Seasonal Variation of Volatile Composition and Odor Activity Value of 'Marion' (*Rubus* spp. *hyb*) and 'Thornless Evergreen' (*R. laciniatus* L.) Blackberries

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ABSTRACT: Volatile compositions of 'Marion' and 'Thornless Evergreen' blackberries from 3 growing seasons were analyzed using gas chromatography-flame ionization detection (GC-FID) and GC-mass spectrometry (GC-MS). Although seasonal variations were present for both cultivars, it was generally observed that the most abundant volatiles in 'Marion' blackberry were acetic, 2/3-methylbutanoic, hexanoic and decanoic acids, ethanol, and linalool, whereas the most abundant volatiles in 'Thornless Evergreen' were 2-heptanol, hexanol, octanol, α-pinene, nopol, and *p*-cymen-8-ol. Compared with 'Marion,' 'Thornless Evergreen' contained significantly more total volatiles, especially in alcohols, terpenoids, and phenols, whereas 'Marion' contained more organic acids. Odor activity values (OAVs) were determined to identify each cultivar's most potent odorants. The compounds with the high odor activity values (OAV > 10) in 'Marion' were ethyl hexanoate, β-ionone, linalool, 2-heptanone, 2-undecanone, α-ionone, and hexanal. The compounds with the high odor activity values (OAV > 10) in 'Thornless Evergreen' were ethyl hexanoate, 2-heptanone, ethyl 2-methylbutanoate, 2-heptanol, 3-methylbutanal, α-pinene, limonene, *p*-cymene, linalool, *t*-2-hexenal, myrtenol, hexanal, 2-methylbutanal, and sabinene.

Keywords: 'Marion', 'Thornless Evergreen', blackberry, seasonal variation, aroma, OAV

Introduction

Blackberry flavor is mainly formed during a brief ripening period and is influenced by internal and external factors. Internal factors are based on plant characteristics such as metabolism and genetic makeup, while external factors are related to fruit growth and cultivation concerns such as climate, soil, fertilization, and harvest date (Forney 2001). Factors affecting blackberry taste, such as sugars, acids, and titratable acidity, have been studied by many researchers (Fitelson 1970; Wrolstad and others 1980; Sapers and others 1985; Plowman 1991). However, compared with other small fruits such as raspberry or strawberry, blackberry aroma study has received very little attention. The limited studies are mainly related to volatile composition in 'Evergreen' cultivar (Scanlan and others 1970; Houchen and others 1972; Gulan and others 1973; Georgilopoulos and Gallois 1987a; Georgilopoulos and Gallois 1987b; Georgilopoulos and Gallois 1988; Humpf and Schreier 1991). Since the early 1980s, 'Marion' has replaced the 'Evergreen' as the leading blackberry cultivar planted in the Pacific Northwest (Finn and others 1997). Compared with 'Evergreen,' 'Marion' is highly preferred by consumers for its aromatic bouquet and intense flavor.

Very few publications report aroma-active compounds in blackberries. Turemis and others (2003) examined the aroma compositions of 5 blackberry cultivars using immersion solid phase micro extraction technique and found furfural and its derivatives to be the most abundant aromatic compounds in those blackberries, while 5-hydroxymethyl furfural to be the "the main specific blackberry-like aromatic compound." Klesk and Qian (2003a, 2003b) studied aroma compounds in 'Thornless Evergreen' and 'Marion' blackberries using dynamic headspace GC/Olfactometry and aroma extract dilution analysis technique and found that the important aroma compounds in 'Marion' and 'Thornless Evergreen' blackberries are 2,3-butanedione, 2-heptanol, linalool, *l*-carvone, β-pinene, thiophene, dimethyl disulfide, dimethyl trisulfide, methional, ethyl 2-methylpropanoate, benzaldehyde, hexanal, 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone, 2-ethyl-4-hydroxy-5-methyl-3(2*H*)-furanone, 4-hydroxy-5-methyl-3(2*H*)-furanone, 4,5-dimethyl-3-hydroxy-2(5*H*)-furanone, and 5-ethyl-3-hydroxy-4-methyl-2(5*H*)-furanone. Because there is no single compound having a "typical" blackberry odor, the authors conclude that the aroma of 'Marion' and 'Thornless Evergreen' blackberries is probably a mixture of these compounds in certain proportions. Blackberry aroma, particularly 'Marion' blackberry aroma, is still poorly understood.

The goal of this work was to study the seasonal variations of volatile compounds for 'Marion' and 'Thornless Evergreen' blackberries and use odor activity values to further elucidate potential aroma contribution of these compounds.

Materials and Methods

Chemicals

Ethyl undecanoate and ethyl decanoate were purchased from Eastman (Rochester, N.Y., U.S.A.). Ethyl hexadecanoate and β-caryophyllene were purchased from Pfaltz & Bauer (Waterbury, Conn., U.S.A.). Limonene, butyl acetate, octyl acetate, 2-heptanone, α- and β-pinene, α-terpineol, 2-nonanone, and 2-undecanone were obtained from K&K Laboratories (Jamaica, N.Y., U.S.A.). Ethanol, 2-methylpropanol, 1-butanol, 2-butanol, 3-methylbutanol, 2-methyl-3-buten-2-ol, 2-pentanol, 1-penten-3-ol, hex-

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anol, *t*-2-hexenol, *cis*-2-hexenol, *t*-3-hexenol, *cis*-3-hexenol, 2-heptanol, heptanol, octanol, nonanol, 2-nonanol, decanol, benzyl alcohol, phenylethyl alcohol, 3-methylbutanal, hexanal, *t*-2-hexenal, 2-butanone, 2-pentanone, acetoin, acetic acid, butanoic acid, 2-methylbutanoic acid, hexanoic acid, *t*-2-hexenoic acid, octanoic acid, decanoic acid, ethyl acetate, ethyl 2-methylbutanoate, ethyl hexanoate, ethyl octanoate, hexyl acetate, *t*-2-hexenyl acetate, α- and β-ionone, eugenol, camphene, linalool, linalool oxide, borneol, α-phellandrene, α-terpinolene, theaspirane, myrtenal, *p*-cymene, γ-terpinene, sabinene, citronellol, 1-terpineol, and myrtenol were obtained from Aldrich Chemical Co. Inc. (Milwaukee, Wis., U.S.A.). Sodium chloride was obtained from Fisher Scientific (Fair Lawn, N.J., U.S.A.). Diethyl ether was obtained from Honeywell Internal Inc. (Muskegon, Mich., U.S.A.). Pentane was obtained from Malinckrodt Baker Inc. (Philipsburg, N.J., U.S.A.).

Blackberry samples

'Marion' and 'Thornless Evergreen' blackberries were grown in Woodburn, Oregon, U.S.A., from 5- and 10-year-old plants. The fruits were machine- and hand-harvested, washed, graded, individually quick-frozen (IQF), and stored at –18 °C. One box of each cultivar (13.6 kg, frozen 5 mo) from the 1999, 2001, and 2002 growing seasons were transported on ice to the laboratory and stored at –23 °C.

