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Investigation of Bound Aroma Constituents of Yellow-Fleshed Nectarines (*Prunus persica* L. Cv. Springbright). Changes in Bound Aroma Profile during Maturation

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Glycosidically bound volatile constituents of yellow-fleshed clingstone nectarines (cv. Springbright) were identified and quantified at three stages of maturity. Glycoconjugates were isolated by LC on a C_{18} reversed phase column with methanol elution followed by hydrolysis with a commercial pectinase enzyme. Forty-five bound aglycons were identified for the first time in yellow-fleshed nectarine. Thirty were terpene derivatives, and the most abundant ones were (*E*)- and (*Z*)-furan linalool oxides, linalool, α-terpineol, (*E*)-pyran linalool oxide, 3,7-dimethylocta-1,5-diene-3,7-diol, linalool hydrate, 8-hydroxy-6,7-dihydrolinalool, (*E*)- and (*Z*)-8-hydroxylinalools, and (*E*)- and (*Z*)-8-hydroxygeraniols. The group of C_{13} norisoprenoids included 3-hydroxy-β-damascone, 3-hydroxy-7,8-dihydro-β-ionone, 3-oxo-α-ionol, 3-hydroxy-7,8-dihydro-β-ionol, 3-hydroxy-β-ionone, 3-oxo-7,8-dihydro-α-ionol, 3-hydroxy-5,6-epoxy-β-ionone, 3-oxo-retro-α-ionol (isomers I and II), 3-hydroxy-7,8-dehydro-β-ionol, 4,5-dihydrovomifoliol, and vomifoliol. Generally, levels of bound compounds, in particular monoterpenols and C_{13} norisoprenoids, increased significantly with maturation. δ-Decalactone was the only lactone found in the enzymatic hydrolysate of yellow-fleshed nectarine, but its level was much lower than that of its free form.

KEYWORDS: Nectarines; *Prunus persica*; flavor; aglycons; C_{13} norisoprenoids; maturation

INTRODUCTION

Contrary to what is commonly believed, nectarines (*Prunus persica* L. Batsch var. *nucipersica*) are not a cross between peaches and plums, but are members of the genus *Prunus* that includes apricots, plums, cherries, almonds, and peaches. Peaches and nectarines differ primarily in that nectarines have a smooth skin, whereas peaches are fuzzy-skinned. Both peaches and nectarines may be freestone—the pit is relatively free of the flesh—or clingstone—the pit adheres to flesh. Although the volatiles of peaches and nectarines have been investigated extensively (*1*−*17*), knowledge of their glycosidically bound aroma is quite limited. Previous studies on apricots, peaches, and yellow plums (*18*) or on white-fleshed nectarines (*10*, *19*) have shown that these fruits contain glycoconjugates of shikimic acid derived metabolites, monoterpenes, and C_{13} norisoprenoids and that these compounds play an important role as flavor precursors. In a previous work (*20*), we studied changes in the physicochemical characteristics and volatile composition of yellow-fleshed clingstone nectarines (cv. Springbright) during "on-tree maturation" and artificial ripening. The objective of this study was to identify the aglycons enzymatically released from the glycoconjugates of nectarines (cv. Springbright) and to determine changes in their levels during on-tree maturity.

EXPERIMENTAL PROCEDURES

Solvents. All solvents used in this study were of high purity and were redistilled before used.

Fruits. Yellow-fleshed clingstone nectarines (*P. persica* L. Batsch var. *nucipersica* cv. Springbright) were obtained from a local commercial orchard (R. Monteux-Caillet - Mouriès - Bouches-du-Rhône, France) in July 2001. The fruits were hand-picked at three different degrees of maturity, which were determined according to size, color, and firmness. The different degrees of maturity were classified as "unripe" (stage I), "commercial-ripe" (stage II), and tree-ripe (stage III). For each stage, ∼10 kg of fruit was washed and cut, and the pits were discarded. Fruits were then sliced into small pieces, immediately frozen with liquid nitrogen, and stored at −25 °C until analysis.

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Chemical Analyses. The total soluble solids content (SS) in juice (%Brix) was determined with an Atago PR-101 digital refractometer. Titratable acidity (TA) was determined by titrating 5 mL of juice to pH 8.1 with 0.1 N NaOH using an automatic titrator Crison Compact II with an autosampler. The individual sugars (glucose, fructose, and saccharose) and organic acids (malic and citric) were determined from 1 mL of juice using a single-injection HPLC technique as described by Doyon et al. (*21*). These measurements were determined in triplicate from the juice obtained from 300 g of fruit after homogenization and centrifugation (8500*g*; 20 min; 4 °C).

