthocyanins was based on the absorbance spectra at 250–600 nm (Hebrero et al., 1988) and on the relative retention times (Williams et al., 1978; Wulf and Nagel, 1978).

Determination of Free Amino Acids. Fruit juice was prepared by squeezing wedges of 5 or 10 fresh or frozen fruits through two layers of cheesecloth. The fruit juice was centrifuged at 25000*g* for 25 min at 4 °C. The supernatant was diluted with

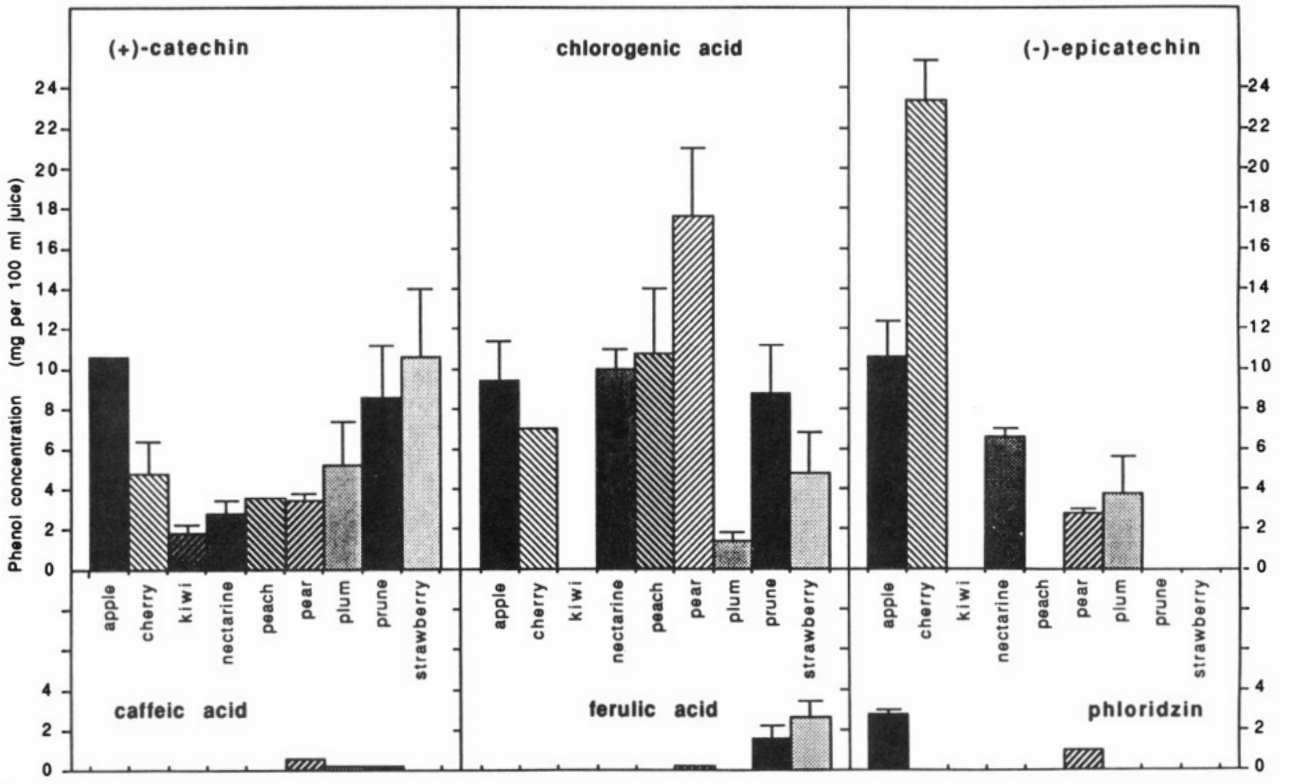

Figure 1. Comparison of processed prune juice with eight other fruits for amounts of phenolics.

water (1:5 and 1:50) and frozen until used for analysis. Lithium buffers were used at a flow rate of 20 mL/h. The eluent was monitored as a ninhydrin complex at 440 and 570 nm.