Extraction of volatile compounds

Three hundred grams of IQF berries were thawed at room temperature for 3 h. The berries were blended in a glass blender jar (Waring Products Div., Dynamics Corp. of America, New Hartford, Conn., U.S.A.) for a total of 40 s. Ethyl undecanoate as the internal standard was added before blending. The puréed fruit was transferred to a 1-L Erlenmeyer flask covered with alumina foil and extracted with 100 mL of distilled pentane:diethyl ether (1:1 v/v) on a platform shaker (Innova 2300; New Brunswick Scientific, Edison, N.J., U.S.A.) at 125 rpm, for 3 h. The solvent and juice were poured into a separatory funnel. The juice was drawn off and returned to the fruit; the organic phase was retained. The extraction procedure was repeated twice, yielding a total volume of 280 mL solvent. Volatile compounds were recovered by using solvent-assisted flavor evaporation (SAFE) at 50 °C under vacuum (Engel and others 1999). The organic SAFE extract was dried with anhydrous Na_2SO_4, concentrated to 2 mL by solvent evaporation, and reduced to a final volume of 0.2 mL with a flow of nitrogen. This extraction was done in triplicate for each cultivar and growing season.

Gas chromatography-flame ionization detection (GC-FID) analysis

The analysis was performed using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector. Samples were analyzed on a DB-Wax column (60 m × 0.32 mm inner diameter cross-linked polyethylene glycol 0.5 μm film thickness; J&W Scientific, Folsom, Calif., U.S.A.). Injector and detector temperatures were 250 °C, nitrogen was used as the carrier gas and column flow rate was 2.0 mL/min at 25 °C, and the 2-μL sample injections were splitless. The oven temperature was programmed for a 4-min hold at 35 °C, then 35 °C to 235 °C at 2 °C/min (30 min hold). Retention indices were estimated in accordance with a modified Kovats method (Van den Dool and Kratz 1963).

Gas chromatography-mass spectrometry (GC-MS) analysis

The same samples as used for GC-FID analysis (2-μL splitless injections) were analyzed using an Agilent 6890 gas chromatograph equipped with an Agilent 5973 mass selective detector. System software control and data management/analysis were performed through Enhanced ChemStation Software, G1701CA v. C.00.01.08 (Agilent Technologies, Inc., Wilmington, Del., U.S.A.). Volatile separation was achieved with the same DB-Wax capillary column used in the GC-FID analyses. A constant helium column flow rate was set at 2 mL/min and the same GC oven temperature programming was set as for the GC-FID analysis. Injector, detector transfer line, and ion source temperatures were 250, 280, and 230 °C, respectively. Electron impact mass spectrometric data from m/z 35 to 300 was collected using a scan rate of 5.27/s, with an ionization voltage of 70 eV. Retention indices were estimated in accordance with a modified Kovats method (Van den Dool and Kratz 1963). Compound identifications were made by comparing mass spectral data from the Wiley 275.L (G1035) Database (Agilent), and confirmed by comparing Kovats retention indices (RI) to the standards or RI reported in the literature.

Quantitative analysis

Volatile compound concentrations were calculated based on comparison of individual volatile peak area from GC-FID response to the peak of the internal standard. Each tabulated experimental value corresponds to the average of the 3 extraction replicates. Odor activity values (OAV) were calculated by dividing the concentrations of aroma compounds in blackberries with their sensory thresholds in water (Patton and Josephson 1957).

Statistical analysis.

An analysis of variance was used to test the variances of volatile concentrations from growing seasons and cultivars. The statistical analysis was performed using the S-PLUS Version 6.1 software (Insightful Corp., Seattle, Wash., U.S.A.).

Results and Discussion

The volatile compositions (ppm) for 'Marion' and 'Thornless Evergreen' through 3 growing seasons are given in Table 1. Seasonal variations and cultivar differences can be inferred by using two-way analysis of variance statistical analysis. These volatile compounds can be summarized according to their chemical classes or biological origins. Based on the total concentration for each chemical class, the most abundant volatiles in 'Marion' were acids, followed by alcohols, terpenes and terpenoids, ketones, esters, aldehydes, and phenols. Comparatively, the most abundant volatiles in 'Thornless Evergreen' were alcohols, followed by terpenes and terpenoids, acids, phenols, ketones, esters, and aldehydes. Based on compound class totals (Table 1), 'Thornless Evergreen' contains much greater amounts of volatiles than 'Marion' (27.33 versus 8.62 ppm). The concentrations of alcohols in 'Thornless Evergreen' are 6 times greater than in 'Marion', whereas the terpenes and terpenoids are 10 times greater. Aldehydes, esters, and ketones are, respectively, about 3, 1.5, and 2 times more concentrated in 'Thornless Evergreen' than those in 'Marion'.

Table 1 data indicates that acids (pungent, cheesy, sour) and alcohols (alcoholic, floral, fruity, green) represent 78.08% (53.83% + 24.25%) of the total volatiles identified in 'Marion.' Terpenes and terpenoids (citrus, piney, terpene-like) account about 10% of the total volatiles while aldehydes (green, fruity, vegetal, 1.62 %), ketones (floral, fruity, 5.10 %), esters (floral, fruity, sweet, 4.64%), and phenols (0.23%) account for the remaining 12%. In the case of 'Thornless Evergreen,' Table 1 data shows that alcohols represent 46.62% of the total volatiles identified, whereas terpenes and terpenoids account for 31.94%. The 6 most abundant volatiles in 'Marion,' totaling 5.34 ppm, were acetic, hexanoic, decanoic and 2/3-me-

Table 1—'Marion' and 'Thornless Evergreen' blackberry volatiles (ppm)

