Volatile Compounds Emitted by Sweet Cherries (*Prunus avium* Cv. Bing) during Fruit Development and Ripening

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Volatile compounds were collected using headspace sampling from intact sweet cherries (*Prunus avium* cv. Bing). Samples were collected at weekly intervals during fruit development and during a 7-day ripening period following harvest at commercial maturity. Thirty-one compounds of several chemical classes were identified including aldehydes, alcohols, esters, a ketone, a volatile acid, and a terpene. Of the compounds identified, ethanol had the highest concentration, but the amounts varied considerably among harvest dates. A number of compounds were detected in all of the samples, while stage of development determined the presence of other compounds. Several esters were detected only during the ripening period following harvest at commercial maturity.

INTRODUCTION

Sweet cherries (*Prunus avium* L.) are a nonclimacteric (Ulrich, 1961) fruit that exhibit a decline in whole fruit respiration rate during development (Blanpied, 1972). Bing sweet cherries, the predominant commercial cultivar in Washington state (Garrett et al., 1986), reach commercial maturity 10–12 weeks after bloom and are highly perishable. Commercial harvest maturity is based primarily on attainment of acceptable fruit color and percent soluble solids (Westwood, 1978).

Volatile compounds contribute to the flavor of processed sweet cherries (Schmid and Grosch, 1986; Poll and Lewis, 1987) and presumably to fresh fruit as well. Twenty compounds were identified in headspace samples from sour cherry juice (Poll and Lewis, 1987). Comparisons between the amounts of seven compounds with high aroma values extracted from sweet and sour cherry juices and jams (Schmid and Grosch, 1986) indicated substantial differences existed between the two fruits. A number of nonvolatile aroma metabolites have also been identified from sour cherry fruit pulp (Schwab et al., 1990).

Substantial qualitative and quantitative differences in volatile compounds have been identified from many different fruits depending on fruit stage of development (Bartley and Schwede, 1989; Brown et al., 1968; Chachin and Iwata, 1988; Dirninger et al., 1989; Engel et al., 1988; Romani and Ku, 1966; Strandzhev, 1975). This type of information can be valuable for determination of fruit maturity and flavor quality but has not been available for sweet cherries. The following, therefore, is a report on volatile compounds emitted from intact sweet cherry fruit during the course of fruit development and a subsequent ripening period following harvest at commercial maturity.

MATERIALS AND METHODS

Sweet cherry fruits were harvested at weekly intervals from mature cherry trees (*Prunus avium* cv. Bing) in a research orchard. Cherries harvested at commercial maturity were ripened at 21 °C for 7 days.

Analysis of Headspace Volatile Compounds. Two replicate samples (500 g of fruit each) were placed into two 4-L glass jars and the jars sealed using Teflon lids with two gas ports. Purified compressed air was passed through each jar, and fruit volatiles were collected on a solid sorbent trap (Tenax TA, 50 mg) connected to the outlet port. The volume of dynamic headspace collected from each replicate was 1 L. Volatiles were introduced into a GC–MS system by thermal desorption and cryofocusing (Farwell et al., 1979). Traps were inserted into a carrier gas loop constructed from Teflon-lined stainless steel tubing, Cajun screw-type fittings, and a six-port Hamilton switching valve. Traps were desorbed with a hot air gun at 200 °C, and a 1-m section of fused silica capillary glass tubing was used as a cryoloop inserted into a Dewar of liquid N_2. Following desorption and cryofocusing, volatiles were introduced to the GC by exchanging the liquid N_2 Dewar for a container of hot (100 °C) water. A Hewlett-Packard 5890A-5971A GC–MSD system equipped with a DB-Wax column (J&W Scientific, 60 m, 0.25 mm i.d., 0.25-μm film thickness) was used for analysis. Conditions for chromatography were an initial oven temperature of 35 °C held for 5 min, increased to 50 °C at 2 °C min^{-1}, increased to 200 °C at 5 °C min^{-1}, and held for 5 min at the final temperature. Linear gas velocity for He carrier was 30 cm s^{-1}. Initial identification of compounds was made using the Wiley–NBS library. Comparison of spectra and retention index with those of standards was used to confirm identification. Quantification of compounds was performed using selected ion monitoring for base peaks and values calculated using response factors generated with standards. Variability between the two replicates was less than 5%.

Fruit Quality. Sweet cherry color and total soluble solids content were measured using a Minolta CR200 Chroma Meter and Atago N1 refractometer, respectively.

