Distribution of Volatile Composition in 'Marion' (*Rubus* Species *Hyb*) Blackberry Pedigree

Xiaofen Du,[†] Chad Finn,[§] and Michael C. Qian*,[†]

[†]Department of Food Science and Technology, Oregon State University, Corvallis, Oregon 97331 and
[§]Horticultural Crops Research Laboratory, Agricultural Research Service, U.S. Department of
Agriculture, Corvallis, Oregon 97330

The distribution of volatile constituents in ancestral genotypes of 'Marion' blackberry's pedigree was investigated over two growing seasons. Each genotype in the pedigree had a specific volatile composition. Red raspberry was dominated by norisoprenoids, lactones, and acids. 'Logan' and 'Olallie' also had a norisoprenoid dominance but at much lower concentrations. The concentration of norisoprenoids in other blackberry genotypes was significantly lower. Terpenes and furanones were predominant in wild 'Himalaya' blackberry, whereas terpenes were the major volatiles in 'Santiam'. 'Marion', a selection from 'Chehalem' and 'Olallie', contained almost all of the volatile compounds in its pedigree at moderate amount. The chiral isomeric ratios of 11 pairs of compounds were also studied. Strong chiral isomeric preference was observed for most of the chiral compounds, and each cultivar had its unique chiral isomeric distribution. An inherent pattern was observed for some volatile compounds in the 'Marion' pedigree. Raspberry and 'Logan' had a very high concentration of β-ionone, but was reduced by half in 'Olallie' and by another half in 'Marion' as the crossing proceeded. A high content of linalool in 'Olallie' and a low content in 'Chehalem' resulted in a moderate content of linalool in their progeny 'Marion'. However, the concentration of furaneol in 'Marion' was higher than in its parents. A high content of (*S*)-linalool in 'Olallie' and a racemic content of (*S*)-,(*R*)-linalool in 'Chehalem' resulted in a preference for the (*S*)-form in 'Marion'.

INTRODUCTION

'Marion' blackberry (*Rubus* sp. L.) was released in 1956 by the cooperative breeding program of the U.S. Department of Agriculture—Agricultural Research Service and the Oregon Agricultural Experiment Station. The pedigree of 'Marion' is quite complicated (**Figure 1**) (*1*). 'Chehalem' and 'Olallie' are the parents of 'Marion'. 'Chehalem' partly originates from wild 'Himalaya'. 'Olallie' has a red raspberry parent in its ancestry. The entire ancestry of 'Marion' is incomplete, and it may never be determined with complete accuracy.

'Marion' has an outstanding aroma and flavor quality; however, its canes are thorny. Consumer preference for 'Marion' flavor has stimulated the breeding program to develop thornless cultivars with 'Marion' type flavor. Blackberry plant breeding is a long process where thousands of seedlings need to be evaluated in the process of developing each new cultivar. Part of the reason the process is slow is that in each stage of evaluation (seedling, selection, advanced selection) it takes 2-3 years for the plants to be mature enough have fruit to evaluate. If the flavor makeups of the parents are known, and the flavor traits are heritable, it could be possible to "formulate" the parents and increase the
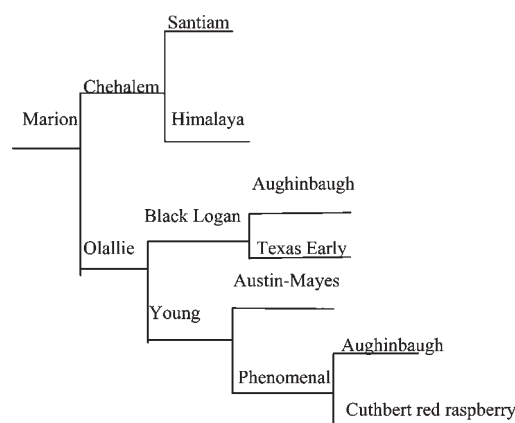

Figure 1. 'Marion' blackberry pedigree.

possibility of breeding in the desirable flavor attribute to new selections.

Breeding in flavor attributes is very complicated, and very few studies have reported the volatile heritability in berry fruits. From the volatile analysis of hybrids, it has been suggested that some compounds such as 3-methyl-2-butenoic and 3-methyl-3-butenoic acids, linalool oxides, α-terpineol, mesifurane, furaneol, alcohols, and esters are inherited in raspberry, strawberry,

*Author to whom correspondence should be addressed [telephone (541) 737-9114; fax (541) 737-1877; e-mail michael.qian@oregonstate.edu].

