Comparison of the Volatile Compounds from Several Commercial Peach Cultivars

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Volatile fractions were prepared from four ripe commercial peach cultivars and two breeding lines by continuous vacuum steam distillation–hexane extraction and analyzed by capillary gas–liquid chromatography and gas–liquid chromatography/mass spectrometry. Thirty-three compounds were identified including five C_6 aldehydes and alcohols, six lactones, five monoterpenes, one sesquiterpene, one ester, three high molecular weight hydrocarbons (C_{21}, C_{23}, C_{25}), and twelve other compounds. Major compounds identified were hexanal, (*E*)-2-hexenal, benzaldehyde, linalool, 6-pentyl-α-pyrone, γ- and δ-decalactones, hexadecanoic acid, and three saturated hydrocarbons. By the use of threshold values and concentrations, odor units were calculated for the major low and medium molecular weight compounds to determine their contribution to peach aroma. Variations in the volatile constituents during maturation were also determined for two peach cultivars. Concentrations of most compounds increased with maturity of fruit. (*E*)-2-Hexenal increased in Cresthaven peaches but decreased in Monroe. Hexanal showed erratic behavior, increasing in Cresthaven and decreasing in Monroe.

Many of the biochemical changes occurring during fruit ripening relate indirectly to quality. Quality was defined by Kramer and Twigg (1966) as the composite of those chemical and physical characteristics that make a product possess consumer appeal and acceptability. One of the most important aspects of these characteristics is fruit flavor.

Several investigations on peach flavor have resulted in the identification of approximately 70 volatile compounds. Lactones have been implicated in peach aroma with informal sensory judgments by Jennings and Sevenants (1964), Sevenants and Jennings (1966, 1971), Broderick (1966, 1975), and Do et al. (1969). Lim (1963), Lim and Romani (1964), and Do et al. (1969) investigated volatile compounds from peaches at different maturity stages and during artificial ripening. Spencer et al. (1978) reported on the relationship between sensory characteristics and relative concentration of the volatile compounds of fresh and cooked peaches. Among the 10 peach varieties investigated, the major differences found were higher concentrations of esters and monoterpenes relative to lactones. However, she reported that the lactones made the major contribution to the "peachy" aroma.

The present investigation was conducted to identify and quantitate the volatile constituents in peach cultivars by gas–liquid chromatography and gas–liquid chromatography/mass spectrometry. Also, the relative contributions of low and medium molecular weight compounds to peach aroma were evaluated.

Variations in the volatile constituents during maturation for two peach cultivars were also determined.

EXPERIMENTAL SECTION

Materials. Tree-ripened peaches were obtained from the Appalachian Fruit Research Station, USDA—ARS, Kearneysville, WV, from the University of Georgia Horticultural Farm, Athens, GA, and from nearby commercial orchards. Fruits were analyzed within 24 h after harvest. Immediately after harvest, the fruits were sorted into three maturity groups (immature, midripe, ripe) on the basis of standard color chips (Delwiche and Baumgardner, 1985). Firmness was determined on the peaches used in the color determinations with a Magness-Taylor fruit pressure tester, Model 30A (Ballauf, Man., Laurel, MD). The sorted samples were used for the analysis of volatile components relative to peach maturation. The cv. Monroe was harvested periodically, starting 80 days after flowering (DAF) (June–August 1988) from the University of Georgia Farm (Athens, GA). These samples were prepared and steam-distilled within 0.5–1.0 h after harvest. Authentic chemical compounds were obtained from commercial sources or synthesized by established methods.

Isolation of Volatiles by Continuous Extraction. Steam distillation–hexane extraction of peach volatiles was performed with a modified Likens–Nickerson extraction apparatus (Schultz et al., 1977). Samples were prepared from five fruits of the same maturity from each cultivar, which were pitted, halved, diced, and composited. A 250-g aliqont was removed and blended with 200 mL of distilled water in a Waring blender. The resulting slurry was transferred to a 3-L round-bottom flask containing 500 mL of distilled water and connected to a Likens–Nickerson head. Hexane (120 mL) was used as the extracting solvent, and the isolation was carried out at 110 mmHg for 4 h. The hexane extract was concentrated to 20 μL by a gentle stream of purified N_2 for GLC/MS and capillary GC analysis. A blank was made by using 700 mL of distilled water under the usual extraction conditions. The hexane extract was concentrated to 20 μL and analyzed by GLC/MS.