RESULTS AND DISCUSSION

Organic Acids. Prune juice was characterized by a predominance of quinic acid, an absence of tartaric acid, and trace amounts or an absence of citric acid (Table I). Compared to other fruit juices, prune DP was relatively low in malic acid. The quinic acid concentration of prune DP was similar to that of kiwi fruit. Except for strawberry and kiwi fruit, the fruit juices contained little ascorbic acid. This may have been due to destruction of some of the ascorbic acid during sample preparation for analysis. Strawberry, kiwi fruit, peach, and nectarine all contained considerable amounts of citric acid. Tartaric acid was absent in all fruit juices except grape juice.

On the basis of these organic acid analyses, only mixing prune juice with pear and plum juices would be difficult to detect. However, pH adjustment with acids is allowed for some fruit juice concentrates. Addition of organic acids to diluted prune juices would change the organic acid profile. In some cases such addition may be detectable; for example, if commercial DL-malic acid were added, the (natural) L-malic to total malic acid ratio would be less than 1. Another concern is that the organic acid composition of fruits is influenced by fruit maturity, geographic origin, and climatic conditions. Especially the ratios of malic to total acids or to other acids can be variable, even within cultivars of the same fruit, as was shown for malic to citric acid ratio in pear (Wrolstad et al., 1981) and strawberry (Reyes et al., 1982) fruits.

Sugars. All processed prune juices were both high in sorbitol and low in sucrose content (Table II). In contrast, fresh prune juices (prune FJ and prune UC) were high in sucrose. Similarly, Kline et al. (1970) found only small amounts of sucrose in juice of dried Imperial and French prunes and no sucrose in juice of California and Robe de Sergent dried prunes. Prunes contain invertase, which has been implicated in the disappearance of sucrose during processing (Wrolstad and Shallenberger, 1981). Flynn and Wendt (1970) have used the presence of sucrose as an indicator of prune juice adulteration.

All prune juices had a glucose to fructose ratio of approximately 1.5. The juices of peach and nectarine also have a glucose to fructose ratio of greater than 1, which is in agreement with the findings of Eheart and Mason (1967). Fresh peach and nectarine juices contained much more sucrose than processed prune juice, but the sucrose could disappear similarly during processing. In contrast to the juices of peach, prune, and nectarine, the juices of apple and pear had much more fructose than glucose. The rest of the fruit juices tested appeared to have about equal amounts of glucose and fructose. Similar results were reported by Flynn and Wendt (1970), Wrolstad et al. (1981), and Wrolstad and Shallenberger (1981).

Consequently, mixing processed prune juices with most of the other fruit juices or with cane sugars, beet sugar, or corn syrup would cause significant changes in the sugar profile. Addition of high-fructose corn syrup would be more difficult to detect but can be determined by stable isotope ratio analysis (Wrolstad et al., 1981; Krueger et al., 1986). This technique can indicate the presence of sugar from C4 (corn) vs C3 (fruits) plants.

In all of the 1989 prune juice samples a trisaccharide, eluting before sucrose, was present in significant amounts. It is composed of the sugars glucose and fructose and an as yet unidentified third component (which may be galactose or *myo*-inositol). This trisaccharide may be raffinose or galactinol.

Hydroxymethylfurfural (HMF) was found in high concentrations in the juice from dried prunes (Table III). HMF is produced in fruit juices from sugars, particularly ketoses, by heating during processing (Pollard and Timberlake, 1971).

