

Investigation of Volatile Constituents in Nectarines. 1. Analytical and Sensory Characterization of Aroma Components in Some Nectarine Cultivars

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Volatile constituents of nectarines (*Prunus persica* L., Batsch var. *nucipersica* Schneid) were isolated by means of liquid-liquid extraction with ether and analyzed by capillary gas chromatography and gas chromatography-mass spectrometry. Aroma patterns (10 lactones, 8 C₆ aldehydes and alcohols, 8 terpenoids, 3 esters, 4 other compounds) were identified and (semi)quantified in four cultivars. Besides C₆ components a series of saturated and unsaturated γ - and δ -lactones ranging from chain length C₆ to C₁₂, with concentration maxima for γ - and δ -decalactone, were a major class of constituents. By determination of odor thresholds and calculation of odor units the significance of lactones and other volatiles (e.g., linalool) to the aroma of nectarines was investigated.

Nectarines (*Prunus persica* L., Batsch var. *nucipersica* Schneid) are members of the same species as peaches and not a cross between peaches and plums as is commonly believed. Their popularity is increasing worldwide, often at the expense of peaches. California nectarine production increased from 24 000 tons in 1955 to 211 000 tons in 1985, almost equaling the production of peaches (243 000 tons in 1985), which slightly decreased during the same period (*California Tree Fruit Agreement*, 1985).

Peach volatiles have been investigated intensively (Maarse and Viischer, 1984), whereas knowledge about flavor and aroma components in nectarines is limited. Lim and Romani (1964) followed volatile fractions at different stages of fruit maturity using gas chromatography, but individual compounds have not been identified as yet. Therefore, analytical characterization of aroma patterns in nectarine cultivars was our first goal.

Lactones were of special interest during these investigations. The intensive "lactonic" aroma was one of the main reasons that led us to choose nectarines as a study subject. Many foods contain γ - and δ -lactones as aroma-contributing components (Maga, 1976). In peaches a number of saturated and unsaturated lactones were identified as volatile constituents (Jennings and Sevenants, 1964; Sevenants and Jennings, 1966, 1971). A special feature of lactones, very often neglected during aroma investigations in the past, is their chirality. Determination of the naturally occurring configuration of chiral aroma constituents at the trace level has been a major aim of research in our recent studies (Tressl and Engel, 1984; Tressl et al., 1985; Engel et al., 1987a). The sensory properties of nectarines indicated that these fruits might be an ideal system for these investigations.

Changes in the distribution of γ - and δ -lactones during the maturation of nectarines and determination of the chiral nature of these constituents will be described in

following papers of this series (Engel et al., 1987b, 1988). In this first paper we report the gas chromatographic-mass spectrometric identification, (semi)quantification, and sensory evaluation of volatiles in nectarines, with special regard to lactone constituents.

EXPERIMENTAL SECTION

Materials and Methods. Four nectarine cultivars (Sunfre, Flavortop, P 62-27, P 89-56) were obtained from orchards of the Horticultural Crops Research Laboratory of the U.S. Department of Agriculture, Fresno, CA. Flavortop and Sunfre are commercially grown cultivars. Flavortop was developed by the U.S. Horticultural Field Station, Fresno, CA (Weinberger, 1970). Sunfre has been jointly released by the USDA in Fresno and the University of Florida (Andrews et al., 1982). P 62-27 (yellow flesh) and P 89-56 (white flesh) are experimental cultivars presently being tested by the USDA in Fresno. The fruits were picked at "tree-ripe" stage and analyzed within 24 h. In our opinion the cultivars Sunfre and P 89-56 showed the most intensive lactonic, peachlike aroma of the material used for investigation in this study. P 89-56 possessed an additional unique flowery note, which is typical for many of the white-flesh cultivars. Flavortop has a more floral, estery character.