Volatile fractions were isolated from ripe Loring and Cresthaven peaches by substituting benzene for hexane during the steam distillation procedure. The recovery efficiencies of the compounds of interest were determined by adding 100 μg of each into 700 mL of distilled water with the distillation procedure described. Recoveries of volatile components were determined based on standard curves with known concentrations of authentic compounds directly injected into the GC. The standard curves were also used to estimate the amount of volatile components obtained from peach samples.

Capillary GLC Analysis. The GLC columns used were a 15 m × 0.25 mm (i.d.) fused silica capillary coated with DB-1 (J&W, Alltech, Inc., Deerfield, IL) and a 15 m × 0.25 mm fused silica capillary coated with Carbowax 20 M-NPA. Injector and detector temperatures were 225 and 280 °C, respectively. For both columns the oven temperature was held at 60 °C for 1 min, then programmed to 90 °C at 3 °C/min, held for 0.5 min,

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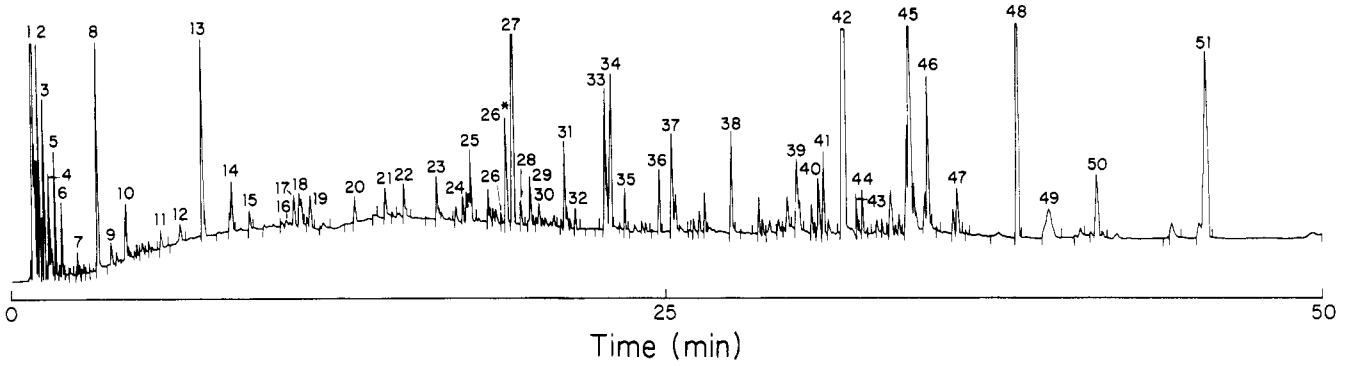

Figure 1. GLC chromatogram of tree-ripe Cresthaven peach volatiles.

Table I. Volatile Compounds Identified in Fresh Peaches by GC/MS Retention Times

compound[a]	peak[b]	Belle of Georgia	Cresthaven	June Gold	Monroe	Bailey	selectn 612615
hexanal	3	5.8	34.3	155.4	79.9	8.6	138.9
(*E*)-2-hexenal	4	6.9	42.8	196.6	96.5	10.4	167.7
hexanol	5	tr[d]	tr	tr	tr	tr	tr
(*E*)-2-hexenol[c]	6	tr	tr	tr	tr	tr	tr
xylene	7	tr	tr	tr	tr	tr	tr
benzaldehyde[c]	8	11.5	79.7	14.4	58.6	11.6	21.3
benzyl alcohol[c]	9	tr	tr	tr	tr	tr	tr
γ-hexalactone[c]	10	tr	tr	tr	tr	tr	tr
linalool[c] + tr nonanal[c]	13	113.5	36.7	128.6	50.4	69.5	147.1
naphthalene	14	tr	tr	tr	tr	tr	tr
α-terpineol[c]	16	tr	tr	tr	tr	tr	tr
benzothiazole	17		tr	tr	tr	tr	tr
1-methylnaphthalene	18	tr	tr	tr	tr	tr	tr
2-pentylfuran	19	tr	tr	tr	tr	tr	tr
(*E*,*E*)-2,4-decadienal	22	tr	tr	tr	tr	tr	tr
methyleugenol	25	tr	tr	tr	tr	tr	tr
6-pentyl-α-pyrone[c]	26*						
dihydroionone	26						
γ-decalactone[c]	27	155.7	74.0	25.4	128.5	77.9	29.3
β-ionone	28	tr	tr	tr	tr	tr	tr
δ-decalactone[c]	29	34.2	4.4	6.5	34.2	21.5	0
α-bergamotene	30	tr	tr	tr	tr	tr	tr
γ-dodecalactone[c]	31	0	0.2	0.03	0	0	0.07
2,6-dichloro-4-nitroaniline (Botran 75W)	37						
dibutyl phthalate	41						
palmitic acid	42						
methyl 3-methoxyoctadecanoate[e]	44						
$C_{21}H_{44}$	45						
$C_{23}H_{48}$	48						
bis(ethylhexyl) phthalate	51						
$C_{25}H_{52}$	51						

