HPLC−DAD−ESIMS Analysis of Phenolic Compounds in Nectarines, Peaches, and Plums

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The phenolic compounds of 25 peach, nectarine, and plum cultivars were studied and quantified by HPLC−DAD−ESIMS. Hydroxycinnamates, procyanidins, flavonols, and anthocyanins were detected and quantified. White and yellow flesh nectarines and peaches, and yellow and red plums, were analyzed at two different maturity stages with consideration of both peel and flesh tissues. HPLC−MS analyses allowed the identification of procyanidin dimers of the B- and A-types, as well as the presence of procyanidin trimers in plums. As a general rule, the peel tissues contained higher amounts of phenolics, and anthocyanins and flavonols were almost exclusively located in this tissue. No clear differences in the phenolic content of nectarines and peaches were detected or between white flesh and yellow flesh cultivars. There was no clear trend in phenolic content with ripening of the different cultivars. Some cultivars, however, had a very high phenolic content. For example, the white flesh nectarine cultivar Brite Pearl (350−460 mg/kg hydroxycinnamates and 430−550 mg/kg procyanidins in flesh) and the yellow flesh cv. Red Jim (180−190 mg/kg hydroxycinnamates and 210−330 mg/kg procyanidins in flesh), contained 10 times more phenolics than cultivars such as Fire Pearl (38−50 mg/kg hydroxycinnamates and 23−30 mg/kg procyanidins in flesh). Among white flesh peaches, cultivars Snow King (300−320 mg/kg hydroxycinnamates and 660−695 mg/kg procyanidins in flesh) and Snow Giant (125−130 mg/kg hydroxycinnamates and 520−540 mg/kg procyanidins in flesh) showed the highest content. The plum cultivars Black Beaut and Angeleno were especially rich in phenolics.

Keywords: *Nectarine; peach; plum; Prunus persica; P. salicina; Rosaceae; phenolics; polyphenols; flavan-3-ols, hydroxycinnamates; flavonols; anthocyanins; HPLC−MS*

INTRODUCTION

Fruit phenolic compounds are relevant in terms of quality, as they have a role in the visual appearance (pigmentation and browning), taste (astringency), and health-promoting properties (free-radical scavengers) of different fruit products (*1*). Epidemiological studies have pointed out that regular consumption of fruits and vegetables imparts health benefits (*2*−*7*), and governmental institutions have recommended minimum daily intakes of fruits and vegetables because of their health-promoting properties. The health benefits related to fruit consumption seem to be related, at least partly, to the content of antioxidant phenolic metabolites. Therefore, there has been a renewed interest in the evaluation of the phenolic content of fruits.

Information available about the phenolic content of fruits is not always complete, and many times is restricted to few cultivars and to a single group of phenolic compounds. Previous work has been reported on peach flavonols (*8*), anthocyanins (*9*), catechins (*10*), and hydroxycinnamates (*11*), and plum flavonols (*12*), catechins (*13*), and hydroxycinnamates (*11*). The data reported, however, are quite limited by the small sample size, the small number of cultivars analyzed, and the phenolic compounds quantified (mainly related to hydrolysis products). To the best of our knowledge, there is no information available about nectarine phenolics.

The aim of the present work was to identify and quantify individual phenolic compounds (Figure 1) in peaches (white flesh and yellow flesh cultivars), nectarines (white flesh and yellow flesh cultivars), and plums (yellow and red) grown in California, at two maturity stages, and comparing peel and flesh tissues.

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MATERIALS AND METHODS

Fruits. All stone fruit cultivars used were obtained from packinghouses in the Fresno area of California between June 2 and September 7, 1999, and transported in an air-conditioned car (for about 3 to 4 h) to Davis. Half the fruits were sampled upon arrival at the Department of Pomology, Postharvest Laboratory, at the University of California, Davis, and the other half were ripened at 20 °C for 5 days before sampling. In each case, 5 replicates of 10 fruits each were selected. The fruit were then peeled and four wedges were cut vertically from each side of each fruit. The flesh and peel were frozen separately in liquid nitrogen and kept at −80 °C until analyzed. At analysis, the frozen fruit was ground to a fine powder in liquid nitrogen before sampling to ensure uniformity. Only 3 of the 5 frozen replicates were analyzed; the other

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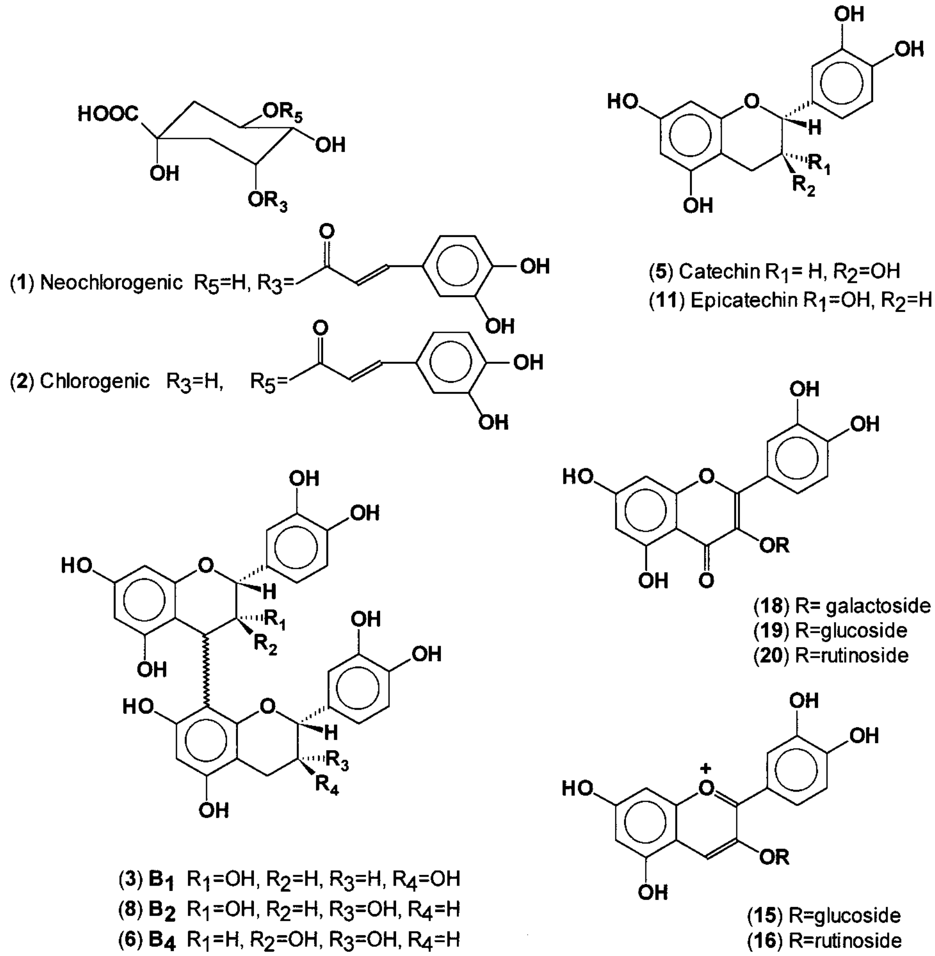

Figure 1. Chemical Structures.

Table 1. Ranges of Maturity and Quality Indices of Stone Fruits Used in This Study at Harvest (Mature) and after Ripening for 5 days at 20 °C (Ripe).

stone fruit	stage	skin color ("a" value)	flesh firmness (Newtons)	soluble solids (%)	titratable acidity (%)	pH
yellow-flesh peaches	mature	0.8−24.4	52.5−74.3	10.1−12.0	0.53−0.97	3.6−3.7
	ripe	5.3−26.6	8.5−19.1	11.2−12.9	0.45−0.87	3.5−3.8
white-flesh peaches	mature	7.1−25.0	28.9−69.8	8.9−13.1	0.15−0.34	4.2−5.0
	ripe	8.9−27.0	5.3−15.6	9.3−13.3	0.13−0.31	4.3−5.0
yellow-flesh nectarines	mature	13.1−30.2	45.4−60.9	11.2−14.8	0.66−1.16	3.5−3.8
	ripe	5.0−29.5	7.1−27.6	11.2−15.3	0.51−1.01	3.6−3.9
white-flesh nectarines	mature	2.6−12.9	51.2−85.0	11.3−13.6	0.31−0.47	3.6−4.2
	ripe	11.5−19.1	13.8−28.0	12.0−14.5	0.28−0.46	3.9−4.3
plums	mature	9.9−13.8	24.5−52.5	9.9−13.8	0.36−1.09	3.5−3.7
	ripe	10.4−14.3	7.6−19.6	10.4−14.3	0.31−0.55	3.6−3.8

2 replicates were to be used only if the extent of variability was excessive among the 3 replicates, which was not found to occur.

For each cultivar, 10 fruit were evaluated initially (harvest maturity) and after 5 days at 20 °C (ripe) for the following maturity and quality indices: skin color (by a Minolta colorimeter), flesh firmness (by a fruit penetrometer with an 8-mm tip), soluble solids content (by a refractometer), titratable acidity (by an automatic titration system), and pH (by a pH meter). The ranges of these indices for each group of stone fruit cultivars are shown in Table 1.

Extraction of Phenolic Compounds. The frozen fruit material (5g) was homogenized in a Polytron (2 min on ice) with 10 mL of extraction solution (water/methanol 2:8 containing 2 mM NaF to inactivate polyphenol oxidases and prevent phenolic degradation due to browning). Homogenates were kept in ice until centrifuged (11500 rpm, 15 min, 2−5 °C, 16000*g*); the supernatant was recovered carefully to prevent contamination with the pellet, and the volume was measured. A 1-mL portion of this extract was filtered through a 0.45-μm filter (Osmonics/MSI Cameo Nylon Filters, Fisher Scientific, Los Angeles, CA) and directly analyzed by HPLC after a period not exceeding 24 h. This extraction procedure recovers 85% of the total soluble anthocyanins, 86% of the hydroxycinnamates and flavonols, and 92% of the procyanidins present in the different plum tissues; phenolic recoveries are even higher in peach and nectarine. A second extraction completed phenolic extraction, as only traces were detected in a third extraction under the same conditions. A second extraction was, however, considered inconvenient because of sample dilution, requiring further concentration that would render the technique less straightforward.