Sample Preparation. After peeling and removal of the stone, 500 g of fruit pulp was homogenized with distilled water (500 mL) in a Waring blender for 30 s. The mixture was transferred immediately to a liquid-liquid extractor, and 250 μ g of the internal standard (S)-(+)-octanol-2 (stock solution: 5 mg in 1 L of H₂O) was introduced. Distilled water was added to the extraction flask contents (total volume 9 L), and the extraction was carried out for 24 h with distilled ether as solvent. The flask containing the solvent (250 mL) was heated in a water bath (45 °C); after the first 12 h of extraction the ether was replaced by a new batch. The aroma extracts were dried over Na₂SO₄ and concentrated (water bath, 45 °C) to a volume of 750 μ L on a Vigreux column.

Capillary Gas Chromatography (GC). Capillary GC investigations were carried out on a 60 m \times 0.322 mm DB-Wax column (0.25- μ m film thickness; J&W Scientific, Inc.) and a 60 m \times 0.315 mm DB-1 column (0.25- μ m film thickness; J&W Scientific). The columns were installed in Hewlett-Packard 5830A gas chromatographs equipped with split injector (1:25) and flame ionization detector (FID). Temperature programs from 50 to 230 °C at 4

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Table I. Volatile Constituents Identified in Nectarines

component ^a	KI DB-Wax	KI DB-1	concentration, $\mu\text{g}/\text{kg}$			Flavortop
			Sunfre	P 89-56	P 62-27	
1. Lactones						
γ -hexalactone	1694	1003	350	350	300	270
γ -heptalactone	1797	1103	40	10	30	10
γ -octalactone	1911	1210	300	100	50	10
δ -octalactone	1964	1234	140	130	30	+ ^b
γ -nonalactone	2024	1315	+	+	+	+
γ -decalactone	2142	1422	1900	2200	650	220
6-pentyl- α -pyrone	2176	1415	280	100	120	70
δ -decalactone	2195	1447	1000	1400	340	190
(<i>Z</i>)-dec-7-en-5-olide	2257	1442	310	260	30	30
γ -dodecalactone	2379	1636	+	230	+	+
2. C ₆ -Aldehydes and Alcohols						
hexanal	1078	772	580	740	600	1950
(<i>E</i>)-3-hexenal	1131	770	+	+	+	+
(<i>Z</i>)-3-hexenal	1138	769	30	+	10	40
(<i>Z</i>)-2-hexenal	1200	815	10	+	10	40
(<i>E</i>)-2-hexenal	1215	822	1340	1900	960	3950
hexanol	1352	847	100	80	50	180
(<i>Z</i>)-3-hexenol	1381	834	30	40	30	110
(<i>E</i>)-2-hexenol	1404	844	100	110	30	170
3. Terpenoids						
α -phellandrene	1162	996	+	+	+	20
α -terpinene	1178	1008	+	+	+	+
β -phellandrene	1208	1018	+	- ^c	+	+
γ -terpinene	1245	1048	30	+	10	30
(<i>Z</i>)- β -ocimene	1232	1026	+	-	+	+
terpinolene	1281	1077	10	-	+	+
linalool	1545	1083	+	-	10	500
hotrienol	1085	1606	50	+	20	90
4. Esters						
hexyl acetate	1270	994	+	+	10	20
(<i>Z</i>)-3-hexenyl acetate	1315	986	20	+	10	50
(<i>E</i>)-2-hexenyl acetate	1331	994	+	+	+	10
5. Others						
benzaldehyde	1516	926	200	170	90	20
acetoin	1282	673	10	+	+	+
furfural	1454	800	+	+	+	+
furfuryl alcohol	1653	826	+	+	+	+

^a Mass spectra identical with those of authentic reference compounds. ^b Concentration less than 10 ppb. ^c Not detected.