[a] Concentration is in ppb. [b] Peaks numbered in order of increasing retention times as shown in Figure 1. [c] Previously identified in peach volatiles. [d] tr = present in less than 1% of volatile fraction based on area of GLC peak. [e] Tentative identification based on mass spectrum.

then programmed to 210 °C at 5 °C/min, and held for 15 min. Injection volume was 1 μL. Kovats indices were determined by coinjection of samples and reference compounds with a series of hydrocarbons (C_{12}–C_{32}).

GLC/Mass Spectral Analysis. Mass spectral analyses were made with an Extrel Model C50/400 (Pittsburg, PA) quadrupole mass spectrometer that was interfaced with a Perkin-Elmer Sigma 300 gas–liquid chromatograph (Norwalk, CT) equipped with a cold on-column injector. Chromatographic separations were made on a 20 m × 0.32 mm (i.d.) fused silica capillary column coated with SE-54. Helium was used as the carrier gas at 0.5 psi. The column oven was programmed from 50 to 100 °C at 2 °C/min, held for 0.5 min, then programmed at 3 °C/min to 220 °C, and held for 40 min.

Mass spectrometer conditions: ion source temperature, 150 °C; scan rate, 200 amu/s; ionization voltage, 70 eV. Data were acquired with Technivent software and interface (St. Louis, MO) and processed on an IBM PC (640K, 40-Mbyte disk) (Boca Raton, FL).

RESULTS AND DISCUSSION

Qualitative Analysis of the Volatile Fraction. Volatile compounds of four commercial peach cultivars (Cresthaven, June Gold, Monroe, Belle of Georgia) and two breeding lines (Selection 612615, Bailey) were isolated by continuous vacuum steam distillation–hexane extraction. These aroma concentrates were judged to possess a peachlike aroma by an informal panel.

The steam-volatile compounds were identified by comparison of mass spectra and GC retention times to those of authentic reference standards. Compounds identified solely on the basis of mass spectral comparisons to published data were designed to be tentively identified.

Thirty-two compounds were identified by GC/MS in this study, of which 13 have been previously reported (Figure 1; Table I). For most varieties, the abundant compounds were (*E*)-2-hexenal, hexanal, benzaldehyde,

Table II. Composition of Peach Lactones[a]

cultivar	C_{10} γ-lactone	C_{10} δ-lactone	6-pentyl-α-pyrone	C_{12} γ-lactone
Belle of Georgia	92.5	1.9	4.1	1.5
Cresthaven	79.5	5.5	11.1	3.7
June Gold	61.3	4.3	34.4	0
Monroe	98.1	1.4	0.5	0
Bailey	77.9	13.6	8.5	0
Selection 612615	47.4	0	48.2	4.4

[a] Based on individual lactone area to total lactone area.

linalool, 6-pentyl-α-pyrone, γ- and δ-decalactone, γ-dodeclactone, palmitic acid, and three normal hydrocarbons (C_{21}, C_{23}, C_{25}). Minor constituents included xylene, naphthalene, benzyl alcohol, α-terpineol, benzothiazole, 2-pentylfuran, (*E*,*E*)-2,4-decadienal, methyleugenol, dihydroionone, ionone, and α-bergamotene. γ-Hexalactone and γ-octalactone were present only in trace levels. The latter was established by GC/MS analysis of its characteristic mass spectrum (*m*/*e* 56, 70, 85, 100, 124) and GLC retention time. 6-Pentyl-α-pyrone (peak 26*) was identified on the basis of comparison of its mass spectra to that published by Jennings and Shibamoto (1980). Also, Kovats indices on Carbowax M-NPA and DB-1 were 2292 and 1520, which are in agreement with data of Engel et al. (1988).

