Comparison of Volatile Compounds from Peach Fruit and Leaves (cv. Monroe) during Maturation

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Variation in the levels of volatile constituents during maturation of peaches was determined by means of capillary gas chromatography. C₆ aldehydes were the major compounds isolated from immature fruit; however, as the fruit matured, levels of the C₆ aldehydes decreased. The final period of peach maturation, 134–143 days after flowering, showed significant increases in benzaldehyde, linalool, and γ - and δ -decalactone. The volatile constituents of peach, nectarine, and plum leaves were found to be very similar with benzaldehyde >64% of the total fraction. Of all the volatile compounds identified in leaves, only seven were found in both peach leaves and mesocarp tissue.

INTRODUCTION

Although many of the physiochemical properties of maturing peaches have been extensively investigated to obtain suitable indices of maturity, the need still remains for objective indices of fruit maturity that correlate with consumer acceptance of the product. One very important index in evaluating fruit quality is aroma.

Lim and Romani (1964) reported volatile constituent concentrations increased with maturation of peaches and nectarines. However, the volatile peach constituents were not identified. Do et al. (1969) studied peaches at different stages of maturity and found the concentration of the major identified components increased with maturation. We have recently found that benzaldehyde, linalool, and the C10 lactones increased during Monroe peach maturation, while the C₆ aldehydes decreased (Horvat et al., 1990). Bayonove (1973), using gas chromatographic techniques, estimated the changes in γ -decalactone levels during maturation. Kemp et al. (1971) isolated peach fruit and foliage volatiles and identified 1.2-dihydro-1.1.6-trimethylnaphthalene as being common to both. We hypothesize that some of the major volatile components may be biosynthesized in the leaves of *Prunus* species and then translocated into the fruit. Evidence for the translocation of sorbitol and sucrose from leaves into fruit has been demonstrated by DeVilliers et al. (1974) and Ishida et al. (1985).

The objective of this study was to identify and quantitate the major volatiles during the maturation of cv. Monroe peaches and to investigate the major volatile components from the leaves of several *Prunus* species.

MATERIALS AND METHODS

Plant Material. Peaches. Fruit were obtained from trees (cv. Monroe) grown at the University of Georgia Horticultural Farm (Watkinsville, GA). The trees were 4 years old and received adequate rainfall and/or irrigation during the summer of 1988. Twelve peaches were harvested during maturation (June 20-August 15), starting at 81 days after flowering (DAF) until about 2 weeks after beginning of fruit drop (140 DAF). Individual peach diameters (long axis) were measured with a vernier caliper to ensure sample uniformity. The average weight of 10-12 peaches was also obtained during maturation. Volatile fractions were prepared from six fruit within 0.5-1 h after harvest.

Leaves. Mature leaves were harvested at times corresponding to immature, midripe, and mature fruit (111, 126, and 143 DAF) from the same trees. Plum and nectarine leaves were harvested twice during the growing season.

Isolation of Volatiles. *Peach*. At each stage of maturity volatiles were isolated from 250 g of blended fruit by continuous steam distillation-hexane extraction using the previously described procedure (Horvat et al., 1990).

Leaves. (A) Twenty leaves were deveined, frozen with liquid nitrogen, ground to a fine powder with a mortar and pestle, and treated with 75% ethanol to inactivate enzyme activity, and the excess solvent was decanted. Twelve grams of leaf powder was transferred to a 350-mL round-bottom flask containing 150 mL of distilled water that was connected to a modified Likens-Nickerson distillation head (Schultz et al., 1977). Fifty milliliters of hexane was used as the extracting solvent. Conditions for vacuum steam distillation of the leaves were the same used for peaches. Hexane extracts were concentrated to 20 μ L with a gentle stream of nitrogen for GC analysis.

(B) To investigate the nonpolar leaf lipid fraction, 12 peach leaves were dipped in 100 mL of hexane. Extract was filtered through Whatman No. 4 filter paper and concentrated to a volume of 0.1 mL by means of a stream of nitrogen gas for GC analysis.

Capillary Gas Chromatography-Mass Spectrometry (GC-MS). For capillary GC investigations, a 15 m \times 0.25 mm (i.d.) fused silica capillary column coated (0.25 μ m thick) with DB-1 (J and W Scientific, Folsom, CA) was used. For determining levels of hexanal, (E)-2-hexenal, benzaldehyde, linalool, and γ - and δ -decalactone in peach mesocarp tissue by GC analysis, standard curves were made by using authentic compounds and reported as parts per billion (ppb). For GC-MS analysis, volatile components were separated with a 30 m \times 0.32 mm (i.d.) fused silica capillary column coated (0.25 μ m thick) with DB-1. Mass spectrometer and conditions used were previously described (Horvat et al., 1990).

RESULTS AND DISCUSSION

Peaches. The growth of peaches is described by a double-sigmoidal curve in which there are three distinct growth periods. A rapid weight increase is observed during the first period, followed by a slower growth rate, and finally an accelerated period in which fruit growth is greatest (Lilleland, 1932). In this study, the fresh weight of Monroe peaches increased from 24 (81 DAF) to 128 g at 140 DAF (Figure 1). There was a significant drop in fresh weight between 140 and 143 DAF, and the fruit developed a peachlike aroma at 130 DAF.

As shown in Figures 2-4 benzaldehyde, linalool, γ -decalactone, and δ -decalactone increased in concentration from 130 to 143 DAF (tree-ripe fruit) for Monroe peaches.



Figure 1. Changes in fresh weight in Monroe peaches during maturation.