Isolation of Glycosidic Extracts. Two hundred grams of frozen fruit, 100 mL of distilled water, and 133.3 g of $(NH_4)_2SO_4$ were homogenized in a Waring blender for 3 min. The pulp was then centrifuged (9000*g*; 30 min; 4 °C), and the clear juice was filtered through glass wool and immediately recentrifuged (20000*g*; 30 min; 4 °C). Fifty milliliters of clear supernatant, diluted twice with distilled water, was subjected to LC on a C_{18} reversed phase column according to the method of Williams et al. (*22*). After being washed with 25 mL of H_2O and 25 mL of pentane/dichloromethane (2:1, v/v), the glycosidic extract was isolated by eluting with 25 mL of MeOH. The extract was dried over anhydrous Na_2SO_4, filtered through glass wool, and concentrated under reduced pressure (rotavapor) to 1 mL. The extract was then transferred into a small vial and concentrated to dryness at 60 °C under a stream of nitrogen.

Enzymatic Hydrolysis. One hundred microliters of citrate−phosphate buffer (0.2 M, pH 5.0) was added to the glycosidic extract, and the mixture was washed five times using 1 mL aliquots of pentane/dichloromethane (2:1, v/v). After the addition of 200 μL of Pectinase AR 2000 (70 mg·mL^{-1}; Gist-Brocades), the mixture was incubated for 16 h at 40 °C. The liberated aglycons were extracted five times with 1 mL aliquots of pentane/dichloromethane (2:1, v/v). The organic layer was dried over anhydrous Na_2SO_4, and 16 μg of 4-nonanol was added as standard. The extract was then concentrated at 40 °C to a final volume of 400 μL using a Dufton column. The extract was stored at −20 °C until analysis. All analyses were performed in triplicate.

GC-FID Conditions. A Varian 3300 gas chromatograph equipped with an on-column injector was used. The flow of hydrogen carrier gas was 1.5 mL/min. The oven was kept at 40 °C for 3 min, then programmed to 245 °C at 3 °C/min, and kept at 245 °C for 20 min. The injector was kept at 20 °C for 0.1 min, then programmed to 245 °C at 180 °C/min, and kept at 245 °C for 85 min. The FID was kept at 245 °C. One microliter of each sample was injected on a DB-Wax (J&W Scientific, Folsom, CA) capillary column (30 m × 0.32 mm i.d., 0.5 μm film thickness). The levels of the volatile compounds were expressed as 4-nonanol equivalents (assuming all of the response factors to be 1). The concentrations are to be considered as relative data because recovery after extraction and calibration factors related to the standard were not determined.

GC-MS Conditions. A Hewlett-Packard 5989 series II gas chromatograph equipped with an on-column injector was used with the same DB-Wax capillary column as above. The flow of helium N60 carrier gas was 1.5 mL/min. The oven and the injector temperature programs were as above. A Hewlett-Packard 5889A mass spectrometer with a quadrupole mass filter was used. Mass spectra were recorded in electronic impact (EI) ionization mode at 70 eV. The transfer line, source, and quadrupole temperatures were set, respectively, at 250, 250, and 120 °C. Mass spectra were scanned in the range *m*/*z* 29−350 amu at 1 s intervals. Identifications were carried out by comparison of linear retention index and EI mass spectra with published data or with data from authentic compounds.

HPLC Conditions. A Waters 600 E liquid chromatograph equipped with a Waters 610 fluid unit pump was used. A variable-wavelength UV−vis detector (Waters 486) set at 210 nm and a differential refractometer (Waters 410) were connected in series and used as detectors. Twenty microliters of each sample, obtained as described under Chemical Analyses, was injected on a 300 mm × 7.8 mm i.d. cation-exchange ICSep ICE-ION-300 column equipped with an ICSep ICE-GC-801/C guard column (Transgenomic, San Jose, CA). The column oven temperature was set at 30 °C, and the flow of mobile phase (0.008 N H_2SO_4) was 0.4 mL/min.

Table 1. Changes[a] in Soluble Solids (SS), Titratable Acidity (TA), and SS/TA Ratio of Yellow-Fleshed Nectarines (Cv. Springbright) at Three Stages of Maturity

compd	stage I	stage II	stage III
SS (% Brix)	10.8 ± 0.1 z	11.6 ± 0.2 y	13.0 ± 0.1 x
TA (g/100 g, reported as malic acid)	1.02 ± 0.05 z	0.86 ± 0.03 y	0.62 ± 0.03 x
SS/TA	10.6 ± 0.5 z	13.6 ± 0.2 y	21.1 ± 0.8 x

[a] Data are given as average ± standard deviation ($n = 3$). Values with different letters are significantly different (based on Newman–Keuls test, $p < 0.05$).