$^{\circ}\text{C}/\text{min}$ (DB Wax) and 50 to 250 $^{\circ}\text{C}$ at 4 $^{\circ}\text{C}/\text{min}$ (DB-1) were used. The injector temperature was 200 $^{\circ}\text{C}$; the detector temperature was maintained at 225 $^{\circ}\text{C}$ (DB-Wax) and 250 $^{\circ}\text{C}$ (DB-1). Helium at a flow rate of 3.5 mL/min was used as a carrier gas. Injection volume was 1 μL . Kovats' indices were determined by coinjection of samples and reference compounds with a series of normal hydrocarbons (C₆-C₂₅).

Capillary Gas Chromatography-Mass Spectrometry. A Finnigan MAT 4500 series quadrupole gas chromatograph-mass spectrometer (GC-MS) coupled with an IncoS data system was used for mass spectrometric analyses. The end of the fused silica column (described above) was inserted directly into the ion source block. The spectra were recorded at an ionization voltage of 70 eV, at an ion source temperature of 180 $^{\circ}\text{C}$, and with a speed of 1 scan/s over a mass range of m/e 33-350.

Odor Thresholds. Reference compounds were purified by preparative gas chromatography, and their odor thresholds were determined in Teflon squeeze bottles according to the procedure described by Guadagni et al. (1973) and Guadagni and Buttery (1978).

RESULTS AND DISCUSSION

Aroma constituents of two commercial (Sunfre, Flavortop) and two experimental (P 89-56, P 62-27) nectarine cultivars were isolated by means of continuous liquid-liquid extraction using diethyl ether as solvent. Direct

extraction of fruit pulp with an organic solvent has some disadvantages such as formation of emulsions or coextraction of gas chromatographically undesirable constituents (e.g., pigments). Nevertheless, in the present study this technique was preferred to headspace or distillation procedures, because a higher yield for the polar lactone constituents was expected. The concentrated extracts had the typical nectarine aroma; there was however a certain lack of "fresh, fruity" and a preponderance of "heavy" notes.

The extracts were investigated by capillary GC and by capillary GC-mass spectrometry. Compound identification was achieved by comparison of gas chromatographic (Kovats indices) and mass spectral data with those of authentic reference compounds. Quantification of the constituents was based on (*S*)-(+)-octanol-2 as internal standard. The determined concentrations are to be considered as approximate values, because calibration factors related to the standard, involving variations in gas chromatographic (FID) response and the recovery after the extraction were not determined. In test extractions with water solutions approximately 90% (related to 2-octanol) of added lactones were reisolated. The results are summarized in Table I.

Lactones. Saturated and unsaturated γ - and δ -lactones from chain length C₆ to C₁₂ constitute a major class of components in nectarines. The cultivars show significant differences in the concentrations of individual lactones.

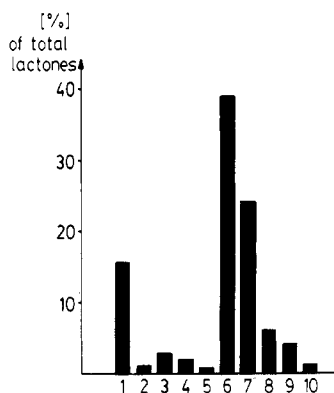


Figure 1. Average distribution of lactones in nectarines. x-Axis lactones: 1 = γ -hexalactone; 2 = γ -heptalactone; 3 = γ -octalactone; 4 = δ -octalactone; 5 = γ -nonalactone; 6 = γ -decalactone; 7 = δ -decalactone; 8 = 6-pentyl- α -pyrone; 9 = (*Z*)-dec-7-en-5-olide; 10 = γ -dodecalactone.

The total amounts of lactones range from 10% of the isolated volatiles in Flavortop to 61% and 63% in Sunfre and P 89-56, respectively. Within the homologous series of lactones, however, there is a common pattern with pronounced maxima for γ - and δ -decalactone. Lactones with even-numbered carbon chains are quantitatively predominant. γ -Heptalactone and γ -nonalactone are only minor constituents; γ -undecalactone, which has a typical peach aroma (Maga, 1976), could not be detected in this study. Whether some of the quantitative differences in the contents of lactones, e.g. the high concentration of γ -dodecalactone in P 89-56, are really specific for the cultivars or due to other factors has to be determined in further experiment. The average distribution of lactones in the nectarine material available in this study is shown in Figure 1.