Figure 2. Changes in benzaldehyde in mesocarp tissue at different stages of fruit maturity.



Figure 3. Changes in linalool in mesocarp tissue at different stages of fruit maturity.



Figure 4. Changes in γ - and δ -decalactones in mesocarp tissue at different stages of fruit maturity.

Hexanal decreased to 3 times its odor threshold, and (E)-2-hexenal decreased to approximately its odor threshold (Figure 5) [hexanal, 4.5 ppb; (E)-2-hexenal, 17 ppb (Buttery et al., 1971)]. Similarly with nectarines Engel et al. (1988) reported the C₆ aldehydes and alcohols decreased significantly during maturation. The two C₆ aldehydes, products of enzyme breakdown of unsaturated fatty acids



Figure 5. Changes in hexanal and (E)-2-hexenal in mesocarp tissue at different stages of fruit maturity.

Table I.	Volatile Compounds	Identified in	Prunus Leaves
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compound	peach,° %	nectarine,° %	plum,° %
hexanal ^d	tr ^e	tr	1.0
(E)-2-hexenal ^d	tr	tr	10.3
(Z)-3-hexenol	tr	tr	tr
benzaldehyde ^d	>95	>95	64.0
benzyl alcohol	tr	tr	tr
ethyl benzoate	tr	tr	tr
(Z)-3-hexenyl butyrate	tr		
methyl salicylate ^d	tr		
ethyl salicylate	tr		
benzoic acid	1.2	tr	tr
eugenold	tr		
(Z)-3-hexenyl benzoate	tr	tr	
benzyl salicylate ^b	tr		tr
palmitic acid	tr	tr	tr
ethyl palmitate	tr	tr	tr
isopropyl palmitate ^b	tr	tr	tr
$C_{21}H_{44}$	tr	tr	1.6
$C_{23}H_{48}$	tr	tr	1.7
$C_{25}H_{52}$	tr	tr	tr

^a Identified by GC-MS and GC retention times. ^b Tentative identification based on mass spectrum. ^c Amount based on GC peak area percent. ^d Previously identified by Kemp et al. (1971). ^e tr, <1% based on GC area percent.

(Tressl et al., 1981), are the major volatile components in immature peaches. Since the peroxidative enzymes were not inactivated during blending of the fruit in this study, the values for hexanal and (E)-2-hexenal presented in Figure 5 are the sum of the endogenous levels plus those formed by enzymatic action during blending and subsequent isolation. Thus, the actual concentrations of the C₆ aldehydes in Monroe peaches and their contribution to peach aroma have not been determined. However, since all isolations were conducted under identical conditions, the levels of C₆ aldehydes can be compared and used to estimate enzyme activities at different stages of maturity.

Linalool, benzaldehyde, and γ - and δ -decalactone levels increased significantly from 134 to 143 DAF. γ -Decalactone increased 24-fold and δ -decalactone 6-fold during this period (Figures 2-4), which is consistent with the results of Do et al. (1969) and Bayonove (1973). Both linalool and γ -decalactone are present in levels above their threshold values in tree-ripe fruit and, therefore, should contribute to peach aroma. The reported threshold value for linalool is 6 ppb and for γ -decalactone is 11 ppb (Buttery et al., 1969; Engel et al., 1988). Benzaldehyde is present below its threshold value of 350 ppb (Buttery et al., 1971) and would not contribute to peach aroma. Results of this study (Figure 3) show that linalool levels increased approximately 5-fold from 130 to 137 DAF, which produced an 8-fold increase in odor units. Although δ -decalactone was present in levels below its threshold value, isolation experiments showed its recovery was only 30% (Horvat et al., 1990). Therefore, its contribution to peach aroma has not been

determined in this investigation. The changes that occur in aroma components after harvest are thought to be determined by the stage of fruit maturity (Lim and Romani, 1964; J. A. Robertson, USDA—ARS, R. B. Russell Agricultural Research Center, Athens, GA, personal communication, 1989).

Leaves. Gas chromatographic and GC-MS analyses revealed the majority of compounds in the volatile leaf fraction were benzenoid, with benzaldehyde constituting better than 95% (Table I). Several of the leaf components previously have been identified in peach fruit, for example, hexanal, (E)-2-hexenal, (Z)-3-hexenol, benzaldehyde, benzyl alcohol, methyl salicylate, and ethyl benzoate (Horvat et al., 1990; Kemp et al., 1971; Do et al., 1969). The levels of the volatile constituents of mature peach leaves remained approximately the same during fruit maturation (111, 126, and 143 DAF). In addition to the lower molecular weight (<200 amu) compounds listed in Table I, palmitic acid, ethyl palmitate, isopropyl palmitate, and the three saturated hydrocarbons $(C_{21}, C_{23}, and C_{25})$ were present in the volatile extracts as well as in the hexane washes of peach leaves. Thus, it appears that these latter compounds are contributed by the leaf wax.

Linalool and C_{10} lactones were formed only in the mesocarp during maturation, since they were not detected in leaves. The C₆ aldehydes were found in leaves and the mesocarp and would suggest that oxidative enzymes are present in both. It is doubtful that translocation of these compounds occurred. The only major volatile compound identified in this study that may be translocated from leaves to mesocarp was benzaldehyde.

The volatile fractions of nectarine and plum leaves were similar to those found in peach leaves (Table I). These results indicate that these constituents are probably endogenous to the *Prunus* genus and are possible precursors of the volatile benzenoid compounds present in fruit.

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