Article

J. Agric. Food Chem., Vol. 58, No. 3, 2010   **1861**

and highbush blueberry (*2−4*). However, it is difficult to make general conclusions of the patterns of inheritance of the volatile compounds in fruits.

More extensive studies on the inheritance of volatile compounds in fruits use a large number of seedlings or progenitors to make a statistical analysis. Most information for aroma inheritability is from studies on strawberry (*5−7*). Aroma analysis shows different models of inheritance of different compounds, which is not surprising considering that the multiplicity of volatile compounds is derived from different biochemical pathways. For instance, methyl anthranilate, a major compound in strawberry, was detectable in only one-fourth of the offspring of a cross between a parent that had fruit with detectable methyl anthranilate with one that had no detectable methyl anthranilate (*5*). This low degree of inheritance suggests that this important compound can be easily lost in the breeding process. Transgressive segregation, where the offspring has levels of compounds higher or lower than either parent is common. For instance in a cross of a strawberry parent whose fruit had no detectable methyl butanoate with one that had low levels, the offspring had fruit that ranged from no detectable methyl butanoate to fruit with levels 5× the level of the parent with detectable levels (*5*).

Very little is known of volatile heritability in blackberries, and the volatile composition in each genotype in the 'Marion' pedigree has not been fully studied. The objective of this study was to investigate the distribution of volatile constituents and enantiomeric ratio of some chiral compounds throughout the 'Marion' pedigree.

MATERIALS AND METHODS

Chemicals. All of the chemical standards used in this study are listed in **Tables 1** and **2**. Methanol (HPLC grade) was from EM Science (Gibbstown, NJ), and dichloromethane (HPLC grade) was from Burdick & Jackson (Muskegon, MI). Standard stock solutions of 7-methyl-3-methylene-1,6-octadiene (myrcene) and 6-heptyloxan-2-one (δ-dodeca-lactone) were prepared in dichloromethane individually at a concentration of 10 mg/mL, and all other stock solutions were prepared in methanol individually. Two sets of internal standards were prepared. Internal standard A was composed of 1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane (eucalyptol), 4-methyl-2-propan-2-ylphenol (isothymol), 4-heptanolide-4,5-dihydro-5-propyl-2(3*H*)-furanone (γ-heptalactone), and 1-(2-hydroxy-5-methylphenyl)ethanone with concentrations of 3.4, 8.3, 7.6, and 3.5 mg/L; internal standard B was 1-(2-hydroxy-5-methylphenyl)ethanone with a concentration of 70 mg/L.

Anhydrous sodium sulfate (99.9%, ACS certified) was supplied by Mallinckrodt Baker (Phillipsburg, NJ). Fructose, glucose, and citric acid were from Lancaster (Ward Hill, MA); sucrose and malic acid were from Spectrum (Gardena, CA). Synthetic juice contained 3.0% fructose, 3.1% glucose, 0.2% sucrose, 0.8% citric acid, and 0.9% malic acid. Citrate buffer solution (0.2 M, pH 3.1) was freshly prepared.

Berry Samples. Fully ripe berry samples including 'Marion', 'Chehalem', 'Santiam', 'Himalaya', 'Olallie', 'Logan', and 'Meeker' red raspberry were hand-harvested from plants growing in research plots at Oregon State University Lewis-Brown Farm in Corvallis, OR, between June and July of the 2007 and 2008 growing seasons. The berries were individually quick frozen (IQF) and stored at −18 °C until analysis. During analysis, 100 g of IQF berry fruit was thawed in a refrigerator (1 °C). Equal weights of distilled water and 1% calcium chloride (final concentration) were added, and the sample was then blended in a glass jar (Waring Products Div., Dynamics Corp. of America, New Hartford, CT) in high-speed pulse mode for 20 s. The puree was centrifuged for 20 min at 5000 rpm. The supernatant was filtered through a Waterman no. 1 filter paper (particle retention > 11 μm), followed by a VWR 413 filter paper (particle retention > 5 μm). The filtered clear juice was used for analysis.

°Brix and Titratable Acidity. °Brix was measured at room temperature using a PAL-1 pocket refractometer (Atago USA, Inc., Bellevue, WA). Titratable acidity was measured by mixing 7 mL of juice sample with 50 mL of boiled water and titrating with 0.1 N NaOH to an end point of pH 8.1 and is reported as percentage of citric acid.