DB-wax RI	Compound	Basis of identifi-cation	'Marion' growing season[a] 2002	2001	1999	ppm[b]	'Thornless Evergreen' growing season[a] 2002	2001	1999	ppm[b]	Main effect of cultivar (*P* value)
	Acids[c]		**5.29**	**5.56**	**3.08**	**4.64**	**5.17**	**1.42**	**1.20**	**2.60**	
1471	Acetic acid	MS, RI	3.69bA[d]	0.85aA	0.86aA	1.80	0.08bB	0.02aB	0.03aB	0.04	<0.01*[e]
1642	Butanoic acid	MS, RI	0.23a	0.20a	0.12b	0.19	0.12b	0.03a	0.04a	0.07	<0.01
1688	2/3-Methylbutanoic acid	MS, RI	0.15bA	0.44a	0.43a	0.34	1.82bB	0.51a	0.52a	0.95	<0.01*
1874	Hexanoic acid	MS, RI	0.91aA	3.22bA	1.18aA	1.77	2.27bB	0.66aB	0.43aB	1.12	<0.01*
2002	*t*-2-Hexenoic acid	MS, RI	0.03aA	0.13b	0.04a	0.07	0.55bB	0.12a	0.10a	0.26	<0.01*
2085	Octanoic acid	MS, RI	0.15	0.19	0.19	0.18	0.06b	0.02a	0.03a	0.04	<0.01
2308	Decanoic acid	MS, RI	0.13a	0.53b	0.26a	0.30	0.27b	0.05a	0.05a	0.12	<0.01
	Alcohols[c]		**1.72**	**2.89**	**1.61**	**2.09**	**21.94**	**8.90**	**7.37**	**12.74**	
955	Ethanol	MS, RI	0.75aA	1.02aA	0.02b	0.60	0.09B	0.03B	0.02	0.05	<0.01*
1045	2-Butanol	MS, RI					0.02	0.01	0.01	0.01	
1060	2-Methyl-3-buten-2-ol	MS, RI					0.12	0.09	0.08	0.10	
1113	2-Methylpropanol	MS, RI					0.24b	0.03a	0.04a	0.10	
1142	2-Pentanol	MS, RI					0.05a	0.02ab	0.03b	0.03	
1167	Butanol	MS, RI	0.02A	0.03	0.03	0.03	0.39bB	0.07a	0.06a	0.17	<0.01*
1181	1-Penten-3-ol	MS, RI					0.06	0.09	0.04	0.06	
1220	2-Methyl/3-methylbutanol	MS, RI	0.02	0.05A	0.04A	0.04	0.03b	0.01aB	0.01aB	0.02	0.02*
1272	3-Methyl-3-buten-1-ol	MS, RIL[f]					0.10b	0.03a	0.03a	0.05	
1344	2-Heptanol	MS, RI	0.18	0.25	0.37	0.27	4.15	3.95	4.06	4.05	<0.01
1378	Hexanol	MS, RI	0.09aA	0.27bA	0.21abA	0.19	4.09bB	1.08aB	0.57aB	1.92	<0.01*
1389	*t*-3-Hexenol	MS, RI					0.09b	0.02a	0.01a	0.04	
1410	*cis*-3-Hexenol	MS, RI	0.10A	0.11	0.16	0.12	0.26bB	0.13a	0.13a	0.17	<0.01*
1432	*t*-2-Hexenol	MS, RI	0.03aA	0.09bA	0.07abA	0.06	0.67bB	0.34aB	0.25aB	0.42	<0.01*
1441	*cis*-2-Hexenol	MS, RI					0.02b	0.01a	0.01a	0.01	
1481	Heptanol	MS, RI					0.15b	0.05a	0.05a	0.08	
1488	6-Methyl-5-hepten-2-ol	MS, RIL[g]	0.02A	0.03	0.04	0.03	0.08bB	0.03a	0.04a	0.05	<0.01*
1538	2-Nonanol	MS, RI	0.03	0.05	0.05	0.04	0.03			0.03	
1573	Octanol	MS, RI	0.09A	0.08A	0.09A	0.09	6.64bB	1.13aB	0.66aB	2.81	<0.01*
1676	Nonanol	MS, RI	0.02A	0.03A	0.03A	0.03	0.53bB	0.12aB	0.12aB	0.26	<0.01*
1738	2-Undecanol	MS, RIL[h]	0.09a	0.24b	0.11a	0.15					
1787	Decanol	MS, RI	0.04A	0.06A	0.03A	0.05	1.54aB	0.42bB	0.24cB	0.73	<0.01*
1912	Benzyl alcohol	MS, RI	0.11aA	0.27b	0.20c	0.19	0.64bB	0.27a	0.22a	0.38	<0.01*
1950	Phenylethyl alcohol	MS, RI	0.04aA	0.09bA	0.06aA	0.06	1.15aB	0.78bB	0.51cB	0.81	<0.01*
2029	4-Phenyl-2-butanol[T]	MS	0.03a	0.07bA	0.05aA	0.05	0.05	0.02B	0.02B	0.03	0.11*
2331	Cinnamic alcohol	MS, RIL[i]	0.06aA	0.15b	0.05aA	0.09	0.75aB	0.17b	0.16cB	0.36	<0.01*
	Aldehydes[c]		**0.17**	**0.15**	**0.10**	**0.14**	**0.55**	**0.41**	**0.15**	**0.37**	
925	2-Methylbutanal	MS, RI					0.02	0.02	0.01	0.01	
929	3-Methylbutanal	MS, RI					0.02	0.01	0.01	0.01	
1098	Hexanal	MS, RI	0.08	0.05	0.06	0.06	0.06	0.08	0.03	0.06	0.77
1119	2-Methyl-2-butenal	MS, RIL[j]					0.02	0.01	0.01	0.01	
1237	*t*-2-Hexenal	MS, RI	0.09A	0.09A	0.04	0.07	0.39aB	0.28aB	0.07b	0.25	<0.01*
1514	*t, t*-2,4-Heptadienal	MS, RIL[k]					0.03	0.01	0.01	0.02	
	Ketones[c]		**0.35**	**0.60**	**0.36**	**0.44**	**1.38**	**0.61**	**0.59**	**0.84**	
918	2-Butanone	MS, RI					0.01	0.01	0.01	0.01	
992	2-Pentanone	MS, RI					0.03b	0.01a	0.01a	0.02	
1006	3-Methyl-3-buten-2-one[T]	MS					0.34	0.27	0.36	0.32	
1200	2-Heptanone	MS, RI	0.04A	0.06A	0.05A	0.05	0.91bB	0.30aB	0.17aB	0.46	<0.01*
1309	Acetoin	MS, RI	0.14bA	0.05aA	0.02a	0.07	0.06bB	0.01aB	0.01a	0.03	<0.01*
1417	2-Nonanone	MS, RI	0.01	0.01	0.03	0.02					
1608	2-Undecanone	MS, RI	0.13a	0.42b	0.23ab	0.26					
1894	α-Ionone	MS, RI	0.01a	0.02b	0.01a	0.01					
1978	β-Ionone	MS, RI	0.02a	0.04b	0.02a	0.03					
	Terpenes and terpenoids[c]		**0.27**	**1.60**	**0.74**	**0.86**	**9.56**	**8.59**	**7.76**	**8.73**	
1029	α-Pinene	MS, RI	0.02a	0.07b	0.04a	0.04	1.54	2.83	2.29	2.22	<0.01
1075	Camphene	MS, RI	0.01a	0.03b	0.02a	0.02	0.13	0.15	0.16	0.15	<0.01
1129	β-Pinene	MS, RI					0.05	0.12	0.11	0.09	
1192	α-Phellandrene	MS, RI					0.04	0.07	0.06	0.05	
1213	Limonene	MS, RI	0.03a	0.07b	0.04ab	0.04	0.29	0.41	0.33	0.34	<0.01
1231	Sabinene	MS, RI					0.90b	0.15a	0.06a	0.37	
1262	γ-Terpinene	MS, RI	0.01	0.02	0.01	0.01	0.02ab	0.03a	0.02b	0.02	<0.01
1288	*p*-Cymene	MS, RI					0.13a	0.23b	0.17ab	0.18	
1301	α-Terpinolene	MS, RI	0.06a	0.19b	0.07a	0.11	0.22ab	0.28a	0.13b	0.21	<0.01
1489	*cis*-Sabinene hydrate	MS, RIL[l]					0.02a	0.04b	0.01a	0.02	
1496	Linalool oxide	MS, RI					0.01			0.01	
1545	Camphor	MS, RIL[f]					0.02	0.02	0.02	0.02	
1562	Linalool	MS, RI	0.08aA	1.03bA	0.49abA	0.53	0.26bB	0.11aB	0.14aB	0.17	<0.01*