Individual Phenolics. Grape juice had a very different and complex phenolic composition (including caffeoyl tar-

Table IV. Comparison of Processed Prune Juices with Juices of Fresh Prune and Nine Other Fruits for Contents of Amino Acids

	amino acid content, mg/L of juice									
juice	aspartic	threonine	serine	proline	glycine	alanine	α-amino-*n*-butyric	valine	isoleucine	leucine
prune DP[a]	526[b]	36 ± 5	36 ± 4	165 ± 36	4 ± 0	59 ± 3	39 ± 1	17 ± 4	14 ± 1	25 ± 5
prune D	703 ± 25	36 ± 4	35 ± 3	130 ± 34	7 ± 0	50 ± 2	36 ± 8	25 ± 2	18 ± 2	17 ± 1
prune C	632 ± 57	31 ± 8	34 ± 2	98 ± 7	5 ± 1	42 ± 3	42 ± 4	17 ± 3	13 ± 2	12 ± 1
prune FJ	425 ± 12	148 ± 15	175 ± 5	309 ± 5	17 ± 1	134 ± 4	ND[c]	80 ± 6	43 ± 4	30 ± 4
prune UC	ND	82 ± 2	66 ± 2	421 ± 93	9 ± 1	43 ± 6	ND	40 ± 9	22 ± 4	15 ± 3
plum	359 ± 42	64 ± 6	147 ± 9	476 ± 87	14 ± 2	198 ± 17	1 ± 1	41 ± 2	19 ± 1	10 ± 1
peach	353 ± 24	85 ± 12	182 ± 20	52 ± 4	16 ± 3	132 ± 22	1 ± 1	42 ± 5	30 ± 3	14 ± 1
cherry	195 ± 8	24 ± 4	27 ± 4	222 ± 47	3 ± 0	7 ± 1	ND	4 ± 0	ND	21 ± 3
nectarine	517 ± 58	95 ± 21	158 ± 11	85 ± 10	14 ± 1	104 ± 16	0.2 ± 0	30 ± 5	19 ± 5	5 ± 0
pear	128 ± 3	6 ± 1	25 ± 4	12 ± 6	1 ± 0	8 ± 1	0.2 ± 0	15 ± 2	13 ± 2	4 ± 1
apple	155 ± 30	4 ± 1	17 ± 11	2 ± 0	1 ± 0	14 ± 0	1 ± 1	5 ± 1	16 ± 2	1 ± 0
grape	77 ± 10	55 ± 2	57 ± 3	1007 ± 32	4 ± 0	172 ± 17	1 ± 1	47 ± 9	33 ± 11	51 ± 12
kiwi fruit	96 ± 2	37 ± 3	27 ± 3	19 ± 1	9 ± 1	36 ± 0	3 ± 0	27 ± 3	19 ± 2	38 ± 3
strawberry	114 ± 6	52 ± 1	107 ± 2	3 ± 0	9 ± 1	144 ± 8	3 ± 0	18 ± 1	7 ± 1	3 ± 0

	amino acid content, mg/L of juice									
juice	tyrosine	methionine	phenyl-alanine	trypto-phan	β-alanine	γ-amino-*n*-butyric	ethanol-amine	*O*-phospho-L-serine	taurine	*O*-phospho-ethanolamine
prune DP	12 ± 0	0.4 ± 0	31 ± 2	7 ± 1	3 ± 0	101 ± 10	3 ± 1	24 ± 6	110 ± 22	79 ± 5
prune D	34 ± 5	ND	28 ± 1	ND	ND	88 ± 5	2 ± 1	ND	118 ± 14	96 ± 4
prune C	14 ± 4	ND	19 ± 3	ND	ND	67 ± 7	1 ± 0	ND	155 ± 12	171 ± 23
prune FJ	27 ± 7	3 ± 4	78 ± 1	6 ± 1	12 ± 0	738 ± 10	5 ± 0	15 ± 0	16 ± 0	5 ± 0
prune UC	18 ± 3	ND	31 ± 4	12 ± 3	10 ± 2	238 ± 57	6 ± 0	6 ± 0	ND	ND
plum	4 ± 0	0.4 ± 0	27 ± 2	8 ± 1	4 ± 1	33 ± 9	4 ± 1	3 ± 0	ND	ND
peach	9 ± 1	0.6 ± 0	27 ± 4	7 ± 3	7 ± 1	37 ± 3	NR	3 ± 0	NR	2 ± 0
cherry	1 ± 0	0.1 ± 0	1 ± 0	62 ± 5	1	37 ± 5	ND	13 ± 1	ND	ND
nectarine	4 ± 0	0.3	15 ± 1	14	5 ± 0	39 ± 4	1 ± 0	5 ± 1	NR	ND
pear	1 ± 0	ND	5 ± 0	8 ± 2	–	–	–	–	–	–
apple	ND	0.3 ± 0	1 ± 0	4 ± 2	–	–	–	–	–	–
grape	26 ± 4	12 ± 3	21 ± 4	45 ± 4	–	–	–	–	–	–
kiwi fruit	11 ± 1	6 ± 1	26 ± 2	34 ± 1	–	–	–	–	–	–
strawberry	4 ± 0	2 ± 0	3 ± 0	18 ± 1	–	–	–	–	–	–