Stir Bar Sorptive Extraction (SBSE)-GC-MS Analysis. Ten milliliters of berry juice was added to a 20 mL vial, to which 3 g of sodium chloride and 20 μL of internal standard A solution were added. A stir bar (Twister) coated with poly(dimethylsiloxane) (PDMS) phase (1 cm length, 0.5 mm thickness, Gerstel Inc., Baltimore, MD) was used to extract volatile compounds. The sample was extracted with the Twister bar for 2 h at a speed of 1000 rpm. After extraction, the Twister bar was rinsed with distilled water, dried with a tissue paper, and placed into a sample holder for GC-MS analysis.

GC-MS analysis was performed using an Agilent 6890 gas chromatograph with a 5973 mass selective detector (Agilent, Santa Clara, CA). Samples were loaded into the TDU by a multipurpose autosampler (Gerstel Inc.). A cooled injection system (CIS4, Gerstel Inc.) was used in the GC-MS system. A glass liner packed with 1 cm of Tenax sorbent (TA, 60/80, Supelco, Bellefonte, PA) was used in the CIS4 injector.

The TDU has an initial temperature of 25 °C. After the sample was loaded, the TDU was heated at a rate of 300 °C/min to a final temperature of 250 °C with a 1 min hold. TDU injection was in splitless mode during thermal desorption, whereas the CIS4 was in a solvent vent mode with a venting flow of 60 mL/min for 4.7 min, at a venting pressure of 22.8 psi. After the solvent vent, the CIS4 was switched to splitless mode for 3.0 min and then changed to split mode with a venting flow of 50 mL/min. The initial temperature of CIS4 was kept at −80 °C for 0.2 min and then ramped at a rate of 10 °C/s to a final temperature of 250 °C with a 10 min hold.

Compound separation was achieved with a DB-WAX column (30 m × 0.25 mm i.d., 0.25 μm film thickness, Phenomenex, Torrance, CA). The oven temperature was programmed at 40 °C for a 2 min hold and then increased to 230 °C at a rate of 4 °C/min with a 6 min hold at the final temperature. A constant helium column flow of 2.5 mL/min was used. A column splitter was used at the end of the column, 1 mL/min column flow was introduced to the MS, and the other 1.5 mL/min column flow was vented out. The MS transfer line and ion source temperatures were 280 and 230 °C, respectively. Electron ionization mass spectrometric data from *m/z* 35 to 350 were collected using a scan rate of 5.27/s, with an ionization voltage of 70 eV.

Standard calibration curves were built up for quantitative analysis. Individual stock solution was diluted in synthetic juice to make the first level mixed standard solution, which was then diluted at a 1:9 (v/v) ratio with synthetic juice to obtain the concentration range (**Table 1**). Twenty microliters of internal standard was added to the diluted solution. Volatiles were then extracted using a stir bar, as done for the sample. Standard calibration curves were obtained through Chemstation software using selected mass ions (**Tables 1** and **2**) and were used to calculate the concentrations of volatile compounds in the samples. Triplicate analysis was performed for each sample.

Solid Phase Extraction (SPE)−Direct Microvial Insert Thermal Desorption GC-MS for Polar Compounds. Polar volatile compounds including butanoic acid, 2-methylbutanoic acid, phenylmethanol, 2-phenylethanol, and Furaneol (**Table 2**) were determined using a SPE−direct microvial insert thermal desorption technique described previously, with some modification (*8*). Ten milliliters of berry juice was passed through a preconditioned Lichrolut-EN cartridge (200 mg, 3 mL, from Merck, Darmstadt, Germany, preconditioned with 5 mL of methanol followed by 10 mL of distilled water). After the sample was loaded, the SPE cartridge was washed with 20 mL of distilled water and then gently dried with air. The retained volatile compounds were eluted with 1 mL of methanol. Twenty microliters of internal standard B was added, and the eluent was dried with anhydrous sodium sulfate. Ten microliters of the extract was loaded into a 200 μL glass insert and placed into the sample holder of the TDU for GC-MS analysis. The TDU and GC-MS conditions were the same as described previously, except that the TDU was heated at a rate of 100 °C/min to the final temperature and the initial CIS4 temperature was kept at 25 °C.

Individual stock solution of butanoic acid, 2-methylbutanoic acid, phenylmethanol, 2-phenylethanol, and Furaneol was diluted in methanol to make the first level mixed standard solution and then diluted with methanol to a serial concentration (**Table 2**). Twenty microliters of internal standard was added to the diluted solution. Ten microliters of solution was used to build the calibration curves.