Table 2. Changes[a] in the Sugar and Organic Acid Contents of Yellow-Fleshed Nectarines (Cv. Springbright) at Three Stages of Maturity

compd	stage I	stage II	stage III
saccharose	5.89 ± 0.07 z	7.28 ± 0.01 y	8.14 ± 0.09 x
fructose	1.03 ± 0.01 z	1.05 ± 0.01 y	0.97 ± 0.02 x
glucose	1.01 ± 0.02 z	1.00 ± 0.01 z	0.95 ± 0.02 y
citric acid	0.48 ± 0.02 z	0.39 ± 0.01 y	0.12 ± 0.01 x
malic acid	0.68 ± 0.01 z	0.69 ± 0.01 y	0.67 ± 0.01 z

[a] Data expressed in g/100 g are given as average ± standard deviation ($n = 3$). Values with different letters are significantly different (based on Newman–Keuls test, $p < 0.05$).

RESULTS AND DISCUSSION

Chemical analyses of yellow-fleshed nectarines during the three described developmental stages are summarized in **Tables 1** and **2**. Levels of soluble solids, the SS/TA ratio, and saccharose levels significantly increased with maturation, whereas levels of titratable acidity and citric acid significantly decreased. Levels of fructose and glucose slightly decreased during maturation, whereas those of malic acid were found to be very similar for the three stages. The levels of fructose were slightly higher than those of glucose, and their ratio remained approximately the same during maturation. Saccharose, accounting for 74−81% of the total sugars in stages I and III, respectively, was correlated with SS ($r^2 = 0.95$; $p < 0.001$). These results are consistent with those previously reported for peaches or nectarines (*4*, *11*, *15*, *23*−*25*).

The glycosidic extracts of yellow-fleshed nectarine juices (cv. Springbright) obtained by C_{18} reversed phase extraction and methanol elution were hydrolyzed enzymatically to release the aglycons. A typical GC-FID separation of aglycons from yellow-fleshed nectarine is shown in **Figure 1**. The enzyme preparation used contains glycosidase activities (β-D-glucosidase, α-L-arabinofuranosidase, α-L-rhamnopyranosidase, and β-D-apiofuranosidase) involved in the hydrolysis of glycosides (*26*, *27*). The identified aglycons and their levels at the three stages of maturation are shown in **Table 3**. Forty-five aglycons were detected and quantified for the first time as bound aroma constituents in yellow-fleshed nectarines. In agreement with previous studies (*10*, *18*, *28*−*35*) the identified aglycons consisted of compounds arising from the fatty acid, shikimate, and terpene metabolisms. The most numerous aglycons were related to the last class, subdivided as monoterpenes and C_{13} norisoprenoids (**Table 4**). The monoterpene group made up >60% of the total level of aglycons in stage I, followed by shikimate and C_{13} norisoprenoid derivatives (20 and 15%, respectively). The relative proportion of monoterpenes decreased and that of C_{13} norisoprenoids increased with maturation to reach about the same percentage (∼40%), whereas the relative proportion of shikimates was unchanged.

Table 3. Levels[a] of Aglycons Identified in Enzymatic Hydrolysates of Glycosidic Extracts of Yellow-Fleshed Nectarines at Three Stages of Maturity