	amino acid content, mg/L of juice									
juice	α-amino-adipic	citruline	glutamine	cysteine	lysine	histidine	arginine	hydroxy-proline	ornithine	1-methyl-L-histidine
prune DP	4 ± 0	37 ± 5	3	4 ± 0	2 ± 0	14 ± 0	2 ± 0	NR	25 ± 16	25
prune D	ND	42 ± 4	3 ± 0	–	–	–	–	–	–	–
prune C	ND	42 ± 2	–	–	–	–	–	–	–	–
prune FJ	4 ± 0	4 ± 3	43 ± 2	76 ± 8	–	–	–	–	–	–
prune UC	5 ± 0	ND	95 ± 23	27 ± 2	–	–	–	–	–	–
plum	10 ± 3	ND	55 ± 3	55 ± 4	2 ± 0	18 ± 2	1 ± 0	2 ± 0	28 ± 7	30 ± 3
peach	6 ± 1	ND	223 ± 48	53 ± 7	3 ± 0	28 ± 3	1 ± 0	8 ± 1	47 ± 10	26 ± 2
cherry	10 ± 1	7 ± 1	168 ± 18	90 ± 4	1 ± 0	40 ± 5	2 ± 0	2 ± 0	11 ± 0	ND
nectarine	ND	15	207 ± 71	86 ± 8	2 ± 0	34 ± 7	1 ± 0	6 ± 1	13 ± 1	ND
pear	–	–	–	38 ± 2	2 ± 0	11 ± 4	0.3 ± 0	–	–	–
apple	–	–	–	1 ± 0	1 ± 0	12 ± 0	1 ± 0	–	–	–
grape	–	–	–	23 ± 1	4 ± 0	50 ± 2	592 ± 15	–	–	–
kiwi fruit	–	–	–	46 ± 2	19 ± 1	41 ± 2	50 ± 8	–	–	–
strawberry	–	–	–	ND	1 ± 0	15 ± 3	8 ± 3	–	–	–

[a] For description of prune juices, see footnote for Table II. [b] Mean ± standard deviation, $n = 3$; if no SD is indicated, $n = 1$. [c] ND, not detected; NR, not resolvable; –, not determined.

tarate) compared to that of any of the other fruit juices (data not shown). The composition of individual phenolics of prune DP is compared with that of the other fruit juices (Figure 1). Catechin was present in all fruits and was the only phenolic compound found in kiwi fruit. Chlorogenic acid was present in all fruits except grape and kiwi fruit. The absence of (−)-epicatechin distinguished prune DP from apple, cherry, nectarine, pear, and plum juices. With respect to the six phenolics for which we assayed, peach had about equal or lower concentrations of phenolics than prune. Strawberry juice was very similar to prune juice in phenolic composition. On the basis of phenolic composition, mixing prune juice with peach or strawberry juice would be difficult to detect. Phloridzin appeared to be present in apple, pear, and fresh, but not processed, prune juice (Table III). However, phloridzin has been confirmed only in the fruit of *Malus* species (Macheix et al., 1990). Another dihydrochalcone probably accounts for the finding in pear and prune. Our results are in general agreement with the findings of Van Buren (1970), Mösel and Herrmann (1974), and Möller and Herrmann (1983). The latter authors also identified neochlorogenic acid and 3′-*p*-coumaroylquinic acid in some pome and stone fruits.