Do et al. (1969) reported the presence of several aromatic compounds: benzyl alcohol, benzyl acetate, ethyl benzoate, methyl salicylate, and hexyl benzoate from benzene extracts of peach mesocarp. Capillary GC–MS and capillary GC analysis in the present study indicated only benzyl alcohol and methyl salicylate to be present when benzene was used as solvent.

Quantitative Analysis of Peach Volatiles. Quantitation of the major low and medium molecular weight (*m*/*e* 200 amu) volatiles was made with response factors calculated from standard curves prepared with authentic compounds. Recovery experiments after vacuum steam distillation–hexane extraction yielded 70% γ-decalactone, 31% δ-decalactone, 85% γ-dodecalactone, 40% hexanal, 63% (*E*)-2-hexenal, 51% benzaldehyde, and 63% linalool. Percentage recovery values represent means of three experiments and possessed an average deviation of ±5%.

Six lactones were identified ranging from C_6 to C_{12} and represent a major class of compounds in peach volatiles. Table II shows the distribution of individual lactones in the peach cultivars investigated. γ-Decalactone was the major lactone found in all peaches examined, except Selection 612615, which had 6-pentyl-α-pyrone and its major component. The distribution of peach lactones differed from those of nectarines (Engel et al., 1988), in that γ-hexalactone and γ-octalactone were present in only trace amounts and 6-pentyl-α-pyrone was generally present in higher levels than δ-decalactone. It is possible that δ-decalactone is present in higher levels in peaches than was observed, since its recovery was 31%. Also, γ-heptalactone, γ-nonalactone, and (*Z*)-dec-7-en-5-olide were not detected in this investigation.

In order to determine the contributions of the individual lactones to peach aroma, odor units (Guadagni et al., 1966) were calculated with the odor thresholds determined by Engel et al. (1988). The odor unit for γ-decalactone was 4.6 odor units and should contribute to peach aroma (Table III). The other lactones were below their odor threshold units and, consequently, do not contribute to peach aroma. Because of the poor recovery of δ-decalactone, its contribution to peach aroma remains uncertain.

Table III. Odor Threshold Units (T_c) and Odor Units (U_0) in Some Peach Cultivars

compound[a]	$T_c(H_2O)$, ppb	U_0[b]
hexanal	4.5	18.7
(*E*)-2-hexenal	17.5	5.8
linalool	6.0	15.8
6-pentyl-α-pyrone	150.0	0.2
C_{10} γ-lactone	11.0	4.6
C_{10} δ-lactone	100.0	0.01
C_{12} γ-lactone	7.0	0.07

[a] Component concentrations (ppb) are the average of Cresthaven, Bailey, June Gold, Selection 612615, and Boone county cultivars. [b] Ratio of average concentration of individual compound (ppb) to its odor threshold (ppb).

Table IV. Major Volatiles from Two Peach Cultivars at Different Maturity Stages[a,b]

volatile compounds	Cresthaven			Monroe		
	green	midripe	ripe	green	midripe	ripe
hexanal	16.4	11.6	34.3	1524	897	15
(*E*)-2-hexenal	8.7	17.7	42.8	1087	730	11
benzaldehyde	112.0	86.9	79.8	10.4	10.4	58.6
linalool	25.3	38.0	36.7	0	12.1	50.4
C_{10} γ-lactone	25.6	27.9	74.0	0	12.1	128.5
C_{10} δ-lactone	0	1.4	4.4	0	3.7	20.0

[a] Values in ppb. [b] Key: green = 109 DAF; midripe = 126 DAF; ripe = 143 DAF.

Other major compounds identified were hexanal, (*E*)-2-hexenal, benzaldehyde, and linalool. Since the enzyme systems were not inactivated before maceration of peach mesocarp, the levels of the two C_6 aldehydes are probably not representative of whole peach (Engel et al., 1988). Nevertheless, both these aldehydes were present above their odor thresholds and should contribute to peach aroma (Buttery et al., 1971) (Table III). Also, linalool would contribute to peach aroma since its level is above the threshold value (Table III).