Table 1—'Marion' and 'Thornless Evergreen' blackberry volatiles (ppm) *(Continued)*

DB-wax RI	Compound	Basis of identifi-cation	'Marion' growing season[a] 2002	2001	1999	ppm[b]	'Thornless Evergreen' growing season[a] 2002	2001	1999	ppm[b]	Main effect of cultivar (*P* value)
1566	Theaspirane (B)	MS, RI	0.01	0.02	0.01	0.01					
1614	4-Terpineol	MS, RIL[f]					0.23	0.20	0.26	0.23	
1618	β-Caryophyllene	MS, RI	0.003a	0.02b	0.01a	0.01					
1659	1-Terpineol	MS, RI					0.01	0.01	0.01	0.01	
1665	Myrtenal	MS, RI					0.01	0.01	0.01	0.01	
1717	1,8-Menthadien-4-ol[T]	MS					0.03b	0.01a	0.02a	0.02	
1721	α-Terpineol	MS, RI					1.47b	0.99a	0.93a	1.13	
1728	*l*-Borneol	MS, RI					0.56b	0.23a	0.38a	0.39	
1766	*t,t*-α-farnesene	MS, RIL[m]	0.04ab	0.05a	0.02b	0.04					
1791	Citronellol	MS, RI					0.01a		0.01a	0.01	
1827	Nopol[T]	MS					1.42a	1.21ab	1.00b	1.21	
1831	Myrtenol	MS, RI					0.14			0.14	
1881	*p*-Cymen-8-ol	MS, RIL[m]	0.01aA	0.10bA	0.03aA	0.05	1.51B	1.17B	1.35B	1.34	<0.01*
2040	Perilla alcohol	MS, RIL[l]					0.32	0.12	0.09	0.18	
	Esters[c]		**0.32**	**0.67**	**0.21**	**0.40**	**1.11**	**0.30**	**0.39**	**0.59**	
905	Ethyl acetate	MS, RI	0.13aA	0.24bA	0.08a	0.15	0.29bB	0.07aB	0.08a	0.15	0.96*
1062	Ethyl 2-methylbutanoate	MS, RI					0.01			0.01	
1088	Butyl acetate	MS, RI					0.01			0.01	
1251	Ethyl hexanoate	MS, RI	0.01ab	0.02aA	0.01b	0.02	0.02b	0.01aB	0.01a	0.01	0.07*
1291	Hexyl acetate	MS, RI	0.02aA	0.15bA	0.04a	0.07	0.04aB	0.03abB	0.01b	0.03	<0.01*
1354	*t*-2-Hexenyl acetate	MS, RI	0.01aA	0.06bA	0.01a	0.03	0.05bB	0.02aB	0.01a	0.03	0.23*
1367	Ethyl *t*-2-hexenoate	MS, RIL[n]					0.02			0.02	
1454	Ethyl octanoate	MS, RI	0.01	0.01	0.01	0.01	0.03	0.03	0.01	0.02	<0.01
1490	Octyl acetate	MS, RI					0.09b	0.02a	0.02a	0.04	
1540	Ethyl 3-hydroxybutanoate	MS, RIL[o]					0.16b	0.03a	0.03a	0.07	
1647	Ethyl decanoate	MS, RI	0.04aA	0.04a	0.02bA	0.03	0.05aB		0.05aB	0.05	<0.01*
1809	Methyl salicylate	MS, RIL[k]	0.03aA	0.11b	0.03aA	0.06	0.19aB	0.07b	0.12cB	0.13	<0.01*
1866	Ethyl dodecanoate	MS, RIL[o]	0.05	0.04	0.01	0.03					
2281	Ethyl hexadecanoate	MS, RI	0.02A	0.02	0.01	0.01	0.15bB	0.01a	0.05a	0.07	<0.01*
	Phenols[c]		**0.02**	**0.02**	**0.02**	**0.02**	**2.35**	**0.35**	**0.45**	**1.27**	
2039	Phenol	MS, RIL[h]					0.06	0.02	0.03	0.04	
2042	Methyl eugenol[T]	MS					0.32			0.32	
2205	Eugenol	MS, RI	0.02A	0.02A	0.02A	0.02	0.80bB	0.18aB	0.23aB	0.41	<0.01*
2264	Elemicin	MS, RIL[p]					1.17b	0.15a	0.19a	0.50	

[a]Means of triplicate samples.
[b]Means of 3 growing seasons; different small letters in the same cultivar and the same row indicate significant differences between seasons ($P < 0.05$).
[c]Class row values are totals.
[d]Different capital letters for the same season and same row indicate significantly different between 2 cultivars ($P < 0.05$).
[e]*, indicates significantly interaction between cultivar and growing season ($P < 0.05$).
[f]Retention index from the literature, Umano and others (2000).
[g]From Jorgensen and others (2000).
[h]From Parada and others (2000).
[i]From Choi and Sawamura (2000).
[j]From Pino and Marbot (2001).
[k]From Vichi and others (2003).
[l]From Verzera and others (2000).
[m]From Buttery and others (2000).
[n]From Dregus and Engel (2003).
[o]From Pino and others (2001).
[p]From Kjeldsen and others (2003).
[T]Tentatively identified by MS only.

thylbutanoic acids, ethanol, and linalool. In 'Thornless Evergreen,' totaling 13.55 ppm, the 6 most abundant volatiles were 2-heptanol, octanol, α-pinene, hexanol, *p*-cymen-8-ol, and nopol.

The major acids found in 'Marion' and 'Thornless Evergreen' blackberries were even-numbered carbon acids, C_2 to C_{10}. Acids were the largest chemical class in 'Marion'. Concentrations of acids varied from season to season for both 'Marion' and 'Thornless Evergreen' blackberries. The dominated acids in 'Marion' were acetic and hexanoic acids, which represented about 77% of total acids. Hexanoic acid was dominated in both 1999 and 2001 growing seasons, whereas acetic acid was dominated in 2002 growing season. The dominated acids in 'Thornless Evergreen' were hexanoic and 2/3-methylbutanoic acids, which represented 80% of total acids. The acids were about 4 times higher in 2002 growing season than in 1999 and 2001 growing seasons. On average, the total acids in 'Marion' were twice as much as in 'Thornless Evergreen'. Most of these acids were probably derived from β-oxidation of fatty acids (Sanz and others 1997). During fruit ripening, fatty acids, more precisely acyl-CoA derivatives, are metabolized to shorter-chain acyl-CoAs by sequentially losing 2 carbons during each round of the β-oxidation cycle (Sanz and others 1997).