Compared to 1988 (Figure 1), we found 50% more catechin, 200% more chlorogenic acid, and large amounts of caffeic acid in the juice from dried prunes in 1989 (Table III). Caffeic acid is a degradation product of chlorogenic as well as neochlorogenic acid, the two most predominant phenols in prune juice. The amount of neochlorogenic acid was approximately 6 times higher in fresh prune juice (prune FJ) compared to that in any of the processed prune juices (data not shown). One possible limitation of the

Table V. Anthocyanins Detected in Fruit Juices Tested

juice	anthocyanin identification[a]	anthocyanin peak area[b]
apple	cyanidin 3-arabinoside	22 ± 6
	cyanidin 7-arabinoside or cyanidin 3-glucoside	27 ± 15
	cyanidin 3-galactoside	260 ± 69
cherry	cyanidin 3-glucoside	189 ± 40
	cyanidin 3-rutinoside	1320 ± 109
	peonidin 3-rutinoside	47 ± 36
grape	cyanidin 3-glucoside	121 ± 33
	delphinidin 3-glucoside	586 ± 110
	malvidin 3-glucoside	2157 ± 375
	peonidin 3-glucoside	478 ± 92
nectarine	cyanidin 3-glucoside	322 ± 51
peach	cyanidin 3-glucoside	180 ± 43
plum	cyanidin 3-glucoside	42 ± 5
strawberry	cyanidin 3-glucoside	70 ± 18
	pelargonidin 3-glucoside	1302 ± 29
	pelargonidin 3-glycoside	78 ± 9

[a] Tentative identification based on retention times and spectral characteristics. Results were compared with those reported by Gross (1987), Hebrero et al. (1988), Hrazdina (1982), Timberlake (1980), Timberlake and Bridle (1982), and Van Buren (1970). [b] Mean ± standard deviation, $n = 3$.

use of phenolic composition data for the determination of the authenticity of prune juice would be the change in phenolic composition by gelatin fining of fruit juices. This can account for the disappearance of up to 50% of the phenols (Bannach, 1984). A second limitation is the variable effect of processing on the phenolic composition of the other juices. The difference in phenolic composition between fresh prune juice FJ and UC (Table III) may be due to some heating and/or prolonged extraction in preparing the FJ sample.

Free Amino Acids. All processed prune juices had high concentrations of citrulline, α-amino-*n*-butyric acid, *O*-phosphoethanolamine, and taurine (Table IV). Prune FJ and prune UC and the juices of the other fruits tested had very small or nondetectable amounts of these amino acids. Threonine, serine, proline, valine, isoleucine, and γ-aminobutyric acid were lower in processed prune juices than in prune FJ and prune UC. Prune DP was much lower in cysteine and glutamine contents than prune FJ, prune UC, and juices of cherry, nectarine, peach, and plum fruits. All prune juices were higher in γ-aminobutyric acid content than the juices of cherry, nectarine, peach, and plum. The prune juices were lower in leucine, methionine, and tryptophan than juices of both kiwi fruit and grape. Cherry juice was relatively high in tryptophan. Grape juice had the highest arginine and proline contents among all fruits included in this study. To avoid the Maillard browning reaction, which occurs when amino acids and sugars are heated together as in the preparation of fruit juice concentrates, cation exchange of amino acids is sometimes allowed. This could alter the amino acid profile of a juice and therefore would reduce the value of amino acid analysis for the determination of juice authenticity (Wrolstad et al., 1981). Glutamic acid and asparagine account for the majority of free amino acids in fruit juice but were not separable by the method used.