The spectrum is qualitatively similar to the pattern of lactones identified in peaches (Jennings and Sevenants, 1964; Sevenants and Jennings, 1966, 1971).

γ -Decalactone is the major lactone in both peaches and nectarines. A comparison with the data of Do et al. (1969) and Mori (1977) shows that nectarines contain significantly higher amounts of δ -decalactone than do peaches.

Two unsaturated lactones, structurally related to δ -decalactone, were identified. The mass spectrum of 6-pentyl- α -pyrone was consistent with that published by Jennings and Shibamoto (1980). Sevenants and Jennings (1971) identified the compounds in peaches. Aroma qualities of 6-pentyl- α -pyrone were described as coconut, peachlike, lactonic, and green (Pittet and Klaiber, 1975).

(*Z*)-Dec-7-en-5-olide (jasmin lactone) was first characterized as an aroma-contributing component in jasmin essence by Winter et al. (1962). The major mass spectral fragments are as follows [*m/e* (%): 99 (100), 71 (71), 55 (35), 41 (27), 43 (24), 42 (13), 39 (13), 81 (11), 68 (10), 108 (8). Yamanishi et al. (1973) identified the compound in Ceylon tea and described its aroma as powerful and fruity, reminiscent of peach and apricot. The sweet odor of gardenia flowers has also been attributed to this lactone (Hattori et al., 1978).

Odor Thresholds. To get an idea of the significance of the lactones to the aroma of nectarines, we determined odor thresholds in water of some of the identified compounds. Quantitation data from cultivar P 89-56 was selected as a basis for odor unit calculations because relatively high lactone concentrations were found in this cultivar. The results are shown in Table II. The odor potency of lactones strongly depends upon the presence of an aliphatic side chain. The threshold of γ -octalactone

Table II. Detection Odor Thresholds (T_c) in Water and Odor Units (U_0) in the Nectarine Cultivar P 89-56 of Some γ - and δ -Lactones

component	$T_c(\text{H}_2\text{O})^a$ ppb	U_0^b
γ-Lactones		
γ -hexalactone	1600	0.1
γ -heptalactone	400	0.02
γ -octalactone	7	14
γ -decalactone	11	183
γ -dodecalactone	7	33
δ-Lactones		
γ -octalactone	400	0.3
δ -decalactone	100	14
6-pentyl- α -pyrone	150	0.7
(<i>Z</i>)-dec-7-en-5-olide	2000	0.1

^a ppb = parts (mL) of compound per billion (10^9) parts (mL) of water. U_0 = ratio of concentration (ppb) of compound in nectarines and odor threshold (ppb).

is more than 200 times lower than the threshold of γ -hexalactone. A comparison of the values determined for γ - and δ -octalactone, and γ - and δ -decalactone, respectively, shows that the structural element of a five-membered ring increases the potency compared to the six-membered ring. The two double bonds in the ring system of 6-pentyl- α -pyrone have only a small effect on its odor potency compared to the saturated analogue δ -decalactone. However, modification of the side chain by a double bond increases the threshold significantly, as shown for jasmin lactone.

Rothe and Thomas (1963) and Guadagni et al. (1966) developed the concepts of aroma values and odor units, respectively, to determine the importance of volatile constituents to the odor of complex mixtures. The ratios of concentration and odor threshold reflect the relative contribution of aroma components to the final aroma of a food. Table II presents odor units calculated on the basis of detection odor thresholds and (approximate) concentrations of lactones in nectarines.

Compounds such as γ -hexalactone, γ -heptalactone, or δ -octalactone are present in nectarines in concentrations below their threshold levels; their odor units are less than 1, and they should have no or only little effect on the aroma of nectarines. On the other hand the odor units demonstrate that γ -decalactone, γ -dodecalactone, δ -decalactone, and γ -octalactone make important contributions to the aroma of nectarines.