no.	RI[b]	compd	assignment[c]	stage I	stage II	stage III
		C6 compounds				
2	1359	hexanol	A	2.5 ± 0.6 z	2.0 ± 0.2 z	6.5 ± 0.8 y
3	1387	(*Z*)-3-hexen-1-ol	A	2.6 ± 0.3 z	3.1 ± 0.4 z	12.5 ± 0.4 y
4	1407	(*E*)-2-hexen-2-ol	A	12.8 ± 1.2 z	8.5 ± 0.7 y	11.7 ± 1.3 z
		monoterpenes				
5a	1438	(*E*)-furan linalool oxide	A	26.4 ± 3.3 z	19.3 ± 2.2 y	18.9 ± 0.9 y
5b	1465	(*Z*)-furan linalool oxide	A	3.3 ± 0.4 z	3.4 ± 0.3 z	5.7 ± 0.4 y
7	1539	linalool	A	37.7 ± 3.6 z	53.6 ± 3.7 y	102.0 ± 2.3 x
9	1688	α-terpineol	A	2.7 ± 0.2 z	6.4 ± 0.3 y	16.7 ± 1.3 x
10	1731	(*E*)-pyran linalool oxide	A	14.8 ± 1.8 z	11.5 ± 1.3 y	14.7 ± 0.6 z
13	1949	3,7-dimethylocta-1,5-diene-3,7-diol	A	36.6 ± 2.0 z	32.7 ± 3.6 z	50.5 ± 6.4 y
14	1981	linalool hydrate	A	2.7 ± 0.5 z	4.3 ± 0.3 y	12.0 ± 0.9 x
17	2220	8-hydroxy-6,7-dihydrolinalool	A	341.8 ± 23.4 z	234.4 ± 21.6 y	243.6 ± 25.8 y
18a	2285	(*E*)-8-hydroxylinalool	A	1333.2 ± 81.1 z	1082.1 ± 53.8 y	1008.0 ± 72.6 y
18b	2327	(*Z*)-8-hydroxylinalool	A	1985.4 ± 105.8 z	1705.3 ± 92.4 y	1724.8 ± 88.6 y
21	2442	uroterpenol	B (*28*)	1.5 ± 0.2 z	1.6 ± 0.3 z	3.8 ± 0.6 y
23a	2567	(*Z*)-8-hydroxynerol	A	17.3 ± 1.4 z	16.4 ± 1.7 z	22.5 ± 3.7 y
23b	2606	(*E*)-8-hydroxynerol	A	35.5 ± 2.3 z	35.3 ± 3.2 z	58.1 ± 7.9 y
25a	2614	(*Z*)-8-hydroxygeraniol	A	39.5 ± 2.4 z	40.4 ± 3.3 z	63.7 ± 9.3 y
25b	2652	(*E*)-8-hydroxygeraniol	A	92.0 ± 7.4 z	99.8 ± 8.4 z	167.9 ± 20.1 y
		shikimic acid derived				
6	1508	benzaldehyde	A	19.6 ± 0.6 z	13.8 ± 0.4 y	15.7 ± 0.8 x
8	1602	methyl benzoate	A	1.1 ± 0.2 z	3.1 ± 0.4 y	nd[d]
11	1869	benzyl alcohol	A	40.1 ± 1.7 z	27.5 ± 2.1 y	39.3 ± 4.3 z
12	1906	2-phenylethanol	A	153.9 ± 13.8 z	139.5 ± 15.0 z	236.7 ± 15.4 y
15	2164	eugenol	A	1047.1 ± 153.9 z	806.6 ± 73.7 y	1210.2 ± 107.3 z
19	2340	chavicol	A	85.4 ± 9.0 z	129.8 ± 14.5 y	305.3 ± 28.0 x
20	2356	isoeugenol	A	0.5 ± 0.1 z	0.7 ± 0.0 y	nd
35	2980	dihydroconiferyl alcohol	A	0.7 ± 0.1 z	1.0 ± 0.2 z	7.9 ± 2.3 y
40		coniferyl alcohol	A	5.3 ± 0.6 z	10.3 ± 0.8 y	9.0 ± 2.0 y
		C_{13} norisoprenoids				
22	2563	3-hydroxy-β-damascone	A	19.5 ± 1.3 z	16.5 ± 1.5 z	25.8 ± 3.9 y
24	2571	3-hydroxy-7,8-dihydro-β-ionone	B (*18*)	34.6 ± 6.0 z	74.2 ± 8.5 y	223.7 ± 20.1 x
26	2667	3-oxo-α-ionol	A	4.7 ± 0.2 z	21.0 ± 1.1 z	42.9 ± 15.5 y
27	2681	3-hydroxy-7,8-dihydro-β-ionol	B (*29*)	180.9 ± 11.3 z	381.1 ± 34.9 y	1279.6 ± 124.4 x
28	2693	3-hydroxy-β-ionone	B (*30*)	18.3 ± 1.4 z	74.5 ± 7.5 y	214.6 ± 16.2 x
29	2732	3-oxo-7,8-dihydro-α-ionol	B (*31*)	1.5 ± 0.9 z	1.2 ± 0.3 z	9.0 ± 1.3 y
30	2739	3-hydroxy-5,6-epoxy-β-ionone	B (*18*)	49.3 ± 4.7 z	48.9 ± 5.2 z	81.9 ± 5.2 y
31a	2752	3-oxo-retro-α-ionol (I)	A	2.7 ± 0.4 z	2.6 ± 0.3 z	7.8 ± 0.3 y
32	2770	3-hydroxy-7,8-dehydro-β-ionol	A	8.1 ± 0.5 z	7.1 ± 0.8 z	12.9 ± 1.6 y
31b	2890	3-oxo-retro-α-ionol (II)	A	7.3 ± 0.9 z	8.1 ± 0.9 z	17.2 ± 1.7 y
33	2905	unknown C_{13} 1[f]	C	98.1 ± 12.5 z	150.8 ± 17.7 z	460.6 ± 47.9 y
36	3017	4,5-dihydrovomifoliol	B (*32*)	41.2 ± 2.9 zy	38.0 ± 3.4 z	50.8 ± 7.5 y
37	3088	unknown C_{13} 2[g]	C	358.9 ± 37.7 z	408.7 ± 43.6 z	902.2 ± 87.7 y
38	3103	unknown C_{13} 3[h]	C	67.7 ± 16.0 z	92.8 ± 5.6 z	266.3 ± 24.6 y
39	3175	vomifoliol	A	45.5 ± 4.6 z	41.8 ± 0.9 z	81.3 ± 18.6 y
		miscellaneous				
1		3-methyl-1-butanol	A	24.9 ± 1.6 z	15.1 ± 0.8 y	13.5 ± 0.5 y
16	2193	δ-decalactone	A	1.8 ± 0.2 z	0.5 ± 0.1 z	31.2 ± 6.1 y
34	2923	hexadecanoic acid	A	6.3 ± 1.1 z	7.7 ± 1.1 z	22.6 ± 5.2 y