HPLC−DAD Analyses. Samples of 20 μL of extracts were analyzed using an HPLC system (Hewlett-Packard 1050 pump) coupled with a photodiode array detector (DAD) (Series 1040M, Series II) and an autosampler (Series 1050), operated by HP ChemStation software. A reversed-phase C_{18} Nucleosil

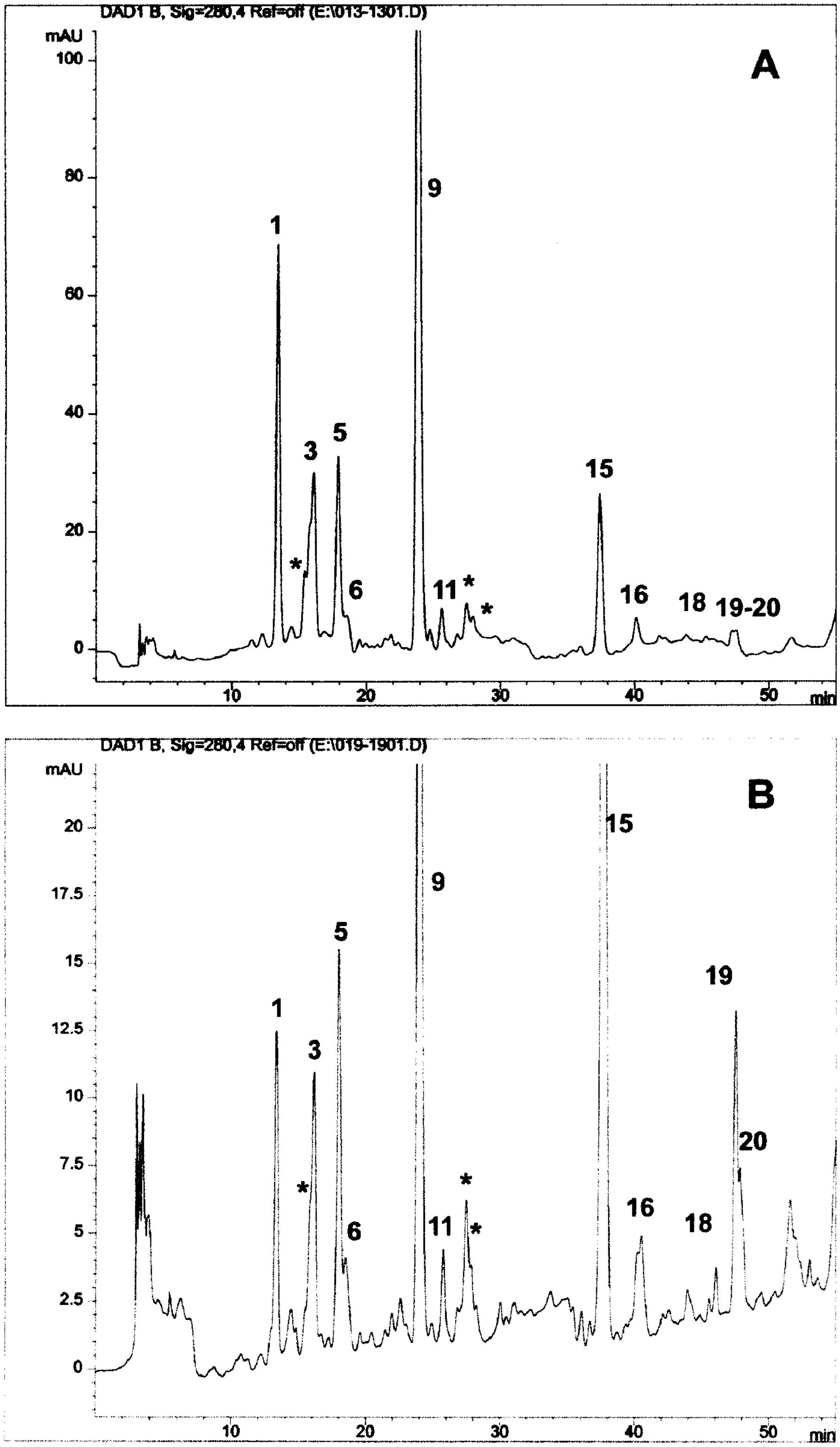

Figure 2. HPLC chromatograms of Brite Pearl cv. nectarine peel extract (**A**) and Summer Sweet cv. peach peel extract (**B**). (**1**) neochlorogenic acid (3-*O*-caffeoyl-quinic); (**3**) procyanidin B1; (**5**) catechin; (**6**) procyanidin B4; (**9**) chlorogenic acid (5-*O*-caffeoyl-quinic); (**11**) epicatechin; (**15**) cyanidin 3-glucoside; (**16**) cyanidin 3-rutinoside; (**18**) quercetin 3-galactoside (tentative); (**19**) quercetin 3-glucoside; and (**20**) quercetin 3-rutinoside; (*) unidentified procyanidins.

column (150 × 4.6 mm i.d.; particle size 5 μm) (MetaChem Technologies, Inc. Torrance, CA) with a guard column containing the same stationary phase (Safeguard holder 5001-CS) was used. Four pumps (A, B, C, and D) were used for mixing the mobile phase to avoid pressure fluctuations due to the mixing of methanol (MeOH) in water. Formic acid (5%) was added to both water and methanol to increase peak resolution before preparing the following mobile phases: 95% water + 5% methanol (A); 88% water + 12% MeOH (B); 20% water + 80% MeOH (C); and MeOH (D). All solvents were HPLC grade. Elution started with 100% A, which remained isocratic until 5 min. A gradient was then used to reach 100% B at 10 min, held isocratic for 3 more minutes. From 13 to 35 min a linear gradient was used to reach 75% B and 25% C, and then 50% B and 50% C at 50 min, and 100% C at 52 min, then maintained isocratic until 57 min. The column was then washed with 100% D at 60 min. The flow rate was 1 mL/min and chromatograms were recorded at 510, 340, and 280 nm.

Table 2. HPLC–DAD and HPLC–ESIMS of Stone Fruit Phenolics

phenolic	no.	Rt HPLC (min)	HPLC–UV–DAD (nm)	HPLC–ESIMS (*m/z*)
Hydroxycinnamates				
neochlorogenic	**1**	13.7	332, 295sh	353, 179
chlorogenic	**9**	24.5	332, 295sh	353, 179
unidentified	**14**	33.8	332, 295sh	335, 287, 179
Flavan 3-ols				
procyanidin dimer	**2**	15.2	280	577, 425, 289
procyanidin B1	**3**	17.1	280	577, 425, 289, 287
procyanidin trimer	**4**	17.9	280	865, 577, 289
catechin	**5**	18.5	280	289
procyanidin B4	**6**	19.1	280	577, 425, 289
procyanidin trimer	**7**	22.5	280	865, 577, 289
procyanidin B2	**8**	23.7	280	577, 425, 407, 289
procyanidin A type dimer	**10**	25.9	280	575, 449, 287, 285
epicatechin	**11**	26.1	280	289
procyanidin A type dimer	**12**	28.1	280	575, 423, 287, 285
procyanidin dimer	**13**	29.4	280	577, 425, 289
Flavonols				
quercetin pentosyl hexoside	**17**	45.4	355, 254	595, 433, 300
quercetin 3- galactoside	**18**	46.5	355, 254	463, 300
quercetin 3-glucoside	**19**	48.5	355, 254	463, 301
quercetin 3-rutinoside	**20**	48.8	355, 254	609, 301
quercetin pentosyle-pentoside	**21**	49.5	355, 254	565, 300
quercetin 3-xyloside	**22**	50.7	355, 254	433, 301
quercetin 3-rhamnoside	**24**	51.9	355, 254	447, 301
Anthocyanins				
cyanidin 3-galactoside	-	36.6	520, 280	447, 284
cyanidin 3-glucoside	**15**	38.5	520, 280	447, 284
cyanidin 3 rutinoside	**16**	41.8	520, 280	593, 284
cyanidin 3-acetylglucoside	**23**	51.5	520, 280	489, 284

The UV spectra of the different compounds were recorded with a diode array detector.

HPLC–MS Analyses. Electrospray mass spectrometric analyses were performed in the negative mode using a Hewlett-Packard 5989A quadrupole instrument equipped with an electrospray interface (HP 59987A). Nitrogen was used as a nebulizing gas at a pressure of 50 psi and a temperature of 300 °C. Column and chromatographic conditions were the same as those used for the HPLC–DAD analyses.

Identification and Quantification of Phenolic Compounds. The phenolic compounds in stone fruit extracts were identified by their UV spectra, recorded with a diode-array-detector, and HPLC–MS (electrospray), and, wherever possible, by chromatographic comparisons with authentic markers. Individual anthocyanins were quantified by comparisons with an external standard of cyanidin 3-rutinoside (Apin Chemicals Ltd., Oxon, UK) at 510 nm; flavonols as quercetin 3-rutinoside at 340 nm; hydroxycinnamic acid derivatives as chlorogenic acid at 340 nm; and flavan 3-ols as catechin at 280 nm (all these markers were from Sigma, St. Louis, MO). Concentrations were expressed as mg/kg fresh weight. Repeatability of the analyses was ± 5%.

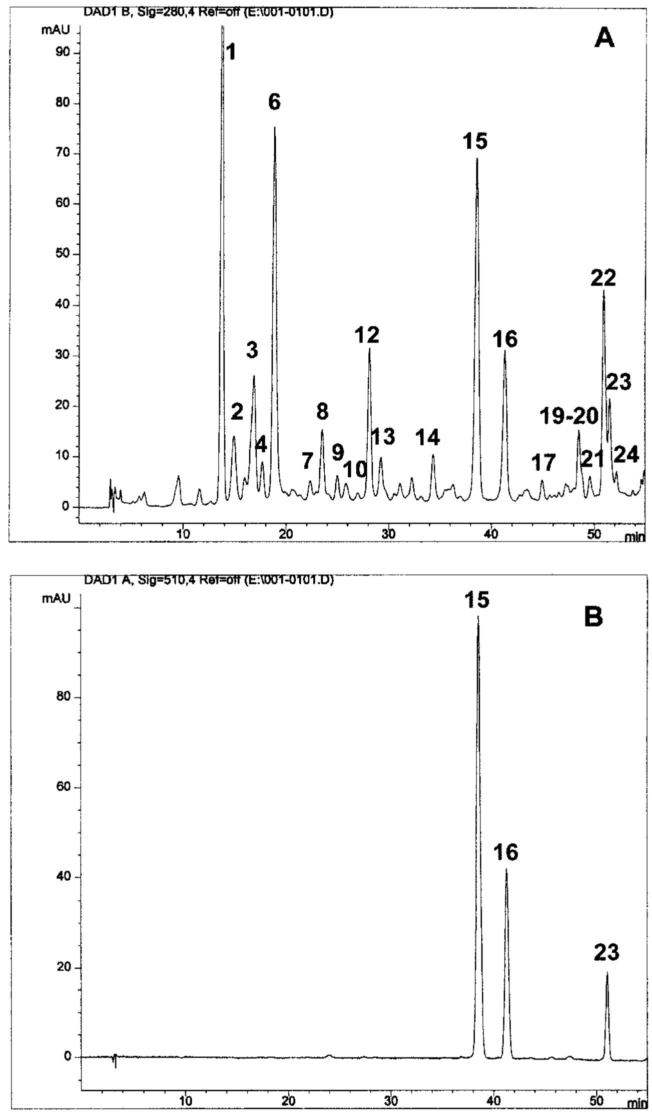

Figure 3. HPLC chromatograms of Black Beaut cv. plum extracts recorded at 280 nm (**A**) and 510 nm (**B**). (**1**) neochlorogenic acid; (**2**) procyanidin dimer; (**3**) procyanidin B1; (**4**) procyanidin trimer; (**6**) procyanidin B4; (**7**) procyanidin trimer; (**8**) procyanidin B2; (**9**) chlorogenic acid; (**10**) procyanidin dimer A-type; (**12**) procyanidin dimer A-type; (**13**) procyanidin dimer; (**14**) unidentified caffeic acid derivative; (**15**) cyanidin 3-glucoside; (**16**) cyanidin 3-rutinoside; (**17**) quercetin hexoside–pentoside; (**19–20**) quercetin 3-glucoside + 3-rutinoside; (**21**) quercetin pentoside–rhamnoside; (**22**) quercetin xyloside; (**23**) cyanidin 3-acetyl-glucoside (tentative); and (**24**) quercetin 3-rhamnoside.