Other Constituents. Beside the lactones, C_6 -aldehydes and alcohols were isolated as major volatiles. As the enzyme systems were not inhibited before the homogenization of the pulp, the concentrations listed in Table I are probably not identical with the amounts of C_6 components present in the intact fruit. They might be increased by additional enzyme-catalyzed breakdown of fatty acid precursors. The values, however, are comparable among the different varieties and reflect their lipoxygenase activities at the tree-ripe stage. Some of the C_6 components, especially the aldehydes, are present at concentrations above their odor threshold levels (hexanal, 4.5 ppb; (*Z*)-3-hexenal, 0.25 ppb; (*E*)-2-hexenal, 17 ppb (Buttery et al., 1971)). They should contribute to nectarine aroma.

The cultivar Flavortop contains the highest amount of terpenoid compound. Linalool is present at a concentration far above (83 odor units) its odor threshold in water of 6 ppb (Buttery et al., 1969). The cooccurrence of the monoterpene alcohols linalool and hotrienol with the monoterpene hydrocarbons listed in Table I is similar to findings reported in grapes (Williams et al., 1982), passion fruit (Engel and Tressl, 1983) and papaya (Schreier et al.,

1985), where these compounds are released from nonvolatile precursors. In peaches the concentrations of linalool and hotrienol also increase during processing as shown by Souty and Reich (1978).

The number of esters identified in this study is very limited, which is probably due to the isolation method chosen; distillation and headspace procedures are superior to direct extraction with ether. Takeoka et al. (1988), who did use distillation and headspace approaches, isolated a complex mixture of saturated and unsaturated esters, which might be biogenetically related to the γ - and δ -lactones identified in this study.

The spectrum of compounds investigated in this study is relatively small, but the analytical data partly reflect the sensorially perceived qualities of some of the cultivars. The exceptionally high concentrations of lactones determined in Sunfre and P 89-56 correlate well with the intensive lactonic aroma of these cultivars; the high amount of linalool might explain the floral note of Flavortop. In the white-flesh cultivar P 89-56 we detected another aroma-intensive constituent (approximate concentration 4000 $\mu\text{g}/\text{kg}$); its mass spectrum (MW 206) indicated an ionone-type compound. The final characterization of this compound, which might be responsible for the unique flowery character of white-flesh cultivars, and the identification of other minor constituents will be part of studies in the coming nectarine season.

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Registry No. γ -Hexalactone, 695-06-7; γ -heptalactone, 105-21-5; γ -octalactone, 104-50-7; δ -octalactone, 698-76-0; γ -nonalactone, 104-61-0; γ -decalactone, 706-14-9; 6-pentyl- α -pyrone, 27593-23-3; 8-decalactone, 705-86-2; (Z)-dec-7-en-5-olide, 100428-67-9; γ -dodecalactone, 2305-05-7; hexanal, 66-25-1; (E)-3-hexenal, 69112-21-6; (Z)-3-hexenal, 6789-80-6; (Z)-2-hexenal, 16635-54-4; (E)-2-hexenal, 6728-26-3; hexanol, 111-27-3; (Z)-3-hexenol, 928-96-1; (E)-2-hexenol, 928-95-0; α -phellandrene, 99-83-2; α -terpinene, 99-86-5; β -phellandrene, 555-10-2; γ -terpinene, 99-85-4; (Z)- β -ocimene, 3338-55-4; terpinolene, 586-62-9; linalool, 78-70-6; hotrienol, 20053-88-7; hexyl acetate, 142-92-7; (Z)-3-hexenyl acetate, 3681-71-8; (E)-2-hexenyl acetate, 2497-18-9; benzaldehyde, 100-52-7; acetoin, 513-86-0; furfural, 98-01-1; furfuryl alcohol, 98-00-0.