Table 1. Chemical Standards and MS Fragments Used for Quantitative Analysis by SBSE Method

chemical	source, purity	quantify ions	qualify ions	slope[a]	intercept	R^2	range[b] (μg/L)
1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane[c] (eucalyptol)	Aldrich, 99%	81	108, 154				
ethyl butanoate	Aldrich, ≥98%	71	60, 88	0.45	+0.02	0.995	0.5−200
hexanal	Aldrich, ≥97%	56	72, 82	0.17	+0.01	0.967	0.5−600
2-methyl-5-(1-methylethyl)-1,3-cyclohexadiene (α-phellandrene)	Aldrich	93	77, 136	0.29	−0.15	0.985	0.5−170
7-methyl-3-methylene-1,6-octadiene (myrcene)	K&K Lab, NY	93	69, 41	0.30	+0.21	0.957	0.5−250
4-methyl-1-(1-methylethyl)-1,3-cyclohexadiene (α-terpinene)	TCI American, 90%	121	93, 136	0.38	−0.11	0.988	0.5−210
1-methyl-4-prop-1-en-2-yl-cyclohexene (limonene)	Aldrich, ≥97%	68	93, 67	0.12	+0.28	0.976	1−390
heptan-2-one	Sigma-Aldrich, 99%	43	58, 71	0.54	+0.07	0.971	0.5−400
methyl hexanoate	Aldrich, ≥99%	74	87, 99	1.81	+0.03	0.994	0.5−180
(E)-hex-2-enal	Aldrich, ≥95%	69	55, 41	0.16	+0.07	0.960	0.5−720
ethyl hexanoate	Aldrich, ≥98%	88	99, 101	1.59	−0.08	0.996	0.5−240
hexyl acetate	Aldrich, ≥98%	56	61, 69	0.95	+0.10	0.993	0.5−200
1-methyl-4-propan-2-ylidenecyclohexene (α-terpinolene)	Aldrich, ≥90%	121	93, 136	0.33	+0.12	0.966	0.5−220
(Z)-hex-3-enyl acetate	Aldrich, ≥98%	67	43, 82	1.68	+0.04	0.991	0.5−170
heptan-2-ol	Aldrich, ≥97%	45	55, 83	0.54	+0.55	0.988	3-2100
(E)-hex-2-enyl acetate	Bedoukian Research	67	100, 82	0.74	+0.17	0.991	0.5−170
hexan-1-ol	Sigma-Aldrich, ≥99%	56	55, 69	0.14	+0.09	0.978	3−1100
(Z)-hex-3-en-1-ol	Bedoukian Research	67	69, 82	0.04	+0.24	0.977	3−900
(E)-hex-2-en-1-ol	Compagnie Parento, Inc.	57	67, 82	0.05	+0.13	0.971	1−1500
6-methyl-2-(oxiran-2-yl)hept-5-en-2-ol (linalool oxide)	Fluka, ≥97%	59	94, 111	0.09	+0.29	0.988	1−2000
oct-1-en-3-ol	Aldrich, ≥98%	57	85, 72	1.10	+0.15	0.987	0.5−350
heptan-1-ol	Eastman Chemical	70	56, 55	0.55	+0.02	0.988	0.5−130
6-methylhept-5-en-2-ol	Aldrich, 99%	95	110, 128	0.69	+0.28	0.997	0.5−150
(2E,4E)-hepta-2,4-dienal	Fluka, ≥97%	81	110, 53	1.11	+0.51	0.970	0.5−250
2,6,6,10-tetramethyl-1-oxaspiro[4.5]dec-9-ene (theaspirane)	Aldrich, ≥85%	138	82, 96	2.25	−0.21	0.994	0.5−400
[c]1-(2-hydroxy-5-methylphenyl)ethanone	Aldrich, 98%	135	150, 107				
3,7-dimethylocta-1,6-dien-3-ol (linalool)	Aldrich, ≥97%	71	93, 121	0.23	+0.17	0.997	5−4140
octan-1-ol	Eastman Chemical	56	84, 70	0.22	+0.65	0.998	2−780
undecan-2-one	Aldrich, 99%	58	43, 59	0.53	−0.12	0.998	0.5−240
4-methyl-1-propan-2-ylcyclohex-3-en-1-ol (4-terpineol)	TCI Japan	71	154, 111	0.50	−0.07	1.000	0.5−440
(1R,5R)-2,7,7-trimethylbicyclo[3.1.1]hept-2-en-4-one (verbenone)	Aldrich, 94%	107	135, 150	0.08	+0.05	0.995	0.5−200
(2S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (borneol)	Aldrich, 97%	95	110, 139	0.94	+0.03	0.995	0.5−100