RESULTS

HPLC–DAD and HPLC–ESIMS Analysis of Stone Fruit Phenolics. In the study of fruit phenolics, the combination of diode array detectors (DAD) and electrospray ionization mass spectrometry detectors (ESIMS) coupled to the HPLC equipment using reversed-phase columns provided a simple and accurate method for the identification and quantification of individual phenolics. The methanol extracts obtained from peel and flesh tissues of different nectarine, peach, and plum cultivars were separated by HPLC, and the UV and MS spectra of the different peaks were recorded. To identify the different phenolics, a number of markers were available, including hydroxycinnamic acid derivatives (chlorogenic acid and green coffee bean extracts), flavan-3-ols (catechin, epicatechin, epigallocatechin, gallocatechin, epigallocatechin gallate, and the dimer procyanidins B1, B2, B4, B7, and C2), flavonols (quercetin 3-glucoside, quercetin 3-rutinoside, and quercetin), and anthocyanins (cyanidin 3-rutinoside and 3-glucoside).

The HPLC–DAD analyses showed that the procyanidin derivatives had a very low response factor, making the quantification of these compounds rather difficult when they are in low concentration. In contrast, the response factor for hydroxycinnamates, flavonols, and anthocyanins was quite good, especially in the specific wavelengths for the different compound types (340 nm for hydroxycinnamates and flavonols and 510 nm for anthocyanins).

Table 3. Hydroxycinnamic Acid Derivatives (mg/kg fresh weight) in White and Yellow Flesh Nectarines (Quantified as Chlorogenic Acid)[a]

cultivar	stage	part	neochlorogenic		chlorogenic		other		total	
			White Flesh Cultivars							
Arctic Star	mature	peel	41.7	(4.3)	338.6	(34.4)	-		380.3	(38.5)
		flesh	30.7	(4.3)	79.1	(15.8)	-		109.8	(19.0)
	ripe	peel	43.2	(3.6)	330.5	(10.8)	12.8	(0.2)	386.5	(11.2)
		flesh	32.6	(1.8)	70.7	(5.7)	-		103.3	(7.2)
Arctic Queen	mature	peel	33.2	(2.9)	176.3	(14.7)	10.4	(0.7)	219.9	(17.0)
		flesh	42.2	(3.9)	85.4	(7.6)	-		127.6	(11.1)
	ripe	peel	48.1	(3.0)	240.5	(4.1)	13.7	(1.7)	302.3	(4.8)
		flesh	44.3	(9.1)	84.4	(19.8)	-		129.0	(28.6)
Arctic Snow	mature	peel	87.0	(18.9)	266.2	(39.3)	8.9	(6.2)	362.2	(54.9)
		flesh	70.3	(17.4)	81.7	(14.3)	-		152.0	(31.6)
	ripe	peel	63.5	(19.0)	189.0	(44.4)	9.9	(6.2)	262.4	(64.4)
		flesh	76.2	(25.7)	90.3	(15.8)	-		166.5	(41.2)
Fire Pearl	mature	peel	21.9	(4.8)	81.1	(16.0)	9.8	(0.5)	112.8	(21.0)
		flesh	14.9	(1.7)	23.1	(3.9)	-		38.0	(5.4)
	ripe	peel	14.8	(1.3)	62.9	(5.8)	-		77.7	(6.9)
		flesh	21.1	(3.8)	29.4	(4.7)	-		50.5	(8.3)
Brite Pearl	mature	peel	124.4	(8.3)	423.5	(10.3)	-		547.9	(17.9)
		flesh	146.9	(19.6)	202.5	(6.7)	-		349.5	(25.4)
	ripe	peel	146.3	(6.2)	580.7	(58.2)	-		727.1	(60.2)
		flesh	183.0	(14.0)	277.1	(25.0)	-		460.1	(28.0)
			Yellow Flesh Cultivars							
Red Jim	mature	peel	63.8	(8.0)	419.5	(76.3)	-		483.1	(84.4)
		flesh	43.4	(4.1)	143.5	(23.5)	-		186.8	(27.6)
	ripe	peel	67.4	(18.1)	362.2	(56.5)	-		429.6	(73.2)
		flesh	48.1	(11.9)	131.8	(30.2)	-		179.9	(41.2)
August Red	mature	peel	67.0	(10.6)	233.1	(13.9)	6.8	(0.2)	306.8	(24.4)
		flesh	59.6	(8.8)	101.8	(8.1)	-		161.5	(16.9)
	ripe	peel	78.8	(9.9)	245.0	(14.6)	5.6	(0.0)	329.3	(23.7)
		flesh	61.9	(13.0)	84.8	(15.7)	-		146.8	(28.7)
Spring Bright	mature	peel	60.1	(6.8)	227.9	(25.3)	19.7	(2.4)	307.7	(34.5)
		flesh	75.1	(15.2)	87.3	(13.2)	-		162.4	(27.1)
	ripe	peel	59.8	(5.3)	241.0	(30.0)	17.0	(2.2)	317.9	(36.8)
		flesh	58.9	(8.0)	84.3	(9.4)	-		143.1	(17.3)
May Glo	mature	peel	24.3	(2.8)	162.1	(19.4)	10.5	(0.2)	196.9	(22.0)
		flesh	23.0	(2.1)	43.7	(4.6)	-		66.7	(6.6)
	ripe	peel	28.2	(3.3)	167.7	(21.8)	9.9	(0.7)	205.7	(25.3)
		flesh	27.3	(1.6)	43.6	(6.8)	-		70.9	(8.2)
September Red	mature	peel	46.6	(13.1)	182.0	(42.2)	10.5	(1.1)	239.1	(56.2)
		flesh	24.0	(4.6)	41.7	(9.1)	-		65.6	(13.6)
	ripe	peel	31.0	(1.2)	106.7	(8.1)	-		137.7	(8.4)
		flesh	24.1	(4.7)	39.0	(5.4)	3.1	(0.7)	66.1	(9.2)

[a] Standard deviations ($n = 3$) in parentheses.

The HPLC−ESIMS analysis of the markers showed that hydroxycinnamates ionized with difficulty under the conditions used, or any other condition that was assayed in this study, showing that the specific sensitivity of the ESIMS detector for this type of compound was smaller than that observed for the other phenolics analyzed. In the case of procyanidins, the dimeric flavan-3-ols ionized better than the monomers (catechin and epicatechin), and as a group ionized much better than the hydroxycinnamates. The ionization of flavonols and anthocyanins was very good.

Nectarines and peaches showed identical phenolic profiles, containing the same individual compounds (Figure 2). The chromatograms recorded at 340 nm showed two main peaks with UV spectra characteristic of caffeic acid derivatives, and with ESIMS spectra as caffeoyl-quinic derivatives (M^+-H, *m/z* 353) The main compound coincided with an authentic marker of chlorogenic acid (5-*O*-caffeoyl-quinic acid), and the secondary compound was identified as neochlorogenic acid (3-*O*-caffeoyl-quinic acid). Other minor compounds with the characteristic spectra of hydroxycinnamic derivatives were detected, but their MS spectra did not allow their identification. In the same chromatogram, three different flavonol peaks were detected. Their UV spectra suggested that they were quercetin derivatives glycosylated at the hydroxyl in the 3 position (*14*). The three flavonols showed the same UV spectrum. Two of the compounds coincided in retention time and UV spectra with those of quercetin 3-glucoside and quercetin 3-rutinoside. The HPLC−MS analysis confirmed these structures, and indicated that the unidentified compound was a quercetin hexoside. Because it eluted with shorter t_R than the glucoside, it was tentatively identified as quercetin 3-galactoside, a compound that had been previously reported in peaches (*8*). In the chromatograms at 280 nm, a number of peaks with UV spectra of flavan-3-ols (maximum at 280 nm) were identified in addition (Figure 2). The main compound of this type was identified as catechin by chromatographic comparison with an authentic marker. In addition, epicatechin was also detected. The dimer procyanidin B1 was also identified by chromatographic comparison with an authentic marker and by its MS spectrum that showed the characteristic fragments at *m/z* 577, 425, and 289 (Table 2) (*15*−*16*). Other minor dimer procyanidins (B4) and other unidentified flavan-3-ols, characterized by the same UV spectrum and the presence of mass ions at *m/z* 289 and 287 were also detected (*15*) (Figure 2). Two anthocyanin pigments were characteristic of the peel of these fruits. They had similar UV−Vis spectra with a maximum around 515 nm in the spectra recorded with the diode-array detector. The main pigment was identified as cyanidin-3-glucoside and the minor one was identified as cyanidin-3-rutinoside. This was confirmed by their ESIMS spectra (Table 2).

The HPLC chromatograms of plum extracts were quite different from those of nectarines and peaches, although they contained the same groups of compounds

Table 4. Flavan 3-ols (mg/kg fresh weight) in White and Yellow Flesh Nectarines (as Catechin)[a]