[a] Data expressed in μg/kg equivalents of 4-nonanol are given as average ± standard deviation ($n = 3$). Values with different letters are significantly different (based on Newman–Keuls test, $p < 0.05$). [b] RI, linear retention index based on a series of *n*-hydrocarbons. [c] A, identities confirmed by comparing mass spectra and retention times with those of authentic standards; B, identities tentatively assigned by comparing mass spectra with those obtained from literature numbered and italicized within parentheses; C, tentatively identified. [d] nd, not determined. [e] Major mass spectral fragments [*m*/*e* (%)]: 83 (100), 85 (81), 45 (41), 55 (35), 68 (25), 124 (22), 96 (21), 82 (21), 43 (20), 73 (19). [f] Major mass spectral fragments [*m*/*e* (%)]: 85 (100), 83 (73), 153 (50), 55 (43), 135 (36), 124 (22), 96 (19), 73 (19), 125 (19), 68 (18). [g] Major mass spectral fragments [*m*/*e* (%)]: 85 (100), 45 (61), 152 (46), 110 (41), 55 (40), 84 (39), 96 (38), 111 (34), 83 (27), 134 (21).

The bound monoterpenic aglycons occurred at two oxidation stage levels (**Figure 2**). The only four monoterpene alcohols at the linalool oxidation stage were two monoterpenols (**7**, **9**) and two monoterpenediols (**14**, **17**). Those at higher oxidation stage were three linalool oxides (**5a**/**b** and **10)** and eight monoterpene diols (**13**, **18a**/**b**, **21**, **23a**/**b**, and **25a**/**b**). Linalool (**7**) and α-terpineol (**9**) are widespread as free aroma volatiles in the plant kingdom and have already been identified as aglycons in other *Prunus* fruits such as apricot, peach, and yellow plum (*18*) and in various other fruits (*35*−*49*). Nevertheless, these compounds had not been observed in the glycosidic fraction of white-fleshed nectarines (*10*), as well as linalool hydrate (**14**), found at much lower levels than linalool (∼1:10), which could be an artifact (*50*). On the contrary, 8-hydroxy-6,7-dihydrolinalool (**17)** was previously identified in white-fleshed nectarine (*10*), in *Prunus* fruits (*18*, *51*), and in various other fruits (*35*, *37*−*39*, *43*, *46*, *52*). The other monoterpenediols 3,7-dimethylocta-1,5-diene-3,7-diol (**13),** (*Z*)- and (*E*)-8-hydroxynerol (**23a**/**b),** and (*Z*)- and (*E*)-8-hydroxygeraniol (**25a**/**b**) were identified for the first time as aglycons in nectarine, but monoterpene **25a** has already been identified as an aglycon in peach (*18*). Contrary to monoterpenols **7** and **9**, the linalool oxides and monoterpenediols have very high sensory detection thresholds (*53*) but could generate aroma compounds during the biotechnological transformation of these fruits (*54*, *55*).

At all maturity stages, the levels of diols **17** and (*E*)- and (*Z*)-8-hydroxylinalool (**18a**/**b**) were much higher than those of the other monoterpenes, accounting for ∼85−90% of the