2-(4-methyl-1-cyclohex-3-enyl) propan-2-ol (α-terpineol)	K&K Lab, NY	59	93, 136	0.15	+0.18	0.999	2−1300
2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-one (carvone)	Aldrich, ≥97%	82	93, 108	0.55	+0.01	1.000	0.5−280
methyl 2-hydroxybenzoate (methyl salicylate)	Lancaster, 98%	120	92, 152	0.75	−0.13	1.000	1−650
3,7-dimethyloct-6-en-1-ol (citronellol)	Aldrich	69	82, 95	0.22	−0.05	0.999	0.5−230
3,7-dimethylocta-2,6-dien-1-ol (nerol)	Sigma, ∼98%	69	121, 93	0.38	+0.23	0.971	0.5−200
(E)-1-(2,6,6-trimethyl-1-cyclohexa-1,3-dienyl)but-2-en-1-one (trans-β-damascenone)	Firmenich	121	105, 190	1.16	−0.42	0.997	0.5−250
2-(7,7-dimethyl-4-bicyclo[3.1.1]hept-3-enyl)ethanol (nopol)	Aldrich, 98%	105	79, 91	0.97	−0.42	0.994	1−500
(3E)-4-(2,6,6-trimethylcyclohex-2-en-1-yl)but-3-en-2-one (α-ionone)	Fluka, 75−90%	121	93, 136	0.93	−0.22	1.000	1−850
hexanoic acid	Aldrich, ≥99.5%	60	87, 73	0.01	+0.18	0.997	10−10500
3, 7-dimethylocta-2,6-dien-1-ol (geraniol)	Aldrich, 98%	69	123, 93	0.50	+0.27	0.999	1−1020
(3E)-4-(2,6,6-trimethylcyclohex-1-en-1-yl)but-3-en-2-one (β-ionone)	Aldrich, ≥97%	177	135, 192	1.78	−0.19	0.998	1−1050
4-phenylbutan-2-ol	Lancaster, 98%	117	91, 132	0.12	+0.33	0.996	1−1120
(4-prop-1-en-2-yl-1-cyclohexenyl)methanol (perilla alcohol)	Aldrich, 96%	79	121, 93	0.10	+0.04	0.999	1−460
octanoic acid	Aldrich	60	73, 101	0.08	+0.15	0.989	5−3800
5-propyloxolan-2-one[c] (γ-heptalactone)	Aldrich, ≥98%	85	56, 110				
4-methoxy-2,5-dimethylfuran-3-one (mesifurane)	Aldrich, ≥97%	142	55, 71	0.18	−0.03	0.998	2−240
5-butyloxolan-2-one (γ-octalactone)	Pfaltz & Bauer Inc.	85	100, 57	4.61	−0.30	0.999	0.5−190
6-propyloxan-2-one (δ-octalactone)	Lancaster, 98%	99	71, 55	0.54	+0.03	0.999	0.5−220
4-methyl-2-propan-2-ylphenol[c] (isothymol)	TCI American, 99%	135	91, 150				
(4-propan-2-ylphenyl)methanol (cumic alcohol)	Aldrich, 97%	135	150, 105	0.12	+0.07	0.995	1−500
5-hexyloxolan-2-one (γ-decalactone)	Aldrich, ≥98%	85	128, 55	0.68	+0.19	0.995	0.5−310
4-allyl-2-methoxyphenol (eugenol)	Aldrich, ≥98%	164	149, 131	0.21	+0.06	0.997	1−470
6-pentyloxan-2-one (δ-decalactone)	Aldrich, ≥98%	99	71, 114	0.16	+0.41	0.981	2−2560
3-phenylprop-2-en-1-ol (cinnamyl alcohol)	TCI American, 97%	92	134, 115	0.008	+0.02	0.976	2−1230
2-methoxy-4-(prop-1-en-1-yl)phenol (isoeugenol)	Aldrich, 98%	164	149, 103	0.21	−0.06	0.996	0.5−330
6-heptyloxan-2-one (δ-dodecalactone)	TCI Japan	99	71, 114	0.48	−0.005	1.000	0.5−210

[a] Values for the slope in the equation $R_{TC}/R_{IS} = \text{slope}(C_{TC}/C_{IS}) + \text{intercept}$, where R_{TC} is the MS response of the target compound, R_{IS} is the MS response of the internal standard, C_{TC} is the concentration of the target compound, and C_{IS} is the concentration of the internal standard. [b] Actual concentration range for standard calibration curve. [c] Internal standard.