cultivar	stage	part	catechin	epicatechin	B1	other procyanidins	total
			White Flesh Cultivars				
Arctic Star	mature	peel	76.6 (17.5)	70.9 (14.1)	68.0 (18.9)	10.9 (6.2)	226.4 (36.1)
		flesh	23.7 (3.3)	21.1 (1.9)	-	-	44.8 (3.2)
	ripe	peel	81.1 (6.8)	103.2 (3.5)	67.4 (4.9)	28.1 (3.3)	279.7 (12.7)
		flesh	19.1 (3.7)	31.3 (0.5)	-	-	50.4 (4.0)
Arctic Queen	mature	peel	75.4 (5.3)	57.6 (9.3)	92.1 (16.8)	31.2 (1.8)	256.3 (21.5)
		flesh	47.7 (7.7)	24.4 (4.4)	53.8 (8.7)	-	125.9 (14.0)
	ripe	peel	113.9 (14.8)	84.2 (9.1)	150.2 (26.7)	38.9 (3.2)	387.2 (36.4)
		flesh	50.3 (15.5)	40.1 (4.7)	67.0 (18.2)	-	157.4 (29.6)
Arctic Snow	mature	peel	195.4 (44.4)	85.4 (15.6)	187.7 (29.1)	97.5 (16.8)	566.0 (74.9)
		flesh	77.4 (7.4)	13.2 (1.8)	115.6 (18.7)	-	206.2 (25.2)
	ripe	peel	165.9 (39.0)	82.7 (9.3)	206.3 (75.5)	67.6 (29.3)	522.5 (145.2)
		flesh	93.5) (19.1	30.4 (15.5)	141.6 (28.5)	7.2 (5.6)	272.8 (67.5)
Fire Pearl	mature	peel	24.9 (6.4)	12.4 (1.8)	27.5 (7.6)	28.8 (5.0)	93.5 (20.5)
		flesh	-	31.2 (3.1)	-	-	31.2 (3.1)
	ripe	peel	20.8 (2.5)	16.6 (1.7)	22.0 (3.7)	74.2 (4.9)	133.6 (8.0)
		flesh	-	23.0 (1.5)	-	-	23.0 (1.5)
Brite Pearl	mature	peel	242.1 (15.6)	42.0 (3.4)	315.7 (17.4)	144.2 (17.6)	744.1 (39.1)
		flesh	172.6 (12.3)	17.9 (6.4)	244.9 (12.2)	113.5 (4.0)	551.0 (30.2)
	ripe	peel	350.9 (48.3)	118.8 (13.3)	448.2 (13.8)	187.8 (47.3)	1105.8 (112.1)
		flesh	236.0 (36.1)	49.7 (2.3)	302.0 (30.6)	82.0 (27.5)	433.7 (55.2)
			Yellow Flesh Cultivars				
Red Jim	mature	peel	238.5 (49.4)	128.8 (28.4)	344.7 (89.1)	32.5 (8.9)	744.5 (143.5)
		flesh	84.7 (9.7)	25.2 (3.1)	226.1 (83.2)	-	336.1 (86.0)
	ripe	peel	237.8 (74.6)	110.1 (12.9)	253.0 (44.8)	20.0 (2.5)	621.2 (133.3)
		flesh	81.0 (6.4)	19.2 (14.4)	114.3 (25.6)	-	214.6 (18.8)
August Red	mature	peel	109.6 (4.2)	74.6 (12.8)	125.4 (7.1)	21.6 (2.5)	331.1 (14.1)
		flesh	37.1 (3.5)	35.4 (11.1)	48.5 (2.8)	-	120.9 (12.4)
	ripe	peel	110.2 (6.6)	96.0 (5.4)	102.1 (3.5)	15.9 (8.5)	324.3 (13.9)
		flesh	25.4 (8.3)	56.4 (29.2)	40.9 (15.7)	-	122.7 (45.1)
Spring bright	mature	peel	46.0 (1.6)	101.7 (6.4)	47.1 (14.6)	50.2 (5.1)	186.1 (43.8)
		flesh	23.2 (1.5)	26.7 (1.7)	41.8 (7.3)	-	91.7 (7.7)
	ripe	peel	53.4 (6.4)	22.4 (3.6)	58.3 (26.3)	52.1 (10.7)	186.1 (43.8)
		flesh	24.4 (3.7)	43.8 (7.0)	36.2 (5.4)	-	80.0 (12.3)
May Glo	mature	peel	45.0 (4.7)	83.6 (4.7)	30.6 (2.6)	21.6 (2.0)	180.7 (6.2)
		flesh	20.1 (2.2)	26.5 (2.2)	-	-	46.7 (1.7)
	ripe	peel	44.4 (12.5)	114.1 (3.6)	32.6 (14.3)	23.3 (2.9)	214.4 (27.8)
		flesh	20.9 (4.8)	36.2 (1.6)	14.3 (3.5)	-	71.4 (8.7)
September Red	mature	peel	41.2 (26.0)	68.4 (4.0)	50.7 (20.9)	51.4 (19.0)	211.6 (68.2)
		flesh	-	13.6 (8.2)	-	-	13.6 (8.2)
	ripe	peel	48.9 (4.5)	59.6 (8.5)	19.5 (1.8)	-	128.0 (4.6)
		flesh	-	30.2 (11.8)	-	-	30.2 (11.8)

[a] Standard deviations ($n = 3$) in parentheses.

Table 5. Flavonols (mg/kg fresh weight) in White and Yellow Flesh Nectarines (as Rutin)[a]

cultivar	stage	part	qu 3-gal (tentative)	qu 3-glc	qu 3-rut	total
			White Flesh Cultivars			
Arctic Star	mature	peel	5.4 (0.3)	18.6 (5.0)	23.3 (5.3)	47.3 (10.5)
		flesh	-	-	-	-
	ripe	peel	17.9 (1.7)	24.6 (5.5)	31.1 (5.9)	73.6 (10.0)
		flesh	-	-	-	-
Arctic Queen	mature	peel	2.5 (0.7)	17.6 (1.0)	24.5 (0.5)	44.6 (0.9)
		flesh	4.8 (0.4)	-	-	4.8 (0.4)
	ripe	peel	13.6 (1.5)	19.9 (3.1)	29.3 (4.2)	62.7 (6.4)
		flesh	10.2 (0.3)	-	-	10.2 (0.3)
Arctic Snow	mature	peel	-	26.1 (5.7)	39.9 (8.2)	66.0 (13.8)
		flesh	-	-	-	-
	ripe	peel	4.3 (1.4)	16.7 (5.3)	24.4 (6.5)	45.4 (10.1)
		flesh	10.5 (1.3)	-	-	10.5 (1.3)
Fire Pearl	mature	peel	4.4 (1.2)	13.0 (2.2)	17.9 (2.0)	35.3 (5.1)
		flesh	7.8 (0.5)	-	-	-
	ripe	peel	6.4 (0.4)	12.9 (1.4)	15.1 (0.2)	34.4 (0.9)
		flesh	7.7 (1.7)	-	-	7.7 (1.7)
Brite Pearl	mature	peel	2.2 (1.9)	12.8 (3.3)	17.0 (4.6)	32.0 (7.9)
		flesh	-	-	-	-
	ripe	peel	6.3 (2.7)	20.3 (4.0)	27.2 (5.1)	53.8 (7.4)
		flesh	7.6 (0.6)	-	-	7.6 (0.6)
			Yellow Flesh Cultivars			
Red Jim	mature	peel	5.5 (1.1)	-	114.2 (5.4)	119.6 (16.4)
		flesh	-	-	-	-
	ripe	peel	8.6 (1.3)	-	82.4 (26.7)	91.1 (27.8)
		flesh	6.9 (0.5)	-	-	6.9 (0.5)
August Red	mature	peel	47.4 (7.2)	2.1 (1.3)	5.4 (2.7)	54.9 (4.6)
		flesh	10.1 (1.1)	-	-	10.1 (1.1)
	ripe	peel	52.1 (16.3)	4.4 (1.8)	11.3 (3.4)	67.8 (17.1)
		flesh	9.9 (1.9)	-	-	9.9 (1.9)
Spring Bright	mature	peel	9.9 (0.7)	14.9 (1.4)	56.9 (9.5)	81.7 (11.7)
		flesh	20.3 (4.0)	-	-	20.4 (4.0)
	ripe	peel	15.3 (0.9)	16.7 (3.5)	56.9 (11.7)	88.9 (16.0)
		flesh	21.1 (0.3)	-	-	21.1 (0.3)
May Glo	mature	peel	7.2 (0.8)	19.5 (2.4)	32.7 (2.9)	59.4 (5.3)
		flesh	4.3 (1.5)	-	-	4.3 (1.5)
	ripe	peel	25.2 (2.8)	14.6 (7.1)	29.4 (6.2)	69.2 (13.1)
		flesh	12.3 (0.5)	-	-	12.3 (0.5)
September Red	mature	peel	2.3 (0.2)	-	60.2 (8.5)	62.5 (8.7)
		flesh	8.4 (0.3)	-	-	8.4 (0.3)
	ripe	peel	7.5 (1.9)	-	41.8 (8.1)	49.3 (9.6)
		flesh	10.5 (1.3)	-	-	10.5 (1.3)

[a] Standard deviations ($n = 3$) in parentheses. Abbreviations: Qu 3-gal, quercetin 3-galactoside; Qu 3-GLC, quercetin 3-glucoside; Qu 3-rut, quercetin 3-rutinoside.

(Figure 3). Plums also contained chlorogenic and neochlorogenic acids and an unidentified caffeic derivative with a M^+-H ion at m/z 335 and the characteristic fragment of caffeic acid at m/z 179 (Table 2). In the 280 nm chromatograms and in the HPLC−ESIMS spectra, the presence of procyanidin derivatives was also detected. These were identified as the dimers procyanidin B1, B4, and B2, by chromatographic comparisons with the authentic markers available, and by their characteristic HPLC−ESIMS spectra (*m*/*z* 577 [M−H]+; *m*/*z* 425, *retro*-Diels−Alder fragment; *m*/*z* 289 and 287, fragments of terminal and remaining catechin residues in the dimer) (*15*). In addition, two A-type procyanidin dimers were detected (characteristic MS fragments at *m*/*z* 575 [M−H]+, *m*/*z* 423, *retro*-Diels−Alder fragment; and *m*/*z* 287 and 285). These A-type dimers showed ESIMS spectra similar to those of the B-type dimers, but showed two mass units less, as expected for this type of molecule with two inter-catechin bonds. Other procyanidin dimers and trimers (characteristic fragments at *m*/*z* 865, 577, and 289) (*16*) were also detected, although they were not fully identified. Flavonols were also detected in the peel extracts of plums. All the detected compounds were quercetin derivatives (characteristic UV spectrum and MS fragments at *m*/*z* 301 and 300) (Table 2). Five different quercetin derivatives (chromatographic peaks) were detected in the chromatograms at 340 and 280 nm (Figure 2) (**17**, **19**−**22**, and **24**). The main peaks were quercetin 3-rutinoside plus minor amounts of quercetin 3-glucoside (**19**−**20**), quercetin 3-pentoside (most probably xyloside as previously reported) (*17*) (**22**), and quercetin 3-rhamnoside (**24**). In addition, the HPLC−MS analyses showed that peak **17** was a quercetin pentosyl hexoside (Table 2) and compound **21** was quercetin pentosyl pentoside. In addition, the HPLC−MS analysis showed minor amounts of quercetin 3-acetylglucoside (*m*/*z* 505, 300) and quercetin acetylrutinoside (*m*/*z* 651, 301) that were not quantified in the HPLC−DAD chromatograms. The chromatograms at 510 nm revealed that plums contain at least four different anthocyanin pigments, depending on the cultivar. The main pigment was always cyanidin 3-glucoside, as in the case of peaches and nectarines, and cyanidin 3-rutinoside was a secondary pigment. In some cultivars cyanidin 3-acetyl glucoside was also detected in small amounts, and it was identified by its characteristic HPLC−MS spectrum and fragments (Table 2). In cv. Santa Rosa cyanidin 3-acetyl glucoside was not observed, but another cyanidin 3-hexoside was detected, eluting with shorter retention times that cyanidin 3-glucoside. This chromatographic behavior suggested that this was cyanidin 3-galactoside, and it was tentatively identified as this compound.

Phenolic Content of White Flesh and Yellow Flesh Nectarines. The hydroxycinnamic acid content of the different nectarine cultivars is shown in Table 3. In all cases the amount of chlorogenic was larger than that of neochlorogenic acid. The content of the peel was generally 2−3 times higher than that of the flesh. When comparing the white flesh and yellow flesh nectarines, there is no general rule that would predict which type of fruit is richer in hydroxycinnamates. Among the white flesh nectarines, cv. Brite Pearl shows a higher content of these compounds. In the ripe stage, it reaches 727 mg/kg hydroxycinnamates in the peel, and 460 mg/kg in the flesh. In contrast, cv. Fire Pearl contains only 78 mg/kg in the peel and 38 mg/kg in the flesh. Among the yellow flesh cultivars, Red Jim is the richest, containing 483 mg/kg in the peel and 187 mg/kg in the flesh at the initial stage. Ripe September Red is the yellow flesh cultivar containing less hydroxycinnamates (138 mg/kg in the peel and 66 mg/kg in the flesh) (Table 3).