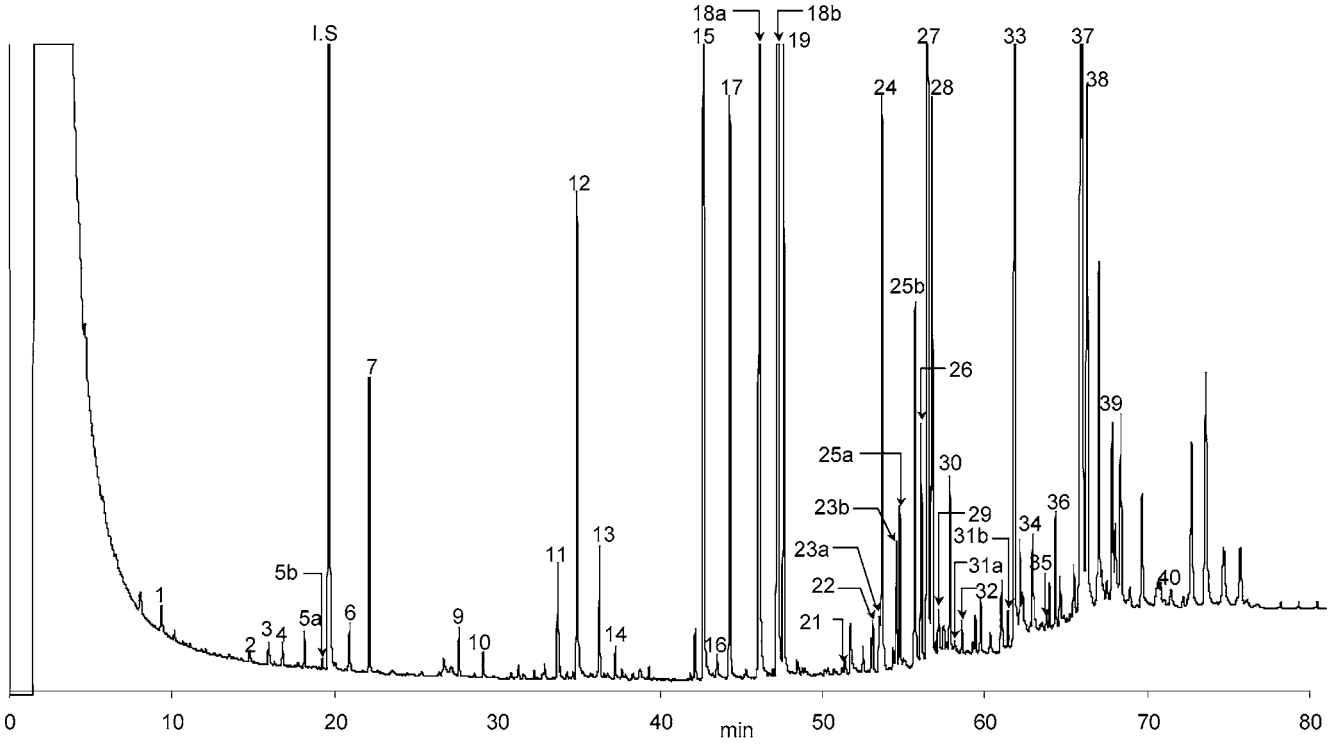

Figure 1. GC-FID separation of aglycons from yellow-fleshed nectarines (cv. Springbright) on a J&W DB-Wax capillary column (30 m × 0.32 mm i.d.; df = 0.5 μm). The numbers correspond to the numbers given in **Table 3**. I.S. = internal standard, 4-nonanol.

Table 4. Relative Proportions[a] of the Main Aglycon Classes of Yellow-Fleshed Nectarines (Cv. Springbright) at Three Stages of Maturity

compd (n)[b]	stage I	stage II	stage III
C_6 compounds (3)	0.28 ± 0.01 z	0.23 ± 0.01 y	0.33 ± 0.04 z
monoterpenes (15)	62.9 ± 1.4 z	57.5 ± 0.4 y	40.0 ± 0.3 x
shikimic acid derived (9)	21.4 ± 1.1 z	19.0 ± 0.1 y	19.6 ± 0.5 y
C_{13} norisoprenoids (15)	14.8 ± 0.3 z	22.9 ± 0.4 y	39.3 ± 0.8 x
miscellaneous (3)	0.52 ± 0.02 z	0.39 ± 0.03 y	0.72 ± 0.05 x

[a] Relative proportions of levels expressed as 4-nonanol equivalents are given as average ± standard deviation (n = 3). Values with different letters are significantly different (based on Newman–Keuls test, p < 0.05). [b] Number of compounds identified in each class.

monoterpene total. Linalool oxides (*E*)- and (*Z*)-furan linalool oxides (**5a**/**b)** and (*E*)-pyran linalool oxide (**10)** have not yet been identified as aglycons in nectarine, but they have been previously detected in glycosidic extracts of apricot or peach (*18*). Uroterpenol (*p*-menth-1-ene-8,9-diol) (**21**), previously detected in Riesling wine (*28*) and found at levels similar to those of linalool hydrate (**14**), could also be an artifact, formed by acid-catalyzed cyclization from glycosides of the major monoterpenes diols **18a/b** (*28*). As shown in **Table 3**, the levels of the bound odorants **7** and **9** increased significantly with maturation. The same trend was observed for the monoterpene-diols **13**, **14**, **23a**/**b**, and **25a**/**b**, but the levels of the most abundant ones, **17** and **18a**/**b**, structurally related to linalool, significantly decreased with increasing maturity. The levels of linalool oxides **5a**/**b** and **10**, although statistically different, were found to be in the same range at different maturation stages.