Volatiles of Peaches at Different Maturities. Capillary gas chromatographic analyses were made on aroma isolates from Cresthaven and Monroe peaches at different maturities on fruit. Concentrations of γ- and δ-decalactone and linalool increased with maturity of fruit; however, benzaldehyde decreased (Table IV). The increase in benzaldehyde in Monroe agrees with the finding of Do et al. (1969). (*E*)-2-Hexenal increased in Cresthaven peaches but decreased in Monroe. Hexanal showed erratic behavior: increasing in Cresthaven and decreasing in Monroe (Table IV).

The observed volatile levels in Monroe peaches at different maturity stages represent more valid data than Cresthaven, since the former fruit were harvested periodically during maturation and analyzed within 0.5–1.0 h after harvest. On the other hand, Cresthaven peaches were sorted into three maturity groups on the basis of color and firmness and analyzed within 1 day after harvest.

The results of this study may be useful in explaining aroma differences among cultivars and fruits subjected to different ripening procedures.

Registry No. $C_{21}H_{44}$, 629-94-7; $C_{23}H_{48}$, 638-67-5; $C_{25}H_{52}$, 629-99-2; hexanal, 66-25-1; (*E*)-2-hexenal, 6728-26-3; hexanol, 111-27-3; (*E*)-2-hexenol, 928-95-0; xylene, 1330-20-7; benzaldehyde, 100-52-7; benzyl alcohol, 100-51-6; γ-hexalactone, 695-06-7; linalool, 78-70-6; nonanal, 124-19-6; naphthalene, 91-20-3; α-terpineol, 98-55-5; benzothiazole, 95-16-9; 1-methylnaphthalene, 90-12-0; 2-pentylfuran, 3777-69-3; (*E*,*E*)-2,4-decadienol, 18409-21-7; methyleugenol, 93-15-2; 6-pentyl-α-pyrone, 27593-23-3; dihydroione, 17283-81-7; γ-decalactone, 706-14-9; δ-decalactone, 705-86-2; β-ionone, 79-77-6; γ-dodecalactone, 2305-05-

7; α-bergamotene, 17699-05-7; 2,6-dichloro-4-nitroaniline, 99-30-9; dibutyl phthalate, 84-74-2; palmitic acid, 57-10-3; methyl 3-methoxyoctadecanoate, 19013-36-6; bis(ethylhexyl) phthalate, 117-81-7.

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Mechanism of Formation of Volatile Compounds by Thermal Degradation of Carotenoids in Aqueous Medium. 1. β-Carotene Degradation

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The study of the degradation of β-carotene during heat treatment at 97 °C in water shows that the kinetics of degradation is the same as that observed in organic solvents. Some volatile compounds produced during this treatment have been previously identified after thermal degradation of homogeneous solutions of β-carotene or after heating of plant products. However, decanal, 4-ethylbenzaldehyde, and cetoisophorone were identified and 2,6-dimethyldecahydronaphthalene and 2-hydroxy-2,6,6-trimethylcyclohexanone were tentatively identified for the first time as degradation products of β-carotene. The influence of temperature on the production of volatile compounds and the kinetics of formation of volatile and nonvolatile compounds shows that dihydroactinidiolide is the first compound produced during heat treatment of β-carotene, its precursor probably being mutatochrome. Kinetics studies indicate that dihydroactinidiolide may also be produced through 5,6-epoxy-β-ionone, which is an important reactional intermediate. This compound acts as precursor for different volatiles such as β-ionone, 2-hydroxy-2,6,6-trimethylcyclohexanone, and 2-hydroxy-2,6,6-trimethylcyclohexane-1-carboxaldehyde.

The formation of volatile compounds by thermal degradation of carotenoids during heat treatment of vegetable products has been mentioned by many authors. Compounds such as β-ionone, damascenone, and dihydroactinidiolide present in tea (Bricout et al., 1967), tobacco (Fujimori et al., 1976; Enzell, 1981), prune (Moutounet, 1978), grapes (Schreier et al., 1976), apricot (Crouzet et al., 1983), and mango (Sakho et al., 1985) are considered as degradative products of β-carotene (Demole and Berthet, 1972; Murray et al., 1972). On the other hand, 1,6,6-trimethyl-1,2-dihydronaphthalene was found in volatile compounds obtained from strawberry (Stoltz et al., 1970) peach or peach leaves (Kemp et al., 1971), or passion fruit (Murray et al., 1972). The presence of this compound is also cited in raw Australian rum (Allan, 1975) or in wine

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