Table 6. Anthocyanins (mg/kg fresh weight) in White and Yellow Flesh Nectarines (as Cyanidin 3-rutinoside)[a]

cultivar	stage	part	Cy-3glc		Cy-3-rut		total	
		White Flesh Cultivars						
Arctic Star	mature	peel	83.6	(8.5)	6.6	(1.2)	92.9	(9.7)
		flesh	-		-		-	
	ripe	peel	126.0	(18.9)	9.5	(1.8)	135.6	(20.5)
		flesh	-		-		-	
Arctic Queen	mature	peel	123.6	(13.7)	4.2	(0.7)	127.8	(14.3)
		flesh	1.3	(0.4)	-		1.3	(0.4)
	ripe	peel	147.5	(31.2)	4.7	(1.0)	152.2	(32.2)
		flesh	6.7	(0.5)	-		6.7	(0.5)
Arctic Snow	mature	peel	109.3	(44.3)	7.9	(3.0)	117.3	(46.9)
		flesh	16.5	(7.2)	-		16.5	(7.2)
	ripe	peel	92.7	(40.6)	6.3	(3.6)	99.0	(43.3)
		flesh	4.3	(3.3)	-		4.3	(3.3)
Fire Pearl	mature	peel	162.4	(16.9)	7.0	(1.3)	169.4	(18.1)
		flesh	2.5	(1.4)	-		2.5	(1.4)
	ripe	peel	165.0	(11.9)	7.8	(1.0)	172.7	(12.8)
		flesh	10.1	(3.0)	-		10.1	(3.0)
Brite Pearl	mature	peel	70.9	(5.3)	3.5	(1.7)	74.4	(7.0)
		flesh	-		-		-	
	ripe	peel	127.3	(19.6)	5.9	(2.1)	133.2	(21.7)
		flesh	-		-		-	
		Yellow Flesh Cultivars						
Red Jim	mature	peel	296.2	(19.2)	16.4	(2.2)	312.6	(21.1)
		flesh	14.6	(4.8)	-		14.6	(4.8)
	ripe	peel	246.6	(19.6)	14.3	(1.6)	260.9	(51.1)
		flesh	13.9	(14.5)	-		13.9	(14.5)
August Red	mature	peel	48.5	(10.6)	0.5	(0.1)	49.3	(11.0)
		flesh	11.6	(4.9)	-		11.6	(4.9)
	ripe	peel	33.5	(5.9)	-		33.5	(5.9)
		flesh	7.8	(1.9)	-		7.8	(1.9)
Spring Bright	mature	peel	256.8	(51.4)	15.2	(4.5)	271.9	(55.9)
		flesh	3.2	(1.3)	-		3.2	(1.3)
	ripe	peel	223.6	(35.2)	12.7	(2.6)	236.4	(37.8)
		flesh	3.2	(1.2)	-		3.2	(1.2)
May Glo	mature	peel	129.8	(8.3)	4.9	(0.4)	134.7	(8.6)
		flesh	-		-		-	
	ripe	peel	125.0	(5.6)	4.8	(0.8)	129.8	(6.4)
		flesh	-		-		-	
September Red	mature	peel	122.7	(8.8)	8.6	(0.4)	131.3	(8.8)
		flesh	23.4	(7.4)	-		23.4	(7.4)
	ripe	peel	77.2	(5.7)	4.8	(0.8)	82.0	(6.4)
		flesh	31.4	(8.8)	-		31.4	(8.8)

[a] Standard deviations ($n = 3$) in parentheses. Abbreviations: Cy-3-GLC, cyanidin 3-glucoside; Cy-3-rut, cyanidin 3-rutinoside.

The flavan-3-ol content of the different cultivars is shown in Table 4. Catechin, epicatechin, procyanidin B1, and other dimeric procyanidins were detected and quantified. The content was generally higher in the peel than in the flesh. Dimeric procyanidins were always detected in the peel, but in some cases, these compounds were not detected in the flesh. Among the white flesh cultivars, ripe cv. Brite Pearl was the richest, containing 1106 mg/kg in the peel and 434 mg/kg in the flesh, but Fire Pearl was the cultivar containing smaller amounts of procyanidins: 93 mg/kg in the peel and 23 mg/kg in the flesh. Among the yellow flesh cultivars, Red Jim was the richest in these compounds, containing 744 mg/kg in the peel and 336 mg/kg in the flesh, and ripe September Red was the one containing the least procyanidins: 128 mg/kg in the peel and 13 mg/kg in the flesh.

The flavonols of nectarines were mainly located in the peel. They were identified as quercetin 3-glucoside and 3-rutinoside. The content variability for these compounds was much smaller than that of the other phenolic metabolites previously mentioned. White flesh nectarines contained similar amounts of both flavonols, whereas yellow flesh fruit produced mainly quercetin 3-rutinoside. Among the white flesh cultivars, ripe Arctic Star showed the largest content (73.6 mg/kg peel) meanwhile Brite Pearl contained only 32 mg/kg. Regarding the yellow flesh nectarines, cv. Red Jim showed the largest flavonol content (119.6 mg/kg peel tissue)

Table 7. Hydroxycinnamic Acid Derivatives (mg/kg fresh weight) in White and Yellow Flesh Peach Cultivars (as Chlorogenic Acid)[a]

cultivar	stage	part	neochlorogenic		chlorogenic		other		total	
			White Flesh Cultivars							
Summer Sweet	mature	peel	24.9	(2.2)	189.3	(16.0)	12.5	(2.3)	226.8	(18.2)
		flesh	31.4	(6.1)	68.2	(17.4)	-		99.6	(17.2)
	ripe	peel	26.3	(4.1)	174.9	(32.1)	8.1	(0.7)	209.2	(35.4)
		flesh	31.0	(2.7)	68.9	(7.9)	-		99.9	(7.4)
Snow King	mature	peel	41.9	(3.0)	366.1	(18.7)	9.6	(0.3)	417.6	(21.3)
		flesh	71.4	(9.7)	229.1	(15.7)	-		301.0	(25.4)
	ripe	peel	47.8	(3.8)	434.7	(96.2)	15.9	(3.8)	498.5	(103.8)
		flesh	79.6	(6.4)	242.2	(14.6)	-		321.8	(18.5)
Snow Giant	mature	peel	74.4	(21.8)	174.9	(22.3)	7.2	(2.3)	256.6	(42.3)
		flesh	78.4	(24.7)	51.8	(5.0)	-		130.2	(28.3)
	ripe	peel	75.0	(22.2)	176.7	(22.3)	10.7	(0.7)	262.4	(44.6)
		flesh	70.8	(19.9)	56.3	(5.5)	-		127.1	(25.3)
Champagne	mature	peel	67.5	(2.3)	159.2	(25.8)	5.3	(0.6)	232.1	(28.0)
		flesh	54.4	(7.9)	37.1	(7.8)	-		91.4	(15.3)
	ripe	peel	87.7	(4.7)	185.9	(10.9)	5.4	(0.8)	279.0	(15.0)
		flesh	60.4	(17.8)	41.5	(16.6)	-		101.9	(33.6)
September Snow	mature	peel	57.2	(13.3)	113.2	(36.1)	5.7	(1.0)	176.1	(48.4)
		flesh	53.4	(11.8)	23.8	(6.3)	-		77.1	(17.9)
	ripe	peel	64.1	(10.7)	107.2	(17.2)	-		171.3	(26.7)
		flesh	50.1	(7.3)	26.4	(5.0)	-		76.5	(12.1)
			Yellow Flesh Cultivars							
Flavorcrest	mature	peel	18.0	(3.8)	134.2	(24.5)	5.3	(2.1)	157.5	(29.7)
		flesh	16.7	(1.4)	51.7	(8.8)	-		68.4	(10.3)
	ripe	peel	18.9	(4.3)	131.1	(26.1)	5.6	(2.2)	155.7	(32.0)
		flesh	17.2	(1.9)	47.4	(6.1)	-		64.6	(8.0)
Spring Lady	mature	peel	38.6	(5.2)	248.9	(14.7)	10.6	(0.8)	298.1	(19.4)
		flesh	49.4	(19.8)	132.1	(37.4)	-		181.5	(57.2)
	ripe	peel	44.1	(11.2)	294.6	(42.3)	8.5	(3.0)	347.4	(49.3)
		flesh	44.7	(4.5)	126.1	(20.9)	-		170.8	(25.2)
Rich Lady	mature	peel	16.2	(3.2)	116.5	(3.7)	14.9	(4.6)	147.6	(7.4)
		flesh	18.8	(3.1)	40.3	(4.6)	-		59.2	(6.7)
	ripe	peel	15.7	(2.4)	124.1	(5.1)	13.7	(2.2)	153.5	(7.7)
		flesh	22.1	(2.0)	43.3	(4.9)	-		65.5	(6.8)
O'Henry	mature	peel	50.7	(2.3)	191.6	(23.9)	16.1	(2.0)	258.4	(25.2)
		flesh	49.2	(2.3)	76.2	(1.3)	-		125.4	(1.9)
	ripe	peel	54.2	(3.8)	191.9	(12.2)	15.0	(2.0)	261.1	(16.0)
		flesh	52.8	(7.2)	79.3	(10.9)	-		132.2	(18.0)
September Sun	mature	peel	45.7	(7.5)	143.0	(30.4)	-		188.7	(37.2)
		flesh	50.6	(5.1)	59.0	(12.3)	-		109.7	(17.4)
	ripe	peel	54.4	(5.7)	182.7	(6.0)	-		236.1	(9.4)
		flesh	65.2	(2.8)	72.9	(5.1)	-		138.0	(5.4)

[a] Standard deviations ($n = 3$) in parentheses.

and ripe September Red contained the smallest amount (49.3 mg/kg peel). The flavonol content of the flesh was very small and restricted to a quercetin hexoside, most probably quercetin 3-galactoside (Table 5).

The anthocyanin pigments of nectarines, cyanidin 3-glucoside and 3-rutinoside, were mainly restricted to the peel (Table 6). However, small amounts of pigments were also detected in some cultivars in the flesh, especially in those tissues that are close to the stone. No clear differences were observed in the pigment contents of white flesh and yellow flesh nectarines. Among white flesh fruits, cv. Fire Pearl showed the largest pigment content (172.7 mg/kg peel), and Brite Pearl showed the smallest (74.7 mg/kg). Regarding the yellow flesh nectarine cultivars, Red Jim showed the largest content (312.6 mg/kg peel), and August Red showed the smallest (33.5 mg/kg peel). It is worth noticing that cv. September Red contains up to 31.4 mg/kg anthocyanins in the flesh, making it the nectarine showing the largest anthocyanin content in this tissue.

Phenolic Content of White Flesh and Yellow Flesh Peaches. The phenolic content of peaches was similar to that observed in nectarines both qualitatively and quantitatively. The hydroxycinnamates neochlorogenic acid and chlorogenic acid were present in all samples. Catechin, epicatechin, and the dimer procyanidin B1 were detected as well as other unidentified dimeric procyanidins. The flavonols quercetin 3-glucoside and 3-rutinoside were detected in the peel of peaches, as were the anthocyanins, cyanidin 3-glucoside, and 3-rutinoside. Anthocyanins were also detected in small amounts in the flesh of some cultivars, and as in the case of nectarines, this pigmentation was particularly located close to the stone.

Among the white flesh cultivars, Snow King showed the highest content of hydroxycinnamates (498.5 mg/kg in the peel and 321.8 mg/kg in the flesh), whereas September Snow showed the smallest content (171.3 mg/kg in the peel and 76.5 mg/kg in the flesh). Chlorogenic acid was always present in larger amounts than neochlorogenic acid. The same trend was observed in the yellow flesh peaches. Spring Lady showed the highest levels in both peel (347.4 mg/kg) and flesh (181.5 mg/kg), and Rich Lady showed the lowest levels (147.6 mg/kg in the peel and 59.2 mg/kg in the flesh) (Table 7).