Table I. Soluble Solids Content of Bing Sweet Cherries at Harvest[a]

harvest date	soluble solids
June 12	15.1 ± 0.4
June 19	15.6 ± 0.4
June 26	23.3 ± 0.8

[a] Values are averages ± SD from measurements of 30 fruits.

RESULTS AND DISCUSSION

Sweet cherry fruit weight (Figure 1), red color (Figure 2), and soluble solids content (Table I) increased as the fruit approached commercial maturity. Sufficient soluble solids content and development of red color had occurred by June 26 to begin commercial harvest in the orchard where these fruits were obtained.

Thirty-one compounds were positively identified from sweet cherry headspace samples during the course of this

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Table II. Volatiles Identified in Headspace Samples Collected from Intact Bing Sweet Cherry Fruits[a]

compound	RI[b]	concn[c] of volatile at harvest date of							
		May 8	May 16	May 22	May 29	June 5	June 12	June 19	June 26
Aldehydes									
propanal	790	164	72	172	224	108	71	84	152
butanal	898	393	75	136	209	116	117	158	779
pentanal	976	486	166	95	210	226	115	143	264
hexanal	1075	2000	740	633	1433	1084	243	257	930
heptanal	1165	1319	264	229	348	273	127	98	279
(*E*)-2-hexenal	1216	3	2	ND[d]	ND	ND	ND	ND	ND
octanal	1286	743	679	461	442	737	80	52	97
nonanal	1394	1611	1112	730	591	1356	176	143	204
decanal	1506	848	1545	1604	406	1963	142	121	306
benzaldehyde	1538	95	130	62	170	80	11	44	85
Alcohols									
2-propanol	931	ND	ND	ND	ND	3828	14	ND	ND
ethanol	934	59700	68550	1748	15500	853	1249	65550	65900
1-butanol	1148	ND	8	ND	ND	12	6	5	ND
1-pentanol	1252	39	12	67	51	29	6	9	19
linalool	1541	5	6	2	1	ND	ND	ND	ND
2-methyl-2,4-pentanediol	1637	27	32	27	98	178	15	97	130
Esters									
ethyl acetate	888	794	1430	208	390	17	58	825	1076
hexyl acetate	1270	25	24	4	10	7	4	5	4
hexyl 2-methylbutyrate	1433	51	107	44	24	27	12	42	46
hexyl hexanoate	1416	218	399	215	103	167	79	124	191
Terpenes									
[C_{10} terpene][e]	1182	90	79	288	230	75	21	20	ND
limonene	1190	8	14	6	ND	ND	ND	ND	ND
Other Compounds									
6-methyl-5-hepten-2-one	1333	109	192	100	122	89	13	31	48
acetic acid	1454	1531	693	1220	2178	755	44	455	126

[a] Values are means of two replicates determined from headspace samples collected from 500-g samples of sweet cherries. [b] RI, retention index, calculated according to the method of Majlat et al. (1974). [c] Concentrations of each compound expressed in picoliters released per kilogram of fruit per hour. [d] ND, not detected. [e] Concentrations are estimates based on response factor calculated from sabinene, a similar C_{10} terpene.

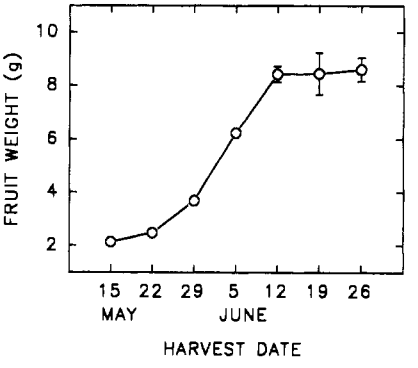

Figure 1. Average fruit weight of Bing cherries during fruit development. Error bars indicate SD of 30 fruit.

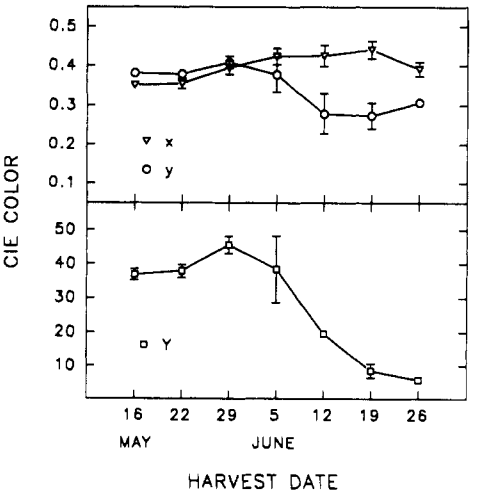

Figure 2. CIE color values for Bing cherries during fruit development. Values are averages ± SD from measurements of 30 fruits.

study (Tables II and III). The majority of these compounds were aldehydes (10), esters (10), or alcohols (8). In addition, one volatile acid (acetic), one ketone (6-methyl-5-hepten-2-one), and one terpene (limonene) were identified by comparison of sample spectra and relative retention times with those of standards. Another compound detected but not positively identified may be a C_{10} terpene on the basis of possible matches with spectra contained in the Wiley–NBS library (Figure 3). Estimates of concentration in headspace samples for the unknown terpene were based on the response factor calculated for sabinene, a similar C_{10} terpene.