Anthocyanins. The anthocyanin composition of the juices of apple, cherry, grape, nectarine, peach, plum, and strawberry is shown in Table V. All of the prune juices and those of kiwi fruit and pear had only trace or nondetectable levels of anthocyanins (data not shown). Therefore, the presence of anthocyanins in prune juice would be a clear mark of adulteration. Complexation of phenolic compounds and/or anthocyanins during processing is probably responsible for the brown color of prune juice.

This effect of processing on the anthocyanin composition is variable (Raynal and Moutounet, 1989). Oxygen and high temperatures are important factors in the degradation of anthocyanins. Also, HMF, furfural, and sugar degradation products accelerate the degradation of anthocyanins (Markakis et al., 1957; Meschter, 1953). A mechanism of anthocyanin degradation in which quinones are formed through oxidation of phenols (especially neochlorogenic acid) plays an important role as described by Raynal and Moutounet (1989). Degradation is enhanced by heat.

Consequently, the small amounts of anthocyanins present in fresh prunes disappear during processing. The amounts of anthocyanins in fresh prunes were too small to allow characterization by means of UV absorption spectra.

Conclusion. Cultivar, cultural practices, season, maturity at harvest, storage conditions, and processing procedures all could affect the fruit juice composition. Cultivar and cultural practices appear to affect the pool of free amino acids only to a small extent (Fernandez-Flores et al., 1970). Sugars are least sensitive to genotypic, geographic, and seasonal variation (Wrolstad and Shallenberger, 1981). Bearing these limitations in mind, adulteration of prune juice with the following fruit juices or sugar syrups can be established:

	presence of	absence or reduced amounts of
apple	high fructose to glucose ratio	quinic acid
cherry	(−)-epicatechin; high tryptophan concentration; cyanidin glycosides	quinic acid; γ-aminobutyric acid
grape	tartaric acid; caffeoyltartaric acid; high tryptophan, arginine, and/or proline concentration; anthocyanins	quinic acid; chlorogenic acid
kiwi fruit	citric acid; high tryptophan concentration	phenolic compounds
nectarine	citric acid; cyanidin 3-glucoside	γ-aminobutyric acid
peach	citric acid; cyanidin 3-glucoside	γ-aminobutyric acid
pear	high glucose to fructose ratio	
plum	cyanidin 3-glucoside	γ-aminobutyric acid
strawberry	citric acid; pelargonidin 3-glucoside	
sugar syrups	C4 sugars and altered sugar profile	

ACKNOWLEDGMENT

Financial support was provided, in part, by the California Prune Advisory Board. We gratefully acknowledge the technical assistance of Chic Nishijima and the late Alec Chordas. We thank Vernon Singleton and Eugene Trousdale for their assistance with the anthocyanin analyses; Quinton Rogers, Stepanie Lee, and Daniel Wong for their help with the amino acid analyses; and Douglas Adams and Vernon Singleton for reviewing the manuscript.

LITERATURE CITED

Bannach, W. Food gelatin in the beverage industries—an important help in juice and wine fining. *Confructa* **1984**, *28* (3), 198–206 (in German).

Eheart, J. F.; Mason, B. S. Sugar and Acid in the Edible Portion of Fruits. *J. Am. Diet. Assoc.* **1967**, *50*, 130–133.

Fernandez-Florez, E.; Kline, D. A.; Johnson, A. R.; Leber, B. L. Quantitative and Qualitative GLC Analysis of Free Amino Acids in Fruits and Fruit Juices. *J. Assoc. Off. Anal. Chem.* **1970**, *53*, 1203–1208.

Fitelson, J. Detection of Adulteration in Fruit Juices by Qualitative Determination of Carbohydrates by Gas-Liquid chromatography. *J. Assoc. Off. Anal. Chem.* **1970**, *53*, 1193–1197.