The alcohol levels in 'Marion' were relatively small. Except for ethanol, most alcohols had concentrations less than 0.5 ppm. In 'Thornless Evergreen', however, many alcohols were present at very high concentrations (>1.0 ppm). The dominant alcohols were 2-heptanol, octanol, and hexanol. Seasonal variations were observed for hexanol (ranging from 0.57 to 4.09 ppm), octanol (ranging from 0.66 to 6.64 ppm), and decanol (ranging from 0.24 to 1.54 ppm). In all cases, the concentrations of hexanol, octanol, and decanol were highest in 2002 growing seasons and lowest in 1999 growing seasons. In contrast, seasonal variations were not obvious for 2-heptanol (range from 3.95 to 4.15 ppm), suggesting different metabolic pathway of 2-heptanol from hexanol, octanol, and decanol in 'Thornless Evergreen' blackberry. It is possible that fatty acids serve as the precursor for hexanol, octanol, and decanol. In addition to hexanol, several other C_6 alcohols (*t*-3-hexenol, *cis*-3-hexenol, *t*-2-hexenol, *cis*-2-hexenol) were also identified. These C_6 alcohols, which typically give green, leafy aromas, could be generated through lipoxygenase pathway of unsaturated linoleic and linolenic acids (Stone and others 1975; Olias and others 1993; Perez and others 1999). In many types of fruits, this enzymatic oxidative degradation starts with acyl hydrolases, which produce polyunsaturated fatty acids from glycolipids, phospholipids, or triacylglycerols. Through the action of LOX and LOX isozymes, linoleic and linolenic acids are degraded and produce fatty acid hydroperoxides. Hydroperoxide lyase converts these fatty acid hydroperoxides to aldehydes and oxoacids, while alcohol dehydrogenase acts on them to produce the corresponding alcohols (Sanz and others 1997).

Aromatic alcohols (benzyl alcohol, phenylethyl alcohol, 4-phenyl-2-butanol, and cinnamic alcohol) were identified in both cultivars. 4-Phenyl-2-butanol had slightly higher concentration in 'Marion' while benzyl alcohol, phenylethyl alcohol and cinnamic alcohol were slightly higher in 'Thornless Evergreen'. It is possible that benzyl alcohol, phenylethyl alcohol, and cinnamic alcohol share the same pathway, with phenylalanine as the common precursor as in other fruits such as apples, kiwi, pineapple, strawberry, tomato, quince, passion fruit, and guava, among others (Williams 1993; Rouseff and Leahy 1995; Leahy and Roderick 1999).

Aldehydes and ketones represented a small percentage of total volatiles in both 'Marion' and 'Thornless Evergreen' blackberries. The dominant aldehyde in 'Thornless Evergreen' was *t*-2-hexenal. *t*-2-Hexenal probably shares the same metabolic pathways of other C_6 compounds, for example, lipoxygenase catalyzed degradation of unsaturated fatty acid, as *t*-2-hexenol was also the major unsaturated C_6 alcohols in 'Thornless Evergreen.' None of the aldehydes were present at large amounts in 'Marion.' 2-Heptanone and 3-methyl-3-buten-2-one were dominant ketones in 'Thornless Evergreen,' while 2-undecanone was found in a large amount in 'Marion.' α- and β-ionones were identified in 'Marion' but not in 'Thornless Evergreen.' Although the exact breeding process of 'Marion' is still a mystery, it has been suspected that raspberry was involved in the breeding process of 'Marion,' and α- and β-ionones have been identified as the major volatile components in red raspberry (Klesk and others 2004).

Esters accounted about 4.6% of the total volatiles in 'Marion' while only about 2.2% in 'Thornless Evergreen'. The compositions of esters were not related to their corresponding acid composition, and ethyl acetate was always dominated in both 'Marion' and 'Evergreen' blackberries. The amount of methyl salicylate was also large in 'Thornless Evergreen'. Esters could be produced from the enzymatic actions on alcohols and acyl CoA's derived from both fatty acid and amino acid metabolism (Wyllie and Fellman 2000).

Terpenes and terpenoids represented 10% of total volatiles for 'Marion' and 32% for 'Thornless Evergreen.' In 'Thornless Evergreen' blackberry, the most abundant terpenes and terpenoids were α-pinene, α-terpineol, nopol, and *p*-cymen-8-ol, whereas 'Marion' had no single terpene or terpenoid in large quantities. High levels of terpenes and terpenoids are probably responsible for the piney, resinous, and citrus odor characters described for 'Thornless Evergreen'(Klesk and Qian 2003a, 2003b). In most fruits, terpenes and terpenoids are probably produced from carbohydrate metabolism through the isoprenoid pathway (Sanz and others 1997). Mevalonic acid (MVA) is considered to be the 1st precursor, which is then converted to isopentenyl diphosphate (IPP). A molecule of isopentenyl diphosphate can be isomerized to dimethylallyl diphosphate (DMAPP) by isopentenyl diphosphate isomerase. DMAPP and IPP can be condensed to form geranyl diphosphate (GPP). From GPP, volatile monoterpenes and terpenoids can be generated through the enzymatic reactions of hydrolysis, cyclizations, and oxidoreductions (Sanz and others 1997).

Because aroma profiles not only depend on volatile concentrations, but also their odor thresholds, odor activity values (OAVs, the ratios of volatile concentrations to thresholds) were calculated to further elucidate aroma contributions of these compounds. Table 2 summarizes the OAVs of aroma compounds in 'Marion' and 'Thornless Evergreen' blackberries, based on published odor thresholds. In 'Marion', 18 aroma compounds had OAVs greater than 1.0, 4 compounds had OAVs between 0.5 and 1.0, and 8 others had OAVs between 0.1 and 0.5. The compounds with the most extreme values (OAV > 10) were ethyl hexanoate (1518.1), β-ionone (282.2), linalool (88.7), 2-heptanone (50.9), 2-undecanone (36.8), α-ionone (23.9), and hexanal (14.2). Except for hexanal, the odor descriptors of these compounds match published 'Marion' aromas such as floral, fruity, sweet, caramel-fruity, and woody (Klesk and Qian 2003a, 2003b). Although the OAVs for hexanal (OAV: 14.2), limonene (OAV: 4.4), and hexanoic acid (OAV: 1.8) imply their possible aroma contributions, their odor descriptors in 'Marion' aroma is lacked, which is likely due to human olfactory dynamics. Olfaction is thought to be a combinatorial approach to recognizing and processing odors with proteinaceous odorant receptors. This theory implies that odor response is characterized by inhibition, suppression, and synergistic effects between odorants (Malnic and others 1999). It is plausible then that the perceived aroma of 'Marion' is a function of these effects acting on any number of the identified aromas. Further, previous blackberry aroma studies identified 5 furanones, compounds with powerful sweet and caramel-fruity aromas (Klesk and Qian 2003b). Although not quantified in this study, these furanones are likely to be important sources of 'Marion' aroma characteristics, while inhibiting or suppressing other strong aromas.