A homologous series of aliphatic aldehydes containing from 3 to 10 carbons was identified (Tables II and III). These compounds were present following all harvests and during fruit ripening following the final harvest. Two other aldehydes, one unsaturated [(*E*)-2-hexenal] and one aromatic (benzaldehyde), were also identified. Benzaldehyde, hexanal, and (*E*)-2-hexenal have previously been identified as important aroma compounds in processed cherries (Schmid and Grosch, 1986). Benzaldehyde and hexanal were present in all samples analyzed in the current study; however, (*E*)-2-hexenal was found in only small amounts and only following the first two harvests. (*E*)-2-Hexenal has been demonstrated to be formed as a result of activity of lipoxygenase and hydroperoxide lyase on linoleic and linolenic acids (Drawert et al., 1966), and amounts would be expected to be greater in processed cherries following disruption of fruit tissue (Frankel, 1982; Schreier, 1984).

A number of primary alcohols were identified at different

Table III. Volatiles Identified in Headspace Samples Collected from Intact Bing Sweet Cherry Fruits Harvested at Commercial Maturity and Ripened at 21 °C for 7 Days[a]

compound	RI[b]	concn[c] of volatile after ripening at 21 °C for 0 days	1 day	2 days	3 days	7 days
		Aldehydes				
propanal	790	152	56	209	126	57
butanal	898	779	18	114	88	32
pentanal	976	264	46	279	212	82
hexanal	1075	930	295	1163	885	453
heptanal	1165	279	40	176	141	36
octanal	1286	97	445	184	198	12
nonanal	1394	204	123	286	411	78
decanal	1506	306	121	292	253	49
benzaldehyde	1538	85	35	95	85	253
		Alcohols				
2-propanol	931	ND[d]	1471	4635	5224	2861
ethanol	934	65900	1475	2117	799	1083
1-butanol	1148	ND	7	6	7	6
1-pentanol	1252	19	6	25	24	15
1-hexanol	1354	ND	9	26	14	194
2-ethyl-1-hexanol	1492	ND	25	48	25	18
2-methyl-2,4-pentanediol	1637	130	91	92	124	22
		Esters				
ethyl acetate	888	1076	41	99	34	15
butyl acetate	1070	ND	47	80	8	5
2-methylbutyl acetate	1110	ND	172	238	7	8
butyl butyrate	1216	ND	27	42	8	ND
butyl 2-methylbutyrate	1231	ND	31	28	ND	ND
ethyl hexanoate	1231	ND	63	81	17	7
hexyl acetate	1270	4	112	150	26	33
hexyl 2-methylbutyrate	1433	46	156	121	59	71
ethyl octanoate	1440	ND	16	17	ND	ND
hexyl hexanoate	1619	191	134	196	133	179
		Other Volatile Compounds				
6-methyl-5-hepten-2-one	1333	48	36	92	58	17
acetic acid	1454	126	24	53	22	93

[a] Values are means of two replicates determined from headspace samples collected from 500-g samples of sweet cherries. [b] RI, retention index calculated according to the method of Majlat et al. (1974). [c] Concentrations of each compound expressed in picoliters released per kilogram of fruit per hour. [d] ND, not detected.

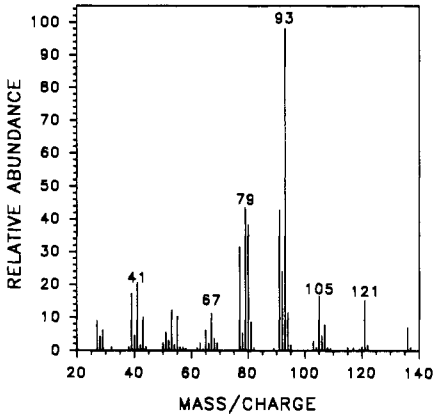

Figure 3. EI mass spectra for unknown volatile compound in Bing cherry headspace samples with retention index of 1182.

developmental stages containing from two to six carbons. In addition, one secondary (2-propanol) and two branched-chain alcohols (2-ethyl-1-hexanol, 2-methyl-2,4-pentanediol) were also present. Ethanol, 1-pentanol, and 2-methyl-2,4-pentanediol were found in all samples. Poll and Lewis (1987) identified ethanol as the major quantitative component of sour cherry juice. 1-Butanol was identified sporadically through the developmental period and in all of the samples during the ripening period. Because 1-butanol concentrations were relatively low when it was detected, headspace sample size may have prevented its detection in the samples where it was not found. This may also have been a limiting factor for other compounds present in low concentrations, e.g., limonene, linalool, and (*E*)-2-hexenal.