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Nectarine Volatiles: Vacuum Steam Distillation versus Headspace Sampling

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The volatile components of fresh, tree-ripened nectarines (*Prunus persica nectarina*) of the Flavortop variety were analyzed by capillary gas chromatography and gas chromatography-mass spectrometry. Samples were prepared by vacuum distillation of the fruit pulp and skin followed by continuous solvent extraction (trichlorofluoromethane-dichloromethane, 9:1, v/v). A total of 62 components were identified in the extract including 21 alcohols, 15 esters, 10 carbonyls, 2 acids, 1 hydrocarbon, and 13 miscellaneous components. Lactones and peroxidation products of unsaturated fatty acids (i.e., C₆ aldehydes and alcohols) were the major constituents of the extract. Headspace analysis of intact fruit yielded the identification of 99 components including 43 esters, 33 hydrocarbons, 10 alcohols, 6 carbonyls, and 7 miscellaneous components.

The nectarine (*Prunus persica nectarina*) is an important commercial crop in the United States. Most of the nectarines sold in the United States are produced in California with over 100 varieties grown commercially in the state. The origins of the fruit are not known, but its history dates back 2000 years and merges into that of the peach (LaRue and Gerdt, 1983). There is controversy over whether the nectarine is a separate and distinct fruit or merely a variety of peach. In contrast to the peach, nectarines lack the fuzz or pubescence of the skin.

Current commercial nectarine varieties are vastly different from varieties produced before World War II. By crossing them with peaches, today's nectarines are larger, firmer, and more highly colored than their forebears. They also have yellow flesh rather than the white flesh that characterized the older varieties.

Despite extensive studies on peach volatiles (van Straten and Maarse, 1983), there are few data on the volatile constituents of nectarine. Lim and Romani (1964) studied volatiles of ripening nectarine (Early Sun Grand variety) using direct headspace sampling but only identified ethylene. Our study was directed toward the identification of nectarine volatiles (Flavortop variety) using two different sampling methods. The Flavortop variety originated in Fresno, CA, and was developed by the U.S. Department of Agriculture. The cultivar was produced from an open-

pollinated seedling of the Fairtime peach (Brooks and Olmo, 1972). The large, ovate fruit possesses a predominantly red over amber skin. The bright yellow flesh is generally streaked throughout with red.

EXPERIMENTAL SECTION

Materials. Fresh, tree-ripened nectarines (*P. persica nectarina*) of the Flavortop variety were obtained from a local orchard in Winters, CA (July-August 1985 and 1986). Ethanox antioxidant 330 was supplied by Ethyl Corp. (Baton Rouge, LA 70820). 3-Octyn-1-ol was obtained from Pfaltz & Bauer, Inc. (Waterbury, CT 06708).

Sampling Techniques. 1. *Vacuum Distillation-Extraction.* The fruit was washed with distilled water and allowed to air-dry. The fruit was cut in half, and the stones were removed and discarded. The skin and pulp were gently blended for 20 s in a Waring blender. The blended material was immediately subjected to vacuum distillation. A separate batch of nectarines was prepared in the same way except both the stones and skin were discarded and only the pulp was sampled.

An aliquot of blended pulp (0.6-0.7 kg) was diluted with distilled water (350 mL) in a 3-L three-neck flask and vacuum-distilled [33-35 °C (1 mmHg)]. The material had a tendency to foam but could be controlled by reducing the pressure gradually. After 2 h a second aliquot of blended fruit (0.6-0.7 kg) and distilled water (350 mL) was added. Distillation continued for an additional 2 h (4 h total), yielding approximately 500 mL of distillate which was collected in two liquid nitrogen cooled traps. A total of 3.9 kg of fruit pulp was distilled in three batches. The originally yellow pulp material was noticeably browned at the end of the distillation. The distillates were combined and immediately frozen until use. The combined distillate was extracted in 250-mL batches for 20 h with 60 mL of Freon 11 (trichlorofluoromethane, bp 23.8 °C) or Freon 11-dichloromethane (9:1, v/v; bp 23.8 °C). Since no nectarine volatiles coeluted with the dichloromethane peak,

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