With regard to the shikimate-derived compounds, benzaldehyde (**6**), benzyl alcohol (**11**), 2-phenylethanol (**12**), eugenol (**15**), dihydroconiferyl alcohol [3-(4′-hydroxy-3′-methoxyphenyl)-propan-1-ol] (**35**), and coniferyl alcohol (**40**) have already been identified as aglycons in *Prunus* species (*10*, *18*) and in various fruits (*35*, *37*−*39*, *43*, *46*, *56*). Methyl benzoate (**8**), chavicol (4-allylphenol) (**19**), and isoeugenol (**20**) were identified for the first time as aglycons in nectarine. Nevertheless, methyl benzoate (**8**), previously identified as one of the main aglycons in lulo fruit pulp (*46*), was probably an artifact formed from benzoic acid. As summarized in **Table 3**, the most significant changes observed with maturation were the increases of the levels of 2-phenylethanol (**12**) and chavicol (**19**). In particular, the levels of **19** showed a 2.6-fold increase in the tree-ripe samples compared to those observed in the unripe samples.

Numerous C_{13} norisoprenoids were found as aglycons in the glycosidic extracts from nectarines (**Figure 3**). Some oxidized C_{13} norisoprenoidic aglycons could be formed as oxidative artifacts from 3-hydroxymegastigmane glycoconjugates during their enzymatic hydrolysis with high concentrations of fungal-derived glycosidase enzyme preparation (*57*). Because 3-oxo-α-damascone, 3-oxo-β-damascone, dehydrovomifoliol, and 3-oxo-7,8-dihydro-α-ionol (**29**) were absent or detected at low levels only in the aglycons liberated from our extracts (**Table 3**), the oxidative activity was probably absent from the enzyme preparation used in this study. These compounds are important aroma constituents (*57*−*60*), and most of those shown in **Table 3** have been previously identified in numerous natural products (*61*). These compounds would derive from the carotenoids of nectarine. Oxygenated carotenoids, neoxanthin (an allenic xanthophyll), violaxanthin (an epoxy xanthophyll), and lutein (a non-epoxy xanthophyll) have been previously identified in nectarines (*62*), and the presence of regiospecific carotenoid cleavage enzymes in quince (*Cydonia oblonga*) and star (*Averrhoa carambola*) fruits (*63*, *64*) has been recently shown. Among the C_{13} norisoprenoids identified in yellow-fleshed glycoside fraction, **22** and **32** were allenic xanthophyll derivatives, **30**, **36**, and **39** were epoxy xanthophyll derivatives, and **24**, **26**−**29**, and **31a/b** were non-epoxy xanthophyll derivatives. 3-Hydroxy-β-damascone (**22**) has been previously reported as a bound constituent in peach (*18*), but its identification as an

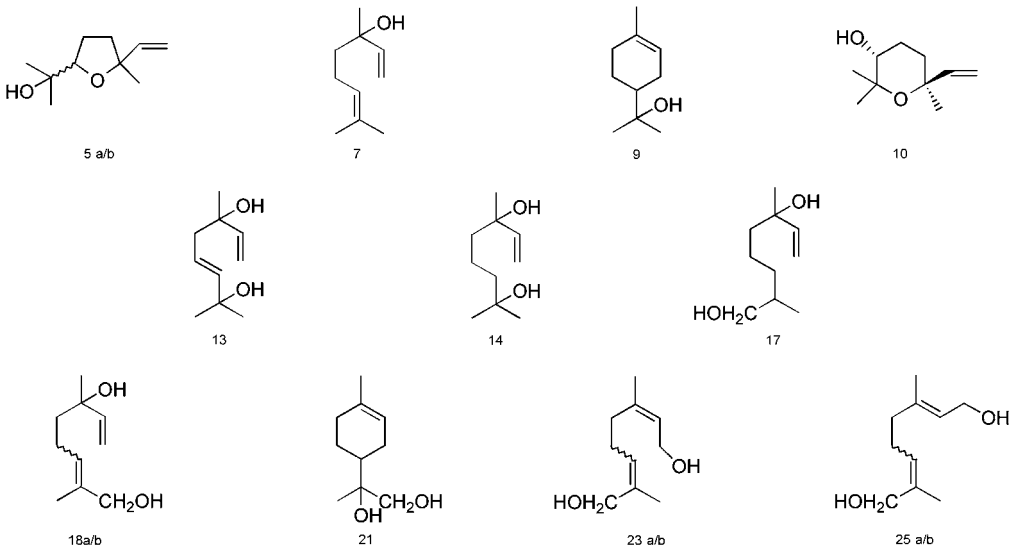

Figure 2. Structures of monoterpenoid aglycons identified in yellow-fleshed nectarines (cv. Springbright).