In the peaches analyzed, catechin, epicatechin, and procyanidin B1 were the main flavan-3-ols in both peel and flesh. In addition, other unidentified procyanidin dimers were detected. The content of catechin was generally higher than that of epicatechin, in agreement with previous studies (*18*−*19*). Among the white flesh cultivars, ripe Snow King (1166 mg/kg in the peel and 696 mg/kg in the flesh) and Snow Giant (1083 mg/kg in the peel and 537 mg/kg in the flesh) showed the largest procyanidin contents. In contrast, ripe Summer Sweet was the least rich in this type of compound (296 mg/kg in the peel and 117 mg/kg in the flesh). The procyanidin content of the yellow flesh peaches was generally smaller than that of the richest white flesh cultivars, with amounts in the peel of around 500−600 mg/kg and in the flesh of 200−350 mg/kg. Flavorcrest was the cultivar showing the smallest amounts of these compounds (Table 8).

As in the case of nectarines, the flavonols of peaches were mainly located in the peel. They were identified as quercetin 3-glucoside and 3-rutinoside. The content variability for these compounds was much smaller than

Table 8. Flavan-3-ols (mg/kg fresh weight) in White and Yellow Flesh Peach Cultivars (as Catechin)[a]

cultivar	stage	part	catechin	epicatechin	B1	other	total
White Flesh Cultivars							
Summer Sweet	mature	peel	124.5 (11.4)	54.5 (3.9)	119.7 (21.1)	42.2 (9.2)	341.0 (43.2)
		flesh	39.2 (6.3)	19.0 (2.8)	35.5 (6.2)	-	93.7 (13.1)
	ripe	peel	104.2 (13.3)	61.9 (12.5)	100.5 (19.1)	30.0 (4.1)	296.5 (26.6)
		flesh	39.7 (3.0)	38.9 (9.2)	38.4 (1.6)	-	117.1 (10.6)
Snow King	mature	peel	316.6 (30.0)	62.0 (17.2)	469.1 (9.0)	250.9 (71.0)	1098.6 (120.1)
		flesh	189.5 (22.5)	32.4 (1.2)	333.4 (14.0)	103.3 (8.3)	658.5 (37.0)
	ripe	peel	311.6 (36.2)	73.0 (18.9)	492.3 (68.1)	288.8 (65.7)	1165.8 (183.1)
		flesh	196.7 (16.2)	35.1 (7.6)	333.1 (37.2)	130.9 (10.3)	695.8 (57.7)
Snow Giant	mature	peel	273.3 (10.1)	73.3 (7.8)	370.7 (47.4)	197.2 (56.8)	914.5 (95.6)
		flesh	189.5 (94.0)	31.5 (19.9)	248.0 (17.8)	51.5 (10.8)	520.5 (95.8)
	ripe	peel	270.0 (18.1)	151.6 (12.7)	322.1 (9.7)	339.3 (21.9)	1083.0 (48.8)
		flesh	138.8 (28.3)	51.9 (4.6)	250.9 (82.6)	95.5 (22.7)	537.0 (86.1)
Champagne	mature	peel	286.9 (40.1)	43.0 (3.3)	328.1 (37.6)	100.5 (36.6)	752.7 (70.8)
		flesh	77.4 (13.3)	20.8 (25.8)	131.8 (40.2)	-	230.0 (53.5)
	ripe	peel	318.9 (8.9)	127.7 (25.6)	354.3 (20.3)	59.9 (10.2)	858.0 (48.6)
		flesh	84.9 (28.1)	38.3 (8.6)	157.4 (43.5)	29.2 (4.6)	309.8 (71.5)
September Snow	mature	peel	178.0 (40.0)	108.6 (15.2)	249.8 (81.5)	105.6 (28.3)	641.9 (165.0)
		flesh	70.8 (19.3)	36.9 (12.9)	76.1 (40.8)	-	183.8 (70.9)
	ripe	peel	149.9 (23.1)	112.1 (57.5)	222.7 (27.8)	84.0 (28.5)	568.8 (135.8)
		flesh	75.6 (11.9)	53.3 (38.1)	87.8 (27.7)	-	216.8 (77.1)
Yellow Flesh Cultivars							
Flavorcrest	mature	peel	93.4 (13.7)	55.9 (8.8)	112.7 (23.4)	48.8 (6.8)	310.7 (30.0)
		flesh	33.7 (6.4)	11.1 (5.1)	42.6 (9.9)	-	87.4 (15.6)
	ripe	peel	84.2 (2.0)	24.9 (9.1)	74.1 (21.6)	42.2 (6.4)	225.4 (14.7)
		flesh	30.1 (4.4)	23.4 (2.2)	39.7 (4.2)	-	93.2 (6.6)
Spring Lady	mature	peel	132.3 (4.1)	67.3 (6.6)	184.9 (10.6)	165.3 (51.1)	549.8 (19.8)
		flesh	97.7 (48.5)	36.2 (9.5)	125.5 (4.6)	107.3 (55.8)	368.7 (113.4)
	ripe	peel	154.3 (30.1)	93.9 (19.9)	221.8 (21.7)	189.3 (54.7)	659.3 (86.4)
		flesh	79.1 (12.3)	43.6 (4.2)	234.3 (37.2)	-	357.0 (51.5)
Rich Lady	mature	peel	175.7 (24.2)	100.2 (22.9)	186.1 (15.1)	111.9 (37.6)	573.9 (37.6)
		flesh	71.3 (6.8)	20.9 (4.7)	108.7 (13.4)	-	200.9 (19.8)
	ripe	peel	163.3 (18.6)	95.6 (26.4)	191.1 (12.9)	98.4 (17.5)	548.4 (28.2)
		flesh	59.8 (5.8)	28.6 (5.2)	96.0 (21.1)	-	184.3 (30.3)
O'Henry	mature	peel	136.3 (10.6)	78.8 (11.9)	246.0 (10.1)	96.1 (15.2)	557.2 (30.6)
		flesh	48.8 (9.6)	9.5 (1.3)	155.1 (20.1)	-	213.5 (20.7)
	ripe	peel	124.6 (12.8)	164.8 (16.3)	298.9 (43.3)	124.7 (21.3)	663.0 (72.2)
		flesh	45.4 (8.1)	32.0 (13.8)	116.4 (53.2)	-	193.9 (69.6)
September Sun	mature	peel	152.2 (20.3)	105.3 (21.6)	169.8 (39.0)	28.3 (8.1)	455.5 (81.4)
		flesh	62.8 (15.9)	44.1 (7.5)	95.9 (51.8)	-	202.8 (51.2)
	ripe	peel	187.1 (19.1)	158.7 (12.9)	240.6 (24.9)	50.3 (5.9)	636.7 (60.3)
		flesh	58.9 (10.3)	59.2 (17.6)	158.3 (13.0)	-	276.4 (37.7)

[a] Standard deviations ($n = 3$) in parentheses.

that of the other phenolic metabolites previously mentioned. White flesh peaches contained similar amounts of both flavonols, whereas yellow flesh fruit produced mainly quercetin 3-rutinoside as it was also observed in nectarines. The white flesh cultivars showed amounts in the range 20−52 mg of flavonols per kg of peel, and much smaller amounts in the flesh (6−10 mg/kg). In the yellow flesh cultivars the range of flavonols in the peel was 35−74 mg/kg, whereas in the flesh it was only 5−20 mg/kg (Table 9).

Peaches also contained anthocyanin pigments that were identified as cyanidin 3-glucoside and 3-rutinoside. In general, white flesh cultivars produced less anthocyanin pigments in the peel than yellow flesh cultivars. Among the yellow flesh cultivars, Rich Lady showed the highestr pigmentation in the peel (337 mg/kg), with significant amounts also found in O'Henry and September Sun; ripe Flavorcrest showed the smallest pigmentation (69 mg/kg) (Table 10). Among the white flesh cultivars, the initial Summer Sweet showed the highest pigmentation (198 mg/kg) and ripe September Snow showed the smallest (54 mg/kg). The pigmentation of the flesh, when it occurred, was always very small, and it was mainly located in the surroundings of the stone (Table 10).

Phenolic Content of Plums. Five plum cultivars were studied: one yellow (Wickson) and four red cultivars. Two of them were pigmented only in the skin (Santa Rosa and Red Beaut); the other two were highly pigmented in the skin and the flesh also contained some red pigmentation (Black Beaut and Angeleno). With regard to the hydroxycinnamic acid derivatives, plums contained mainly neochlorogenic acid, and much smaller amounts of chlorogenic acid (Table 11). In addition, some other hydroxycinnamates were also detected by their characteristic UV spectra, and quantified as chlorogenic acid. The cultivar showing the highest hydroxycinnamate content was Red Beaut, and Angeleno showed the smallest amount. When the flavan-3-ol derivatives were analyzed, no catechin or epicatechin was detected in significant amounts. However, dimeric and trimeric forms of catechin were detected by HPLC−MS and quantified. All the plums analyzed were quite rich in this type of compound, being richer in the skin than in the flesh (Table 12). These compounds were especially abundant in cultivars Black Beaut, Wickson, and Angeleno (more than 1 g/kg fresh weight in the case of the peels). No clear tendency in the flavan-3-ol content of plums was observed with ripening, as Angeleno and Black Beaut increased their content, but Wickson decreased its content. These results are significant from the taste point of view, as these kinds of compounds are responsible for the astringency of plums.

When the flavonols were analyzed, these compounds were detected in significant amounts only in the skins, as happened in the case of nectarines and peaches. Six different peaks were identified in the HPLC chromatograms and quantified. All were quercetin derivatives, with different sugar substitutions, and the aglycon quercetin was also detected, although in rather small amounts (Table 13). The main flavonoids detected were quercetin 3-glucoside and quercetin 3-rutinoside, which were quantified in a single peak as they could not be separated under the chromatographic conditions used in the present work, and quercetin 3-xyloside. The cultivar showing the largest content of flavonols was Black Beaut, whereas Angeleno was the cultivar showing the smallest flavonoid content. All the analyzed cultivars showed the same flavonoid pattern, with the exception of Angeleno, in which the quercetin pentosyl