In 'Thornless Evergreen', 30 aroma compounds had OAVs greater than 1.0, 5 compounds had OAVs between 0.5 and 1.0, and 12 others had OAVs between 0.1 and 0.5. The compounds with the most extreme values (OAV > 10) were ethyl hexanoate (1184.2), 2-heptanone (461.5), ethyl 2-methylbutanoate (103.4), 2-heptanol (57.9), 3-methylbutanal (39.2), α-pinene (35.9), limonene (34.4), *p*-cymene (28.5), linalool (28.1), *t*-2-hexenal (24.9), myrtenol (19.7), hexanal (12.9), 2-methylbutanal (11.5), and sabinene (10.0). The odor descriptors of these compounds match published 'Thornless Evergreen' aromas such as spicy, green, herbaceous, fruity, and sweet (Klesk and Qian 2003b). However, the data do not provide unambiguous guidance to reproduce blackberry aroma. To clearly determine which of the identified odor-active volatiles contribute to the distinctive aromas of 'Marion' and 'Thornless Evergreen' blackberries, including those volatiles that add subtle background aromas required for a "natural, complete" blackberry aroma, further studies are required. In addition, volatile composition may change during the storage as well as during the freezing and thawing process.

Conclusions

Seasonal variations were observed for some volatile compounds in both 'Marion' and 'Thornless Evergreen' blackberries. In 'Marion,' these compounds were mainly acids. In 'Thornless Evergreen,' seasonal variations were mainly noted for acids, alcohols, and a few terpenoids. These variations and magnitude of changes appear random with regards to growing season. Volatile compositions of 'Marion' and 'Thornless Evergreen' blackberries were quite

Table 2—OAV[a] of aroma compounds in 'Marion' and 'Thornless Evergreen' blackberries

DB-wax RI	Compound	Aroma descriptors[b]	Odor threshold[c] (ppm)	'Marion' (ppm)[d]	OAV	'Thornless Evergreen' (ppm)[d]	OAV
	Acids						
1471	Acetic acid	vinegar	60	1.80	< 0.1	0.04	< 0.1
1642	Butanoic acid	rancid, cheesy	1	0.19	0.2	0.07	< 0.1
1685	2/3-Methylbutanoic acid	rancid, cheesy	4.7/0.25	0.34	1.4	0.95	3.8
1874	Hexanoic acid	rancid	1	1.77	1.8	1.12	1.1
2002	*t*-2-Hexenoic acid	fatty, rancid	1	0.07	< 0.1	0.26	0.3
2085	Octanoic acid	sour, goaty	0.91	0.18	0.2	0.04	<0.1
2308	Decanoic acid	rancid, soapy	1	0.30	0.3	0.12	0.1
	Alcohols						
955	Ethanol	alcoholic	16	0.60	< 0.1	0.05	<0.1
1045	2-Butanol	alcoholic	16			0.01	<0.1
1060	2-Methyl-3-buten-2-ol	herbaceous	100			0.10	<0.1
1113	2-Methylpropanol	wine-like	16			0.10	<0.1
1142	2-Pentanol	green, fusel oil	8.1			0.03	<0.1
1167	Butanol	alcoholic	28	0.03	< 0.1	0.17	<0.1
1181	1-Penten-3-ol	green	0.4			0.06	0.2
1220	2/3-Methylbutanol	wine-like	20/0.41	0.04	<0.1	0.02	<0.1
1272	3-Methyl-3-buten-1-ol	herbaceous	unknown			0.05	
1344	2-Heptanol	fruity, herbaceous	0.07	0.27	3.8	4.05	57.9
1378	Hexanol	fruity	2.5	0.19	< 0.1	1.92	0.8
1389	*t*-3-Hexenol	green	1.55			0.04	< 0.1
1410	*cis*-3-Hexenol	green, leaf	0.1	0.12	1.2	0.17	1.7
1432	*t*-2-Hexenol	green	0.1	0.06	0.6	0.42	4.2
1441	*cis*-2-Hexenol	green	unknown			0.01	
1481	Heptanol	fatty, pungent	0.33			0.08	0.3
1488	6-Methyl-5-hepten-2-ol	unknown	2	0.03	< 0.1	0.05	< 0.1
1538	2-Nonanol	fruity, green	0.058	0.04	0.8	0.03	0.6
1573	Octanol	sweet, rose-like	0.875	0.09	0.1	2.81	3.2
1676	Nonanol	rose-orange	1	0.03	<0.1	0.26	0.3
1738	2-Undecanol	fruity	0.041	0.15	3.6		
1787	Decanol	fruity, floral, fatty	0.775	0.05	<0.1	0.73	0.9
1912	Benzyl alcohol	Sweet, cherry	0.1	0.19	1.9	0.38	3.8
1950	Phenylethyl alcohol	rose-like	1	0.06	<0.1	0.81	0.8
2029	4-Phenyl-2-butanol	floral	unknown	0.05		0.03	
2331	Cinnamic alcohol	floral	1	0.09	<0.1	0.36	0.4
	Aldehydes						
925	2-Methylbutanal	green, malty	0.0013			0.01	11.5
929	3-Methylbutanal	fresh grass, cocoa	0.00035			0.01	39.2
1098	Hexanal	green, unripe fruit	0.0045	0.06	14.2	0.06	12.9
1119	2-Methyl-2-butenal	fresh, fruity	0.5			0.01	<0.1
1237	*t*-2-Hexenal	green, leaf	0.01	0.07	7.5	0.25	24.9
1514	*t,t*-2,4-Heptadienal	fatty, green	0.049[e]			0.02	0.4
	Ketones						
918	2-Butanone	acetone-like	80[f]			0.01	<0.1
992	2-Pentanone	ethereal	0.01			0.02	2.0
1006	3-Methyl-3-buten-2-one	unknown	unknown			0.32	
1200	2-Heptanone	fruity	0.001	0.05	50.9	0.46	461.5
1309	Acetoin	buttery	8	0.07	<0.1	0.03	<0.1
1417	2-Nonanone	fruity	0.041	0.02	0.4		
1608	2-Undecanone	orange	0.007	0.26	36.8		
1894	α-Ionone	violet-like	0.0006	0.01	23.9		
1978	β-Ionone	violet-like, fruity	0.0001	0.03	282.2		
	Terpenes and terpenoids						
1029	α-Pinene	pine, resinous	0.062	0.04	0.7	2.22	35.9
1075	Camphene	terpene	1.98[g]	0.02	< 0.1	0.15	< 0.1
1129	β-Pinene	woody, resinous	0.082			0.09	1.1
1192	α-Phellandrene	sweet, rose-like	0.2			0.05	0.3
1213	Limonene	lemon-like	0.01	0.04	4.4	0.34	34.4
1231	Sabinene	woody	0.037			0.37	10.0
1262	γ-Terpinene	fruity, lemon-like	unknown	0.01		0.02	
1288	*p*-Cymene	carrot-like	0.0062			0.18	28.5
1301	α-Terpinolene	sweet, piney	0.2	0.11	0.5	0.21	1.1
1496	Linalool oxide	woody, floral	unknown			0.01	
1545	Camphor	medicinal, woody	4.6			0.02	< 0.1
1562	Linalool	floral, citrus	0.006	0.53	88.7	0.17	28.1
1566	Theaspirane (B)	ionone-like, fruity	unknown	0.01			
1614	4-Terpineol	earthy, lilac	6.4			0.23	< 0.1
1618	β-Caryophyllene	terpeney, spicy	0.064	0.01	0.2		