Flynn, C.; Wendt, A. S. Sugars in Prune Juice by GLC Separation of Trimethylsilylated Derivatives. *J. Assoc. Off. Anal. Chem.* **1970**, *53*, 1067–1070.

Gross, J. *Pigments in Fruit*; Academic Press: New York, 1987; pp 59–85.

Hebrero, E.; Santos-Buelga, C.; Rivas-Gonzalo, J. C. High Performance Liquid Chromatography-diode Array Spectroscopy Identification of Anthocyanins of Vitis Vinifera Variety Tempranillo. *Am. J. Enol. Vitic.* **1988**, *39*, 227–233.

Henning, W.; Herrmann, K. Flavonol Glycosides of Plums of the Species Prunus domestica L. and Prunus salicina Lindley 12. Phenolics of Fruits. *Z. Lebensm. Unters. Forsch.* **1980**, *171*, 111–118.

Hrazdina, G. Anthocyanins. In *The flavonoids*; Harborne, J. B., Mabry, T. J., Eds.; Chapman and Hall: London, 1982; pp 135–188.

Ishii, Y. Sugar Components of Some Dry Fruits. *J. Jpn. Soc. Nutr. Food Sci.* **1983**, *36*, 53–55.

Kline, D. A.; Fernandez-Florez, E.; Johnson, A. R. Quantitative Determination of Sugars in Fruits by GLC Separation of TMS Derivatives. *J. Assoc. Off. Anal. Chem.* **1970**, *53*, 1198–1202.

Krueger, D. A.; Krueger, R. G.; Krueger, H. W. Carbon isotope ratios of various fruits. *J. Assoc. Off. Anal. Chem.* **1986**, *69*, 1035–1036.

Luh, B. S. Nectar, pulpy juices and fruit juice blends in fruit and vegetable processing technology. In *Fruit and Vegetable Juice Processing Technology*, 3rd ed.; Nelson, P. E., Tressler, D. K., Eds.; AVI: Westport, CT, 1980; pp 471–476.

Macheix, J.-J.; Fleuriet, A.; Billot, J. *Fruit Phenolics*; CRC Press: Boca Raton, FL, 1990; p 80.

Markakis, P.; Livingston, G. E.; Fellers, C. R. Quantitative aspects of strawberry pigments degradation. *Food Res.* **1957**, *22*, 117–130.

Meschter, E. E. Effects of carbohydrates and other factors on strawberry products. *J. Agric. Food Chem.* **1953**, *1*, 574–579.

Möller, B.; Herrmann, K. Quinic Acid Esters of Hydroxycinnamic Acids in Stone and Pome Fruits. *Phytochemistry* **1983**, *22*, 477–481.

Mösel, H. D.; Herrmann, K. The Phenolics of Fruits III. The Contents of Catechins and Hydroxycinnamic Acids in Pome and Stone Fruits. *Z. Lebensm. Unter. Forsch.* **1974**, *154*, 6–11.

Pollard, A.; Timberlake, C. F. Fruit Juices. In *The Biochemistry of Fruits and Their Products*; Hulme, A. C., Ed.; Academic Press: New York, 1971; Vol. 2, pp 573–621.

Raynal, J.; Moutounet, M. Intervention of Phenolic Compounds in Plum Technology. 2. Mechanisms of Anthocyanin Degradation. *J. Agric. Food Chem.* **1989**, *37*, 1051–1053.

Reyes, F. G. R.; Wrolstad, R. E.; Cornwell, C. J. Comparison of Enzymic, Gas-Liquid Chromatographic, and High Performance Liquid Chromatographic Methods for Determining Sugars and Organic Acids in Strawberries at Three Stages of Maturity. *J. Assoc. Off. Anal. Chem.* **1982**, *65*, 126–131.

Timberlake, C. F. Anthocyanins-Occurrence, Extraction and Chemistry. *Food Chem.* **1980**, *5*, 69–80.