Table 9. Flavonols (mg/kg fresh weight) in White and Yellow Flesh Peach Cultivars (as Quercetin 3-Rutinoside)

cultivar	stage	part	qu 3 gal (tentative)	qu 3-GLC	qu 3 rut	total
			White Flesh Cultivars			
Summer Sweet	mature	peel	3.3 (1.0)	21.1 (6.3)	28.2 (6.1)	52.2 (11.4)
		flesh	6.0 (0.2)	-	-	6.0 (0.2)
	ripe	peel	9.2 (1.0)	14.3 (3.3)	17.5 (3.0)	41.0 (7.1)
		flesh	11.4 (2.3)	-	-	11.4 (2.3)
Snow King	mature	peel	-	7.8 (0.8)	12.9 (1.0)	20.7 (1.5)
		flesh	-	-	-	-
	ripe	peel	-	20.6 (12.5)	27.1 (11.9)	47.7 (27.4)
		flesh	7.2 (1.6)	-	-	7.2 (1.6)
Snow Giant	mature	peel	4.4 (1.8)	11.4 (4.0)	19.7 (5.0)	35.6 (7.6)
		flesh	-	-	-	-
	ripe	peel	8.3 (0.4)	10.4 (2.5)	15.2 (7.1)	33.9 (7.6)
		flesh	6.1 (1.4)	-	-	6.1 (1.4)
Champagne	mature	peel	-	6.1 (1.9)	16.1 (3.8)	22.2 (5.7)
		flesh	6.8 (1.0)	-	-	6.8 (1.0)
	ripe	peel	9.6 (1.1)	5.2 (1.2)	14.9 (4.3)	29.7 (5.4)
		flesh	10.4 (1.8)	-	-	10.4 (1.8)
September Snow	mature	peel	-	10.2 (2.4)	21.7 (14.9)	31.9 (13.0)
		flesh	6.5 (0.4)	-	-	6.5 (0.4)
	ripe	peel	10.1 (7.8)	-	26.9 (17.3)	37.0 (12.7)
		flesh	7.3 (0.1)	-	-	7.3 (0.1)
			Yellow Flesh Cultivars			
Flavorcrest	mature	peel	13.4 (3.7)	13.1 (3.1)	18.2 (3.5)	44.7 (3.1)
		flesh	7.1 (1.2)	-	-	7.1 (1.2)
	ripe	peel	-	14.1 (1.8)	20.7 (3.5)	34.8 (5.2)
		flesh	13.8 (0.9)	-	-	13.8 (0.9)
Spring Lady	mature	peel	-	21.1 (3.6)	28.7 (2.4)	49.9 (6.0)
		flesh	8.9 (2.6)	-	-	8.9 (2.6)
	ripe	peel	20.9 (2.6)	21.3 (6.3)	28.3 (6.0)	70.5 (9.7)
		flesh	19.2 (2.5)	-	-	19.2 (2.5)
Rich Lady	mature	peel	3.2 (0.6)	17.5 (2.5)	39.3 (4.5)	60.0 (6.5)
		flesh	4.8 (1.9)	-	-	4.8 (1.9)
	ripe	peel	12.8 (0.8)	17.9 (1.8)	37.9 (1.6)	68.6 (1.1)
		flesh	12.4 (3.0)	-	-	12.4 (3.0)
O'Henry	mature	peel	4.8 (4.7)	2.8 (0.4)	34.0 (4.3)	41.7 (8.3)
		flesh	9.9 (1.0)	-	-	9.9 (1.0)
	ripe	peel	2.7 (1.5)	12.7 (2.0)	28.1 (4.8)	43.5 (5.0)
		flesh	18.4 (3.3)	-	-	18.4 (3.3)
September Sun	mature	peel	30.3 (14.9)	9.1 (3.1)	5.2 (0.9)	44.6 (18.6)
		flesh	11.5 (3.3)	-	-	11.5 (3.3)
	ripe	peel	40.2 (12.0)	20.7 (2.4)	13.3 (1.4)	74.1 (12.3)
		flesh	19.3 (3.4)	-	-	19.3 (3.4)

[a] Standard deviations ($n = 3$) in parentheses. Abbreviations: Qu 3-gal, quercetin 3-galactoside; Qu 3-GLC, quercetin 3-glucoside; Qu-3-rut, quercetin 3-rutinoside.

hexoside (**15**) was not detected. The anthocyanins were present in only the red cultivars, as expected, but in some cases, in over-ripe Wickson plums, a red pigmentation was also detected. The main pigments responsible for this pigmentation in plums were cyanidin 3-glucoside and 3-rutinoside. However, in Red Beaut, Black Beaut, and Angeleno, the presence of small amounts of cyanidin 3-acetyl glucoside was also detected, and in the case of Santa Rosa, small amounts of cyanidin 3-galactoside were found. The higher pigmentation was observed in the peels of Angeleno that contained more than 1 g of anthocyanins per kg fresh weight of skins (Table 14).

DISCUSSION

Previous studies on peach phenolics showed that chlorogenic acid (5-*O*-caffeoyl-quinic) was the main hydroxycinnamic derivative, with minor amounts of neochlorogenic (3-*O*-caffeoyl-quinic) and cryptochlorogenic (4-*O*-caffeoyl-quinic) acids (*17*). The results of this study confirm that chlorogenic is the main hydroxycinamate of peaches and plums, but cryptochlorogenic was not detected. With regard to flavan-3-ols, catechin was reported as the main one, with smaller amounts of epicatechin, gallocatechin, and epigallocatechin. The present study has confirmed that catechin was the main monomeric flavan-3-ol, and that epicatechin was also present in smaller amounts. However, gallocatechin and epigallocatechin were not detected. In addition some procyanidin dimers were identified (B1 and B4) as well as other unidentified dimers. The occurrence of procyanidins B2, B3, and B4 has already been reported in peaches (*18*−*19*) and procyanidin B3 could coincide with one of the unidentified B-type procyanidin dimers that were detected in the HPLC−ESIMS analysis of peach and nectarine extracts. Previous studies have shown the occurrence of quercetin 3-glucoside, 3-galactoside, and 3-rutinoside in peaches, as well as some kaempferol derivatives (*17*). The study of these peach and nectarine cultivars has confirmed the occurrence of the quercetin derivatives, although the kaempferol analogues were not detected. Previous studies have only found cyanidin 3-glucoside and 3-rutinoside as anthocyanin pigments in peaches. The present study has confirmed that only these two pigments are present in peaches and nectarines.

Previous studies on plum phenolics have shown differences among the phenolic contents of *Prunus domestica*, *P. spinosa*, and *P. salicina* (*17*). These reports have shown that plums contain mainly neochlorogenic acid with smaller amounts of chlorogenic and cryptochlorogenic acids. In the cultivars analyzed in the present work, only chlorogenic and neochlorogenic acids were detected, as well as an unidentified caffeic acid derivative. No cryptochlorogenic acid was detected. The present study confirms that neochlorogenic acid is the main hydroxycinnamic acid derivative in plums. The presence of cyanidin 3-glucoside and 3-rutinoside, as well as the occurrence of peonidin analogues, have been reported in plums, although *P. salicina* contained only the cyanidin derivatives (*17*). In the plum cultivars analyzed here, we have not identified any peonidin derivative, although in addition to the previously reported anthocyanins, cyanidin 3-galactoside and cyanidin 3-acetyl-glucoside were detected in some cultivars. Regarding flavan-3-ols, previous papers reported the occurrence of catechin and epicatechin in plums (*17*).

Table 10. Anthocyanins (mg/kg fresh weight) in White and Yellow Flesh Peach Cultivars (as Cyanidin 3-rutinoside)

cultivar	stage	part	cy 3-GLC		cy 3-rut		total	
		White Flesh Cultivars						
Summer Sweet	mature	peel	187.3	(21.4)	10.7	(1.0)	198.1	(21.9)
		flesh	-		-		-	
	ripe	peel	114.2	(17.1)	8.6	(1.7)	122.9	(18.6)
		flesh	-		-		-	
Snow King	mature	peel	117.7	(17.6)	4.8	(1.7)	122.5	(19.3)
		flesh	5.1	(1.8)	-		5.1	(1.8)
	ripe	peel	118.7	(17.7)	5.1	(1.3)	123.8	(19.1)
		flesh	17.6	(4.9)	-		17.6	(4.9)
Snow Giant	mature	peel	128.0	(36.0)	8.1	(4.4)	136.1	(39.9)
		flesh	6.6	(1.6)	-		6.6	(1.6)
	ripe	peel	132.8	(4.0)	9.7	(0.2)	142.6	(4.0)
		flesh	-		-		-	
Champagne	mature	peel	70.5	(8.2)	5.5	(0.8)	76.1	(9.0)
		flesh	7.9	(0.3)	-		7.9	(0.3)
	ripe	peel	53.5	(16.3)	3.6	(1.8)	57.1	(17.6)
		flesh	6.4	(2.9)	-		6.4	(2.9)
September Snow	mature	peel	61.1	(15.7)	4.9	(0.9)	66.1	(16.6)
		flesh	-		-		-	
	ripe	peel	52.4	(12.9)	1.8	(0.8)	54.4	(12.1)
		flesh	2.7	(2.4)	-		2.7	(2.4)
Yellow Flesh Cultivars								
Flavorcrest	mature	peel	83.6	(29.3)	3.9	(1.9)	87.5	(31.1)
		flesh	-		-		-	
	ripe	peel	66.2	(7.0)	2.8	(1.4)	69.1	(8.3)
		flesh	-		-		-	
Spring Lady	mature	peel	105.9	(11.7)	4.9	(0.9)	110.8	(12.6)
		flesh	-		-		-	
	ripe	peel	80.7	(38.3)	4.9	(2.2)	85.6	(40.4)
		flesh	-		-		-	
Rich Lady	mature	peel	325.1	(82.4)	11.5	(2.6)	336.6	(84.8)
		flesh	-		-		-	
	ripe	peel	264.4	(22.9)	9.2	(0.9)	273.6	(23.7)
		flesh	-		-		-	
O'Henry	mature	peel	240.7	(10.4)	12.2	(0.4)	252.9	(10.8)
		flesh	8.7	(1.7)	-		8.7	(1.7)
	ripe	peel	224.0	(41.5)	10.5	(2.3)	234.5	(48.8)
		flesh	8.1	(1.9)	-		8.1	(1.9)
September Sun	mature	peel	126.0	(52.2)	6.8	(3.2)	132.8	(53.1)
		flesh	7.3	(2.3)	-		7.3	(2.3)
	ripe	peel	168.9	(70.0)	6.9	(4.4)	175.8	(74.4)
		flesh	3.7	(1.2)	-		3.7	(1.2)

[a] Standard deviations ($n = 3$) are shown in brackets. Abbreviaitons: Cy 3-GLC, cyanidin 3-glucoside; Cy 3-rut, cyanidin 3-rutinoside.

Table 11. Hydroxycinnamic Acid Derivatives (mg/kg fresh weight) in Plum Cultivars (as Chlorogenic acid)

cultivar	stage	part	neochlorogenic		chlorogenic		other		total	
Angeleno	mature	peel	40.0	(11.3)	-		75.0	(5.2)	115.0	(15.1)
		flesh	17.3	(3.9)	-		-		17.3	(3.9)
	ripe	peel	40.3	(11.3)	3.3	(0.3)	85.4	(19.2)	129.0	(16.1)
		flesh	16.3	(2.3)	-		-		16.3	(2.3)
Black Beaut	mature	peel	225.3	(0.3)	12.9	(0.3)	43.9	(2.2)	282.2	(2.1)
		flesh	103.2	(3.1)	-		10.2	(0.2)	113.5	(3.2)
	ripe	peel	242.1	(6.2)	12.7	(0.9)	45.9	(2.2)	300.8	(7.0)
		flesh	110.9	(5.7)	-		11.0	(1.4)	121.9	(6.4)
Santa Rosa	mature	peel	238.4	(40.1)	21.6	(4.1)	11.2	(1.3)	271.1	(44.8)
		flesh	127.5	(9.4)	4.5	(0.9)	-		132.0	(8.6)
	ripe	peel	276.6	(12.8)	21.8	(2.3)	12.7	(1.7)	311.2	(13.4)
		flesh	138.0	(9.5)	3.7	(0.6)	-		141.7	(9.7)
Red Beaut	mature	peel	326.6	(20.4)	14.2	(1.4)	34.1	(5.0)	374.9	(25.4)
		flesh	183.7	(5.8)	3.5	(0.2)	6.8	(0.3)	194.0	(5.7)
	ripe	peel	342.6	(20.9)	14.6	(0.5)	16.8	(3.7)	373.9	(23.8)
		flesh	181.9	(5.3)	4.1	(0.9)	-		186.0	(4.6)
Wickson	mature	peel	135.1	(6.6)	6.1	(0.7)	39.5	(4.1)	180.7	(10.7)
		flesh	86.6	(3.8)	3.3	(0.3)	-		89.9	(3.6)
	ripe	peel	130.4	(11.6)	5.0	(0.4)	36.2	(2.0)	171.6	(14.1)
		flesh	81.4	(6.9)	-		-		81.4	(6.9)

[a] Standard deviations ($n = 3$) in parentheses.