Chiral Analysis. Volatile compounds in berry samples were isolated using the same procedures as described previously (both SBSE and SPE methods); however, internal standards were not added. Separation was achieved using a Cyclosil B column (30 m × 0.25 mm i.d., 0.25 μm film thickness, Agilent). The oven temperature was programmed at 40 °C for a 2 min hold and then increased to 230 °C at a rate of 5 °C/min, with a 5 min hold at the final temperature. Authentic standards (R)-limonene (Sigma-Aldrich, Milwaukee, WI), (S)-limonene (Aldrich, Milwaukee, WI), (R)-linalool (Fluka, Buchs, Switzerland), (R)-2-heptanol (Aldrich), and (R)-terpinen-4-ol (Aldrich) were used for identification. All other isomeric

Table 2. Chemical Standards and MS Fragments Used for Quantitative Analysis by SPE Method

chemical	source, purity	quantify ions	qualify ions	slope[a]	intercept	R^2	range[b] (μg/L)
1-(2-hydroxy-5-methylphenyl)ethanone[c]	Aldrich, 98%	135	150, 107				
butanoic acid	Aldrich, ≥99%	60	73, 55	0.39	−0.19	0.995	70−93000
2-methylbutanoic acid	Aldrich	60	45, 87	0.50	−0.20	0.997	70−95160
phenylmethanol	Sigma-Aldrich, 99.8%	108	107, 77	0.51	−0.09	0.992	40−49430
2-phenylethanol	Sigma-Aldrich, ≥99%	91	92, 122	1.20	−0.006	0.993	40−47530
4-hydroxy-2,5-dimethylfuran-3-one (Furaneol)	Fluka, ≥99%	128	57, 85	1.79	−0.30	0.975	230−105000

[a] Values for the slope in the equation $R_{TC}/R_{IS} = \text{slope}(C_{TC}/C_{IS}) + \text{intercept}$, where R_{TC} is the MS response of the target compound, R_{IS} is the MS response of the internal standard, C_{TC} is the concentration of the target compound, and C_{IS} is the concentration of the internal standard. [b] Actual concentration range for standard calibration curve. [c] Internal standard.

Table 3. °Brix, Titratable Acidity (TA), and Soluble Solids Content to TA Ratio for the Genotypes Representing 'Marion' Blackberry's Pedigree

	2007			2008		
	°Brix	TA	ratio	°Brix	TA	ratio
Marion	14.0	1.7	8.2	11.4	1.2	9.5
Chehalem	15.6	3.2	4.8	14.6	3.1	4.8
Santiam	15.6	1.7	9.2	17.0	1.4	11.9
Himalaya	14.0	1.0	13.6	14.4	1.0	14.8
Olallie	13.8	1.8	7.5	16.8	1.7	9.7
Logan	20.2	3.1	6.4	14.2	2.2	6.4
Meeker, red raspberry	13.8	1.3	10.7	16.2	1.8	8.9

compounds were tentatively identified on the basis of literature reports using a similar column and compounds identified in fruits. The isomeric ratio was determined using the relative total mass ion abundance of the compound.

Statistical Analysis. The S-PLUS version 7.0 software (Insightful Corp., Seattle, WA) was used to test the statistical variances of volatile constituents from two growing seasons. Triplicate analysis was performed for each sample from each growing season, and a *t* test was conducted to test the growing season variance of each volatile compound; ANOVA (analysis of variance) was applied for the test of the variance of each volatile compound among different cultivars.

RESULTS AND DISCUSSION

°Brix and Titratable Acidity. In this study, seven cultivars that reflected genotypes in 'Marion's pedigree in two growing seasons were collected: 'Marion', 'Chehalem', 'Santiam', 'Himalaya', 'Olallie' blackberry; 'Logan', a raspberry−blackberry hybrid; and 'Meeker' red raspberry. °Brix, titratable acidity, and the ratio of soluble solids content to titratable acidity are presented in **Table 3**. Although seasonal variation was observed for some cultivars, the soluble solids content to titratable acidity ratio was relatively consistent for each individual cultivar harvested in two years, suggesting the fruit maturity was similar in both years because the ratio of soluble solids content to titratable acidity is a good indicator of fruit maturity (9).