Table 2—OAV[a] of aroma compounds in 'Marion' and 'Thornless Evergreen' blackberries *(Continued)*

DB-wax RI	Compound	Aroma descriptors[b]	Odor threshold[c] (ppm)	'Marion' (ppm)[d]	OAV	'Thornless Evergreen' (ppm)[d]	OAV
1659	1-Terpineol	woody, musty	unknown			0.01	
1665	Myrtenal	spicy, cinnamon	unknown			0.01	
1717	1,8-Menthadien-4-ol	unknown	unknown			0.02	
1721	α-Terpineol	lilac	0.33			1.13	3.4
1728	*l*-Borneol	pungent, mint	0.14			0.39	2.8
1766	*t,t* -α-farnesene	sweet, flowery	unknown	0.04			
1791	Citronellol	sweet, floral	0.062			0.01	0.1
1827	Nopol	camphoraceous	unknown			1.21	
1831	Myrtenol	flowery, mint	0.007			0.14	19.7
1881	*p*-Cymen-8-ol	musty	unknown	0.05		1.34	
2040	Perilla alcohol	green, fatty	1.66[g]			0.18	0.1
2137	*p*-Cymen-α-ol	unknown	unknown			0.21	
	Esters						
905	Ethyl acetate	fruity, floral	25	0.15	< 0.1	0.15	<0.1
1062	Ethyl 2-methylbutanoate	fruity, pineapple	0.000091			0.01	103.4
1088	Butyl acetate	fruity, pineapple	0.01			0.01	1.3
1251	Ethyl hexanoate	fruity, banana	0.00001	0.02	1518.1	0.01	1184.2
1291	Hexyl acetate	sweet, fruity	0.01	0.07	7.1	0.03	3.0
1354	*t*-2-Hexenyl acetate	fruity, green	unknown	0.01		0.03	
1367	Ethyl *t*-2-hexenoate	fruity, pineapple	unknown			0.01	
1454	Ethyl octanoate	fruity, floral	0.005	0.01	1.6	0.02	4.6
1490	Octyl acetate	fruity, floral	0.047			0.04	0.9
1540	Ethyl 3-hydroxybutanoate	marshmallow	20[h]			0.07	<0.1
1647	Ethyl decanoate	fruity	0.122	0.03	0.3	0.05	0.4
1809	Methyl salicylate	green	0.04	0.06	1.4	0.13	3.2
1866	Ethyl dodecanoate	fruity	3.5	0.03	<0.1		<0.1
2281	Ethyl hexadecanoate	waxy	2	0.01	<0.1	0.07	<0.1
	Phenols						
2039	Phenol	medicinal	5.5			0.04	<0.1
2042	Methyl eugenol	clove	0.775			0.32	0.4
2205	Eugenol	clove, pungent	0.15	0.02	0.1	0.41	2.7
2264	Elemicin	woody, floral	22[i]			0.50	< 0.1

[a]Odor activity value(s).
[b]Aroma descriptors from the literature (Bauer and others 1997; Burdock 2001; Klesk and Qian 2003a, 2003b; Lee and others 2001; Perez and others 2002; Pino and others 2001).
[c]Thresholds in water from Van Gemert (1999) unless noted otherwise.
[d]Means of 3 growing seasons.
[e]Lillard and others (1962).
[f]Tan and Siebert (2004).
[g]Padrayuttawat and others (1997).
[h]Cullere and others (2004).
[i]Moshonas and Shaw (1978).

different. 'Thornless Evergreen' had many more volatiles than 'Marion.' While more acids were found in 'Marion,' more alcohols, terpenes, and terpenoids were found in 'Thornless Evergreen'. The OAVs reported in this study corroborate published aroma descriptions of the 2 cultivars; however, sensory recombination study is needed to confirm the results.

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References

Bauer K, Garbe D, Surburg H. 1997. Common fragrance and flavor materials: preparation, properties and uses, 3rd ed. Weinheim, Germany: Wiley-VCH. 278 p.

Burdock GA. 2001. Fenaroli's handbook of flavor ingredients. 4th ed. Boca Raton, Fla.: CRC Press. 1834 p.

Buttery RG, Light DM, Nam Y, Merrill GB, Roitman JN. 2000. Volatile components of green walnut husks. J Agric Food Chem 48(7):2858–61.

Choi HS, Sawamura M. 2000. Composition of the essential oil of *Citrus tamurana* Hort. ex Tanaka (Hyuganatsu). J Agric Food Chem 48(10):4868–73.

Cullere L, Escudero A, Cacho J, Ferreira V. 2004. Gas chromatography-olfactometry and chemical quantitative study of the aroma of six premium quality Spanish aged red wines. J Agric Food Chem 52(6):1653–60.

Dregus M, Engel KH. 2003. Volatile constituents of uncooked rhubarb (*Rheum rhabarbarum* L.) stalks. J Agric Food Chem 51(22):6530–6.

Engel W, Bahr W, Schieberle P. 1999. Solvent-assisted flavor evaporation—a new and versatile technique for the careful and direct isolation of aroma compounds from complex food matrices. Z Lebensm-Unters Forsch 209(3/4):237–41.

Finn C, Strik B, Lawrence FJ. 1997. 'Marion' trailing blackberry. Fruit Variet J 51(3):130–3.

Fitelson J. 1970. Detection of adulteration in fruit juices by qualitative determination of carbohydrates by gas-liquid chromatography. J Assoc Offic Anal Chem 53(6):1193–7.

Forney CF. 2001. Horticultural and other factors affecting aroma volatile composition of small fruit. Hort Tech 11(4):529–38.

Jorgensen U, Hansen M, Christensen LP, Jensen K, Kaack K. 2000. Olfactory and quantitative analysis of aroma compounds in elder flower (*Sambucus nigra* L.) drink processed from five cultivars. J Agric Food Chem 48(6):2376–83.

Georgilopoulos DN, Gallois AN. 1987a. Aroma compounds of fresh blackberries (*Rubus laciniata* L.). Z Lebensm-Unters Forsch 184(5):374–80.

Georgilopoulos DN, Gallois AN. 1987b. Volatile flavor compounds in heated blackberry juices. Z Lebensm-Unters Forsch 185(4):299–306.

Georgilopoulos DN, Gallois AN. 1988. Flavour compounds of a commercial concentrated blackberry juice. Food Chem 28(2):141–8.

Gulan MP, Veek MH, Scanlan RA, Libbey LM. 1973. Compounds identified in commercial blackberry essence. J Agric Food Chem 21(4):741.

Houchen M, Scanlan RA, Libbey LM, Bills DD. 1972. Possible precursor for 1-methyl-4-isopropenylbenzene in commercial blackberry flavor essence. J Agric Food Chem 20(1):170.