The present analysis has shown, however, that the main flavan 3-ol derivatives in plums are procyanidin dimers (B1, B2, B4, and A-type dimers), and trimers (these in smaller amounts). Catechin and epicatechin were not detected in significant amounts in the plum cultivars analyzed here. The occurrence of A-type dimers in some plum cultivars is of some interest, as this kind of compound has been previously reported only in cranberry fruits (*20*) and it may have antibacterial activity. A number of flavonols have already been described in

Table 12. Flavan 3-ols (mg/kg fresh weight) in Plum Cultivars (as Catechin)[a]

cultivar	stage	part	B1	B4	B2	A-type dimers	other	total
Angeleno	mature	peel	80.6 (15.4)	52.1 (29.3)	339.9 (69.8)	477.4 (66.0)	308.5 (52.1)	1151.1 (208.0)
		flesh	31.2 (15.0)	159.0 (54.6)	120.1 (42.1)	-	66.8 (14.8)	377.3 (125.8)
	ripe	peel	94.9 (11.3)	183.3 (21.1)	343.9 (52.1)	564.8 (101.8)	237.0 (46.2)	1393.6 (205.4)
		flesh	48.5 (10.8)	165.7 (16.2)	110.6 (18.2)	-	60.5 (9.0)	385.4 (53.5)
Black Beaut	mature	peel	291.5 (3.7)	677.6 (24.0)	137.3 (2.8)	256.8 (10.1)	287.3 (20.8)	1650.6 (19.6)
		flesh	136.0 (24.4)	136.8 (5.1)	88.0 (4.5)	103.0 (9.2)	102.3 (19.8)	566.1 (51.0)
	ripe	peel	251.8 (18.0)	710.5 (23.4)	118.6 (9.2)	276.0 (7.0)	479.9 (50.7)	1836.8 (96.2)
		flesh	161.9 (10.4)	142.8 (9.1)	94.4 (3.8)	105.6 (4.4)	113.7 (23.4)	618.3 (2.3)
Santa Rosa	mature	peel	90.0 (16.0)	90.1 (21.9)	73.4 (10.1)	-	408.7 (95.3)	662.2 (133.1)
		flesh	121.0 (37.2)	58.0 (6.0)	-	-	-	179.0 (39.7)
	ripe	peel	81.1 (10.0)	105.7 (12.3)	117.0 (51.8)	33.5 (14.3)	411.8 (55.3)	749.1 (124.5)
		flesh	100.5 (5.4)	59.4 (2.6)	77.2 (22.2)	-	-	237.1 (24.2)
Red Beaut	mature	peel	268.3 (62.1)	253.1 (52.4)	72.1 (18.6)	75.3 (10.1)	204.7 (33.9)	847.4 (171.1)
		flesh	40.7 (11.4)	41.8 (2.1)	41.4 (2.8)	37.2 (2.8)	20.8 (6.4)	181.9 (15.1)
	ripe	peel	115.3 (80.0)	280.0 (58.0)	85.3 (15.4)	75.5 (13.8)	430.1 (122.8)	986.3 (202.0)
		flesh	17.9 (3.1)	43.6 (4.8)	39.5 (6.2)	37.0 (4.3)	83.5 (44.1)	221.5 (43.4)
Wickson	mature	peel	539.9 (12.5)	484.8 (28.2)	-	77.6 (5.7)	431.7 (34.1)	1533.9 (53.7)
		flesh	110.1 (17.2)	45.7 (6.0)	-	-	-	155.8 (22.5)
	ripe	peel	473.2 (30.8)	416.0 (35.9)	-	52.4 (4.5)	417.8 (50.0)	1254.6 (103.2)
		flesh	96.7 (3.9)	41.8 (0.8)	-	-	-	138.5 (4.0)

[a] Standard deviations ($n = 3$) in parentheses.

Table 13. Flavonol Glycosides (mg/kg fresh weight) in the Peel of Plum Cultivars (as quercetin 3-rutinoside)[a]

cultivar	stage	**17**	**19−20**	**21**	**22**	**24**	other	total
Angeleno	mature	-	60.6 (0.7)	8.1 (1.0)	56.5 (2.2)	17.8 (1.3)	-	143.0 (4.7)
	ripe	-	73.3 (8.4)	11.9 (0.3)	74.3 (2.7)	26.5 (1.7)	-	186.0 (9.0)
Black Beaut	mature	8.4 (0.4)	76.2 (8.6)	18.6 (3.5)	128.9 (17.9)	67.1 (8.2)	13.0 (2.0)	312.1 (36.4)
	ripe	8.7 (1.2)	89.3 (8.8)	19.8 (3.3)	145.2 (17.0)	75.1 (12.2)	14.0 (2.5)	352.1 (42.2)
Santa Rosa	mature	14.4 (3.2)	91.8 (18.4)	19.7 (6.2)	101.2 (31.6)	31.1 (15.2)	23.8 (5.0)	282.3 (72.7)
	ripe	9.3 (2.8)	102.7 (11.3)	16.8 (2.3)	105.4 (15.7)	38.2 (6.0)	26.7 (5.6)	299.2 (27.6)
Red Beaut	mature	5.1 (0.2)	16.3 (3.4)	18.2 (2.3)	105.2 (23.7)	50.2 (10.4)	15.0 (0.5)	209.9 (37.5)
	ripe	4.7 (4.0)	7.8 (4.1)	14.6 (4.5)	82.1 (5.6)	40.5 (3.1)	16.4 (8.8)	166.2 (15.0)
Wickson	mature	6.0 (1.6)	77.7 (23.8)	11.5 (5.9)	95.2 (34.2)	35.7 (18.4)	6.6 (3.5)	232.7 (82.7)
	ripe	5.8 (1.0)	68.7 (9.0)	9.8 (1.6)	83.4 (14.3)	31.3 (4.1)	5.2 (2.3)	204.2 (31.4)

[a] **17**, Quercetin pentoxyl hexoside; **19−20**, quercetin glucoside + quercetin rutinoside; **21**, quercetin pentosyl pentoside; **22**, quercetin xyloside (tentative); **24**, quercetin rhamnoside; other, other quercetin glycosides. Standard deviations ($n = 3$) in parentheses.

Table 14. Anthocyanins (mg/kg fresh weight) in Plum Cultivars (as cyanidin 3-rutinoside)[a]

cultivar	stage	part	cy 3-GLC	cy 3-rut	cy 3-GLC acetyl (tentative)	cy 3gal (tentative)	total
Angeleno	mature	peel	860.5 (11.9)	525.3 (2.0)	9.4 (0.7)	-	1395.2 (10.6)
		flesh	3.9 (2.2)	1.9 (0.9)	-	-	5.8 (3.1)
	ripe	peel	1039.3 (263.1)	565.9 (124.6)	9.5 (0.9)	-	1614.7 (386.5)
		flesh	3.2 (2.2)	1.8 (0.7)	-	-	5.0 (2.9)
Black Beaut	mature	peel	269.8 (54.7)	100.1 (14.3)	32.9 (4.3)	-	402.8 (70.6)
		flesh	20.9 (2.9)	7.5 (0.7)	-	-	28.4 (3.5)
	ripe	peel	519.7 (23.5)	127.3 (3.1)	43.6 (1.7)	-	690.6 (23.9)
		flesh	22.7 (3.3)	5.7 (0.2)	-	-	28.4 (3.1)
Santa Rosa	mature	peel	128.0 (36.5)	65.9 (18.9)	-	18.1 (4.9)	212.0 (60.0)
		flesh	-	-	-	-	-
	ripe	peel	175.1 (16.6)	70.7 (7.5)	-	27.2 (2.8)	273.0 (26.5)
		flesh	-	-	-	-	-
Red Beaut	mature	peel	85.0 (10.7)	47.6 (8.8)	9.5 (2.5)	-	142.1 (21.8)
		flesh	-	-	-	-	-
	ripe	peel	79.3 (6.4)	42.0 (2.3)	7.9 (0.5)	-	129.1 (8.5)
		flesh	-	-	-	-	-
Wickson	mature	peel	-	-	-	-	-
		flesh	-	-	-	-	-
	ripe	peel	-	-	-	-	-
		flesh	-	-	-	-	-

[a] Standard deviations ($n = 3$) in parentheses. Abbreviations: Cy 3-GLC, cyanidin 3-glucoside; Cy 3-rut, cyanidin 3-rutinoside; Cy 3-gal, cyanidin 3-galactoside; Cy 3- GLC-acetyl, cyanidin 3-acetyl-glucoside.

plums. *Prunus domestica* was characterized by the occurrence of kaempferol 3-rutinoside, 3-glucoside, 3-galactoside, and 3-arabinoside-7-rhamnoside, in addition to the quercetin analogues plus quercetin 3-xyloside and 3-rhamnoside (*17*). *P. salicina* had similar flavonols to those of *P. domestica*, and *P. spinosa* had only the quercetin derivatives (*17*), as did the plum cultivars analyzed in the present study. It is possible, however, that under the chromatographic conditions used in this study (a single chromatographic analysis for all phenolic compounds), some minor kaempferol derivatives were not detected.

Concerning the content of phenolic compounds in stone fruit, it should be noted that the hydroxycinnamic acid derivatives content of the peach and nectarine analyzed cultivars is generally higher (100−200 mg/kg f.w.) than that previously reported for other cultivars (20-120 mg/kg f.w.) (*18*). A similar trend was observed when analyzing flavan-3-ols, as the content previously reported was generally smaller in other cultivars (10−100 mg/kg) (*10, 18, 19, 21*) than in the cultivars studied in the present work, in which the content reached more than 1000 mg/kg f.w. of procyanidins in some cases. Especially rich in phenolics were the nectarine cultivars Brite Pearl and Red Jim and the peach cultivars Snow King and Snow Giant. This contrasts with the small phenolic content of some nectarines such as Fire Pearl. The feature of white flesh or yellow flesh did not affect the phenolic content of the studied cultivars. Regarding the two ripening stages analyzed, no clear differences were observed, as some cultivars contained higher phenolic content in the less ripe stage, whereas others showed higher phenolic content in the fully ripe stage. This agrees with previous reports showing that there is no general rule correlating phenolic content with ripening stage (*17*).

In the case of plums, previous work had reported relatively small amounts of flavan-3-ols (mainly catechin and epicatechin) in plums (20−40 mg/kg f.w.) (*10*) but the amounts quantified in the present study were much larger. These results agree with those published in a recent study on plum flavan-3-ols in which a similar content of procyanidins was reported (500 mg/kg) (*21*). This can be explained by the analytical methods used in the present work that allowed the quantification of all the different procyanidins present in the extracts, even if they were not completely identified. Outstanding in their phenolic content were the plum cultivars Black Beaut and Angeleno.

These results are of interest, as the phenolic content of fruits can be related to their antioxidant activity and their health-promoting properties.

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