Volatile Distribution in 'Marion' Pedigree. The volatile compounds in 'Marion's pedigree were very diverse, and it was challenging to analyze all volatile compounds using a single method. In this study, SBSE-GC-MS and SPE−microvial insert thermal desorption GC-MS were used to analyze a wide range of compounds. Approximately 80 compounds in 'Marion's pedigree (**Table 4**) were quantified.

Overall, the most abundant volatile compounds in the genotypes were lipid derivatives, followed by terpenes. A large amount of norisoprenoids and shikimic acid derivatives also existed. Two furanone compounds including mesifurane and Furaneol were quantified. However, the compounds in each category did not distribute evenly among the cultivars. Among the compounds analyzed, about half of them presented significant seasonal variations ($p < 0.01$). Compounds from shikimic acid derivatives

and lipid derivatives had higher seasonal variations than terpenes, norisoprenoids, and furanones.

Volatile patterns varied greatly in the genotypes in 'Marion's pedigree. The volatile pattern in raspberry was completely different from that of the blackberries. 'Meeker' predominated by norisoprenoids, lactones, and acids and contained only small amounts of other volatiles, which was in agreement with the literature (10, 11). 'Logan' and 'Olallie', which have red raspberry parents in their ancestry, had a dominance of norisoprenoids, as did 'Meeker' red raspberry, but at much lower concentration. The concentration of norisoprenoids in blackberry genotypes was significantly lower.

Wild 'Himalaya' blackberry was dominated by terpenes and furanones, but had only trace levels of norisoprenoids and esters. The predominant volatiles in 'Santiam' were terpenes. 'Chehalem', a selection from the progenies of 'Santiam' × 'Himalaya', had characteristics from both of its parents. 'Chehalem' had a dominant volatile composition for terpenes, but the concentration was much lower than in 'Santiam'. 'Chehalem' contained a small amount of alcohols, carbonyls, and furanones, similar to its parent 'Santiam'; it also had trace levels of norisoprenoids and esters, similar to its parent 'Himalaya'. 'Marion', a selection from 'Chehalem' and 'Olallie', contained almost all of the volatile compounds in its pedigree at moderate amounts. It had a very balanced volatile pattern as reported previously (12).

(*i*) *Terpenes.* Terpenes have very diverse flavor, ranging from turpentine and resinous impressions to citrus and flowery notes. 'Marion' had almost the complete terpene spectrum; however, the concentration of most terpene compounds was very low. All other cultivars contained much higher terpene levels, especially 'Olallie' and 'Logan'. 'Olallie' and 'Logan' had high concentrations of myrcene, limonene, α-terpinolene, linalool, α-terpineol, nerol, and geraniol. The terpene profile in raspberry was completely different from that of blackberries. Only two-thirds of terpenes were identified in 'Meeker' raspberry; the major compounds were α-phellandrene, α-terpinene, linalool, 4-terpineol, α-terpineol, verbenone, myrtenol, nerol, and geraniol, in agreement with a previous study (13).

Linalool was one of the most important aroma compounds in blackberries, contributing to a floral note (12, 14, 15). 'Logan' had a very high content of linalool, as did its progeny 'Olallie'. Both 'Santiam' and 'Himalaya' had relatively low linalool contents; their progeny 'Chehalem' had only half the linalool compared with its parents. It is interesting to note that a low content of linalool in its maternal parent, 'Chehalem', and a high content of linalool in its paternal parent, 'Olallie', gave 'Marion' an intermediate level of linalool. The pattern suggested that linalool could be inherited in an additive fashion in blackberry. Linalool was reported to be highly heritable in strawberries (5). Similarly, a high content of *p*-cymen-8-ol in 'Himalaya' and a low content in 'Santiam' resulted in an intermediate level in 'Chehalem'. However, the inheritance pattern was not obvious

Table 4. Volatile Concentration (Micrograms per Kilogram ± SD) in Berries from the Genotypes Representing 'Marion' Blackberry's Pedigree[a]