Humpf HU, Schreier P. 1991. Bound aroma compounds from the fruit and the leaves of blackberry (*Rubus laciniata* L.). J Agric Food Chem 39(10):1830–2.

Kjeldsen F, Christensen LP, Edelenbos M. 2003. Changes in volatile compounds of carrots (*Daucus carota* L.) during refrigerated and frozen storage. J Agric

Food Chem 51(18):5400–7.
Klesk K, Qian M. 2003a. Preliminary aroma comparison of Marion (*Rubus* spp. *hyb*) and Evergreen (*R. laciniatus* L.) blackberries by dynamic headspace/OSME technique. J Food Sci 68(2):697–700.
Klesk K, Qian M. 2003b. Aroma extract dilution analysis of cv. Marion (*Rubus* spp. *hyb*) and cv. Evergreen (*R. laciniatus* L.) blackberries. J Agric Food Chem 51(11):3436–41.
Klesk K, Qian M, Martin R. 2004. Aroma extract dilution analysis of cv. Meeker (*Rubus idaeus* L.) red raspberries from Oregon and Washington. J Agric Food Chem 52(16):5155–61.
Leahy M, Roderick RG. 1999. Fruit flavor biogenesis. In: Teranishi R, Wick EL, Hornstein I, editors. Flavor chemistry: thirty years of progress. New York: Kluwer Academic/Plenum Publishers. p 275–85.
Lee GH, Suriyaphan O, Cadwallader KR. 2001. Aroma components of cooked tail meat of American lobster (*Homarus americanus*). J Agric Food Chem 49(9):4324–32.
Lillard DA, Montgomery MW, Day EA. 1962. Flavor threshold values of certain carbonyl compounds in milk. J Dairy Sci 45(5):660.
Malnic B, Hirono J, Sato T, Buck LB. 1999. Combinatorial receptor codes for odors. Cell 96(5):713–23
Moshonas MG, Shaw PE. 1978. Compounds new to essential orange oil from fruit treated with abscission chemicals. J Agric Food Chem 26(6):1288–90.
Olias JM, Perez AG, Rios JJ, Sanz LC. 1993. Aroma of virgin olive oil: biogenesis of the "green" odor notes. J Agric Food Chem 41(12):2368–73.
Padrayuttawat A, Yoshizawa T, Tamura H, Tokunaga T. 1997. Optical isomers and odor thresholds of volatile constituents in *Citrus sudachi*. Food Sci Technol Int, Tokyo 3(4):402–8
Parada F, Duque C, Fujimoto Y. 2000. Free and bound volatile composition and characterization of some glucoconjugates as aroma precursors in melon de olor fruit pulp (*Sicana odorifera*). J Agric Food Chem 48(12):6200–4.
Patton S, Josephson D. 1957. A method for determining significance of volatile flavor compounds in foods. Food Res 22(3):316–8
Perez AG, Sanz C, Olias R, Olias JM. 1999. Lipoxygenase and hydroperoxide lyase activities in ripening strawberry fruits. J Agric Food Chem 47(1):249–53.
Perez RA, Sanchez-Brunete C, Calvo RM, Tadeo JL. 2002. Analysis of volatiles from Spanish honeys by solid-phase microextraction and gas chromatography-mass spectrometry. J Agric Food Chem 50(9):2633–7.
Pino JA, Marbot R. 2001. Volatile flavor constituents of acerola (*Malpighia emarginata* DC.) fruit. J Agric Food Chem 49(12):5880–2.
Pino JA, Marbot R, Vazquez C. 2001. Characterization of volatiles in strawberry guava (*Psidium cattleianum* Sabine) fruit. J Agric Food Chem 49(12):5883–7.
Plowman JE. 1991. Sugars and acids of raspberries, blackberries and other brambles. Lebensm Wiss Technol 24(1):113–5.
Rouseff RL, Leahy MM. 1995. Advances in fruit flavor research: an overview. In: Rouseff R, Leahy M, editors. Fruit flavors: biogenesis, characterization, and authentication. Washington, D.C.: American Chemical Society. p 1–6.
Sanz C, Olias J, Perez A. 1997. Aroma biochemistry of fruits and vegetables. In: Tomás-Barberán, FA, Robins RJ, editors. Phytochemistry of fruit and vegetables. New York: Oxford Univ. Press, New York. p 125–55.
Sapers GM, Burgher AM, Phillips JG, Galletta GJ. 1985. Composition and color of fruit and juice of thornless blackberry cultivars. J Amer Soc Hort Sci 110(2):243–8.
Scanlan RA, Bills DD, Libbey LM. 1970. Blackberry flavor components of commercial essence. J Agric Food Chem 18(4):744.
Stone EJ, Hall RM, Kazeniac SJ. 1975. Formation of aldehydes and alcohols in tomato fruit from U14c [uranium-carbon isotope]-labeled linolenic and linoleic acids. J Food Sci 40(6):1138–41.
Tan Y, Siebert KJ. 2004. Quantitative structure-activity relationship modeling of alcohol, ester, aldehyde, and ketone flavor thresholds in beer from molecular features. J Agric Food Chem 52(10):3057–64.
Turemis N, Kafkas E, Kafkas S, Kurkcuoglu M, Baser KHC. 2003. Determination of aroma compounds in blackberry by GC/MS analysis. Chem Natural Compd 39(2):174–6.
Umano K, Hagi Y, Nakahara K, Shoji A, Shibamoto T. 2000. Volatile chemicals identified in extracts from leaves of Japanese mugwort (*Artemisia princeps* Pamp.). J Agric Food Chem 48(8):3463–9.
Van den Dool H, Kratz PD. 1963. A generalization of the retention index system including linear temperature programmed gas-liquid partition chromatography. J Chromatogr 11(4):463–71.
Van Gemert LJ. 1999. Odour threshold values in water. In: Van Germert LJ, editor. Compilations of odour threshold values in air and water. Huizen, The Netherlands: Boelens Aroma Chemical Information Service. p 1–122.
Verzera A, Trozzi A, Cotroneo A, Lorenzo D, Dellacassa E. 2000. Uruguayan essential oil. 12. Composition of Nova and Satsuma mandarin oils. J Agric Food Chem 48(7):2903–9.
Vichi S, Pizzale L, Conte LS, Buxaderas S, Lopez-Tamames E. 2003. Solid-phase microextraction in the analysis of virgin olive oil volatile fraction: characterization of virgin olive oils from two distinct geographical areas of northern Italy. J Agric Food Chem 51(22):6572–7.
Williams P. 1993. Hydrolytic flavor release in fruit and wines through hydrolysis of nonvolatile precursors. In: Acree TE, Teranishi R, editors. Flavor science : sensible principles and techniques. Washington, D.C.: American Chemical Society. p 287–308.
Wrolstad RE, Culbertson JD, Nagaki DA, Madero CF. 1980. Sugars and nonvolatile acids of blackberries. J Agric Food Chem 28(3):553–8.
Wyllie SG, Fellman JK. 2000. Formation of volatile branched chain esters in bananas (*Musa sapientum* L.). J Agric Food Chem 48(8):3493–6.