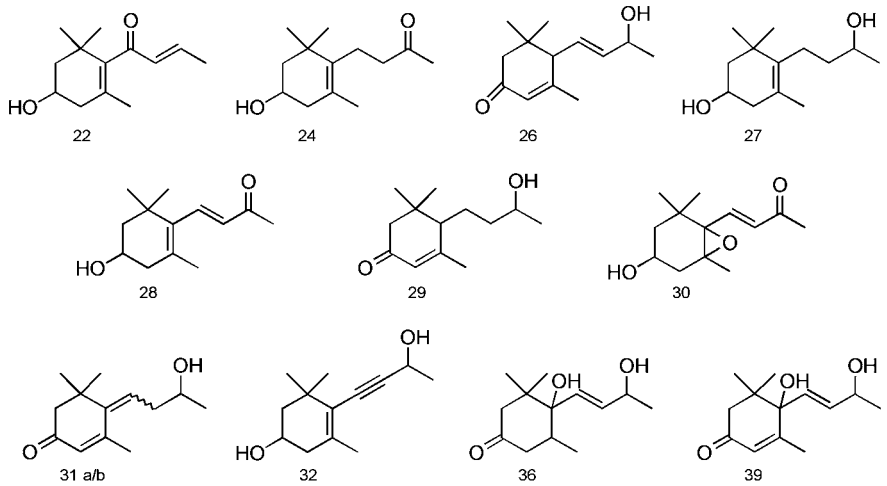

Figure 3. Structures of C_{13} norisoprenoid aglycons identified in yellow-fleshed nectarines (cv. Springbright).

aglycon in nectarine has never been reported. The acetylenic diol **32** (3-hydroxy-7,8-dehydro-β-ionol) has not yet been reported in *Prunus* species. This compound is of particular interest due to its important role as a precursor of damascenone, a potent flavor compound, (*65*, *66*). Among epoxy xanthophyll derivatives, 3-hydroxy-5,6-epoxy-β-ionone (**30**) has already been identified in different *Prunus* species such as apricot, peach, and yellow plum (*18*), but it is the first report of its occurrence in a bound form in nectarines. 4,5-Dihydrovomifoliol (**36**) has not yet been reported in *Prunus* species. On the contrary, vomifoliol (**39**) and the non-epoxy xanthophyll derivatives 3-hydroxy-7,8-dihydro-β-ionone (**24**), 3-oxo-α-ionol (**26**), 3-hydroxy-7,8-dihydro-β-ionol (**27**), 3-hydroxy-β-ionone (**28**), and 3-oxo-7,8-dihydro-α-ionol (**29**) have already been reported as bound constituents in white-fleshed nectarine (*10*) or in *Prunus* species (*18*). The bound form of 3-oxo-retro-α-ionol (isomer I) (**31a**) has not yet been reported in *Prunus* species, whereas the bound form of isomer II (**31b**) had been previously identified in white-fleshed nectarine (*10*). Last, three aglycons, **33**, **37**, and **38**, were tentatively identified as unknown norisoprenoids according to their mass spectra. As reported in **Table 3**, the levels of the C_{13} norisoprenoid aglycons significantly increased with maturation, those of **26**−**29**, **31a**/**b**, **33**, **37**, and **38** showing a 3−12-fold increase in tree-ripe samples compared to those in unripe nectarines. The increase of the levels of these carotenoid degradation products with maturation was similar to that observed previously in grape (*67*).

With regard to miscellaneous constituents, it is noteworthy that only one lactone, δ-decalactone (**16**), was found in the enzymatic hydrolysates of yellow-fleshed nectarine glycosides. Indeed, lactones are key aroma compounds in nectarines (*7*, *8*). This compound, previously reported as a bound compound in raspberry (*35*) or in pineapple (*68*), has already been identified in enzymatic hydrolysates of white-fleshed nectarine (*10*) and peach glycosides (*51*). As δ-decalactone (**16**) has no chemical function able to be glycosylated, its glycosylated precursors are probably glycoconjugates of the corresponding hydroxyacid. Such structurally related derivatives were reported previously for whiskey (*69*) and marmelo lactones (*70*); the latter were reported previously in the enzymatic hydrolysates of peach glycosides (*18*). In our opinion, the occurrence of free δ-decalactone, or of free 5-hydroxydecanoic acid, in these glycosidic extracts was not consistent with the absence in the same extracts of other γ- or δ-lactones, identified as volatiles of yellow-fleshed nectarines (*20*). In particular, γ-hexalactone, more polar and more abundant than δ-decalactone, would be extracted more efficiently in the conditions used in this study to obtain nectarine glycosides. Furthermore, just before the enzymatic hydrolysis step, the glycosidic extract was extensively washed with pentane/dichloromethane (2:1, v/v) in order to eliminate possible

remaining volatiles (see Experimental Procedures). As observed for free δ-decalactone (*20*), the levels of its bound form, much lower than those of its free form, were found to be significantly higher in the tree-ripe samples compared to the earlier stages.

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