Timberlake, C. F.; Bridle, P. Distribution of Anthocyanins in Food Plants. In *Anthocyanins as Food Colors*; Markakis, P., Ed.; Academic Press: New York, 1982; pp 125–162.

Van Buren, J. Fruit Phenolics. In *The Biochemistry of Fruits and Their Products*; Hulme, A. C., Ed.; Academic Press: New York, 1970; Vol. 1, pp 269–300.

Williams, M.; Hrazdina, G.; Wilkinson, M. M.; Sweeny, J. G.; Iacobucci, G. A. High-pressure Liquid Chromatographic Separation of 3-Glucosides, 3,5-Diglucosides, 3-(6-O-p-Coumaryl)Glucosides and 3-(6-O-p-Coumarylglucoside)-5-Glucosides of Anthocyanidins. *J. Chromatogr.* **1978**, *155*, 389–398.

Wrolstad, R. E.; Shallenberger, R. S. Free Sugar and Sorbitol in Fruits—A Compilation From the Literature. *J. Assoc. Off. Anal. Chem.* **1981**, *64*, 91–103.

Wrolstad, R. E.; Cornwell, C. J.; Culbertson, J. D.; Reyes, F. G. R. Establishing Criteria for Determining the Authenticity of Fruit Juice Concentrates. In *Quality of Selected Fruits and Vegetables of North America*; Teranishi, R., Barrera-Benitez, H., Eds.; ACS Symposium Series 170; American Chemical Society: Washington, DC, 1981; pp 77–91.

Wulf, L. W.; Nagel, C. W. High-pressure Liquid Chromatographic Separation of Anthocyanins of Vitis vinifera. *Am. J. Enol. Vitic.* **1978**, *29*, 42–49.

Received for review February 13, 1992. Accepted February 21, 1992.

Registry No. HMF, 67-47-0; sucrose, 57-50-1; glucose, 50-99-7; fructose, 57-48-7; sorbitol, 50-70-4; (+)-catechin, 154-23-4; chlorogenic acid, 327-97-9; phloridzin, 60-81-1; caffeic acid, 331-39-5; aspartic acid, 56-84-8; threonine, 72-19-5; serine, 56-45-1; proline, 147-85-3; glycine, 56-40-6; alanine, 56-41-7; α-aminobutyric acid, 80-60-4; valine, 72-18-4; isoleucine, 73-32-5; leucine, 61-90-5; α-aminoadipic acid, 542-32-5; citrulline, 372-75-8; glutamine, 56-85-9; cysteine, 52-90-4; lysine, 56-87-1; histidine, 71-00-1; arginine, 74-79-3; hydroxyproline, 51-35-4; ornithine, 70-26-8; 1-methyl-L-histidine, 332-80-9; (−)-epicatechin, 490-46-0; ferulic acid, 1135-24-6; cyanidin 3-arabinoside, 27214-72-8; cyanidin 3-galactoside, 27214-71-7; cyanidin 3-glucoside, 7084-24-4; cyanidin 3-rutinoside, 18719-76-1; peonidin 3-rutinoside, 27539-32-8; delphinidin 3-glucoside, 6906-38-3; malvidin 3-glucoside, 7228-78-6; peonidin 3-glucoside, 6906-39-4; pelargonidin 3-glucoside, 18466-51-8; citric acid, 77-92-9; ascorbic acid, 50-81-7; malic acid, 6915-15-7; quinic acid, 77-95-2; tartaric acid, 87-69-4; tyrosine, 60-18-4; methionine, 63-68-3; phenylalanine, 63-91-2; tryptophan, 73-22-3; β-alanine, 107-95-9; γ-aminobutyric acid, 56-12-2; ethanolamine, 75-04-7; taurine, 107-35-7; *O*-phospho-L-serine, 407-41-0; *O*-phosphoethanolamine, 1071-23-4.