Ethanol had the highest concentration of the volatile compounds detected, the amount on some sampling dates being nearly 50 times that of the next largest component (Tables II and III). Ethanol concentrations varied considerably among harvest dates and declined dramatically during the first day following harvest at commercial maturity. The variation in ethanol concentrations during development could arise from fluctuations in the amount of carbohydrate metabolized during glycolysis. If pyruvate were produced in amounts greater than what could be utilized in the tricarboxylic acid (TCA) cycle, the excess could be metabolized to ethanol. The concentration of ethanol declined rapidly during the ripening period (Table III). The rapid loss could have been due to acceleration of ripening after fruit removal from the tree and more efficient entry of pyruvate into the TCA cycle. The rapid loss of ethanol present at commercial harvest could also result from a high rate of ethanol diffusion out of the fruit due to the low diffusive resistance of sweet cherries (Patterson, 1981).

Several esters, ethyl acetate, hexyl acetate, hexyl 2-methylbutyrate, and hexyl hexanoate, were present in fruits from all harvests and during ripening (Tables II and III). The presence of these compounds may indicate that alcohol acetyltransferase, an enzyme catalyzing ester synthesis in other fruit species (Harada et al., 1985; Ueda et al., 1990), is active throughout development. Several other esters, butyl acetate, 2-methylbutyl acetate, butyl butyrate, butyl 2-methylbutyrate, ethyl hexanoate, and ethyl octanoate,

were detected only from cherries allowed to ripen following the final harvest. The maximum concentrations of these compounds were reached on days 1 and 2 after harvest and declined thereafter. Concentrations of butyl butyrate, butyl 2-methylbutyrate, and ethyl octanoate decreased to undetectable levels by day 3 or day 7. The presence of these compounds only after a ripening period following harvest may be a factor influencing sweet cherry flavor and may be due to mobilization of substrate and or increased activity of enzymes involved in ester synthesis.

One qualitative difference detected in the volatile samples collected from fruits harvested at commercial maturity compared to those of previous harvests was the absence of the unidentified C_{10} terpene (Table II). The lack of detection of this compound associated with attainment of commercial maturity could possibly serve as an additional indicator of fruit maturity provided the association was demonstrated during several successive growing seasons.

Compounds identified represent the major volatiles detectable from intact Bing sweet cherry fruits using Tenax traps for collection. Additional compounds may be detectable using destructive sampling techniques (i.e., steam distillation, vacuum extraction) to collect compounds with insufficient volatility to evaporate from intact fruit and compounds that are not efficiently entrained on Tenax. Destructive sampling may also result in the creation of products of lipoxygenase or other enzymes that exhibit increased activity following homogenization of fruit tissues (Bartley and Schwede, 1989) or by release from glycosylated compounds (Schwab et al., 1990).

ACKNOWLEDGMENT

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Registry No. Propanal, 123-38-6; butanal, 123-72-8; pentanal, 110-62-3; hexanal, 66-25-1; heptanal, 111-71-7; (*E*)-2-hexenal, 6728-26-3; octanal, 124-13-0; nonanal, 124-19-6; decanal, 112-31-2; benzaldehyde, 100-52-7; 2-propanol, 67-63-0; ethanol, 64-17-5; 1-butanol, 71-36-3; 1-pentanol, 71-41-0; linalool, 78-70-6; 2-methyl-2,4-pentanediol, 107-41-5; ethyl acetate, 141-78-6; hexyl acetate, 142-92-7; hexyl 2-methylbutyrate, 10032-15-2; hexyl hexanoate, 6378-65-0; limonene, 138-86-3; 6-methyl-5-hepten-2-one, 110-93-0; 1-hexanol, 111-27-3; 2-ethyl-1-hexanol, 104-76-7; butyl acetate, 123-86-4; 2-methylbutyl acetate, 624-41-9; butyl butyrate, 109-21-7; butyl 2-methylbutyrate, 15706-73-7; ethyl hexanoate, 123-66-0; ethyl octanoate, 106-32-1.