RI	compound	year	Marion	Chehalem	Santiam	Himalaya	Olallie	Logan	red raspberry (cv. Meeker)
	terpenes	2007	**619**	**1446**	**1604**	**3537**	**3611**	**3707**	**1000**
		2008	**839**	**1675**	**2395**	**2990**	**1854**	**5190**	**672**
1165	α-phellandrene	2007	9.5 ± 0.2bA	9.8 ± 0.1bA	16 ± 1cB	34 ± 3 dB	ND	ND	96 ± 4eB
		2008	10.4 ± 0.1bB	10.8 ± 0.4bB	12 ± 1bA	28 ± 5cA	ND	ND	25 ± 1cA
1169	myrcene	2007	7.2 ± 0.2bA	6.1 ± 0.2bA	23 ± 3cA	4.4 ± 0.8abA	95 ± 3 dB	125 ± 4dA	ND
		2008	7.1 ± 0.3aA	6.8 ± 0.1aA	68 ± 3bB	4.3 ± 0.5aA	48 ± 8bA	252 ± 4cB	38 ± 7bB
1180	α-terpinene	2007	8.5 ± 0.2aA	11.8 ± 0.3aA	30 ± 1bA	48 ± 1cA	15 ± 2abB	25 ± 1bA	80 ± 10 dB
		2008	8.0 ± 0.1aA	13.9 ± 0.1aB	58 ± 4cB	63 ± 1cB	11.1 ± 0.7aA	38.0 ± 0.1bB	34 ± 4bA
1202	limonene	2007	ND	ND	10 ± 1bA	ND	85 ± 3cB	203 ± 12dA	ND
		2008	ND	3.5 ± 0.6bB	23 ± 1cB	ND	32 ± 5dA	352 ± 3eB	ND
1276	α-terpinolene	2007	6.6 ± 0.1abB	ND	12.7 ± 0.6bA	25.3 ± 0.5cA	66 ± 2 dB	185 ± 9ea	0.8 ± 0.1aA
		2008	3.0 ± 0.1aA	0.9 ± 0.1aA	42 ± 4bB	35 ± 3bB	32 ± 1bA	250 ± 30cB	0.6 ± 0.001aA
1341	(Z)-rose oxide[b]	2007	1.9 ± 0.1bA	2.53 ± 0.04cB	12.9 ± 0.7eB	ND	2.0 ± 0.4bcB	7.1 ± 0.4 dB	ND
		2008	1.4 ± 0.1bcA	1.8 ± 0.1cA	10.6 ± 0.7eA	ND	1.1 ± 0.1bA	3.5 ± 0.1dA	ND
1354	(E)-rose oxide[b]	2007	ND	ND	4.9 ± 0.1bA	ND	ND	ND	ND
		2008	ND	ND	4.8 ± 0.1bA	ND	ND	ND	ND
1425	(Z)-linalool oxide	2007	4.1 ± 0.2cB	2.0 ± 0.5bB	2.3 ± 0.2bB	2.0 ± 0.2bA	5.9 ± 0.7eB	5.1 ± 0.9 dB	ND
		2008	2.03 ± 0.05cA	1.3 ± 0.1bA	-aA	1.8 ± 0.1cA	2.8 ± 0.2dA	4.6 ± 0.1eA	ND
1451	(E)-linalool oxide	2007	1.8 ± 0.1cA	1.0 ± 0.1bA	2.5 ± 0.1 dB	0.8 ± 0.1bA	3.5 ± 0.5eB	3.5 ± 0.5eA	ND
		2008	1.8 ± 0.1cA	0.76 ± 0.05bA	1.5 ± 0.07cA	0.8 ± 0.1bA	2.3 ± 0.2dA	4.05 ± 0.03eA	ND
1532	linalool	2007	190 ± 25bA	24 ± 1aA	70 ± 3aA	52 ± 1aB	1797 ± 38 dB	1500 ± 38cA	70 ± 2aB
		2008	194 ± 3bA	23 ± 1aA	70 ± 7aA	43 ± 2aA	800 ± 30cA	1790 ± 40 dB	42 ± 1aA
1577	4-terpineol	2007	7.1 ± 0.1aB	16.5 ± 0.4bA	38 ± 1cA	201 ± 1dA	4.7 ± 0.7aB	12 ± 1bA	214 ± 4eB
		2008	6.3 ± 0.2abA	15.2 ± 0.4bA	65 ± 1 dB	190 ± 10eA	3.5 ± 0.01aA	14.0 ± 0.3bB	50.6 ± 0.3cA
1581	1-p-mentha-9-al[b]	2007	6.0 ± 0.2eB	3.4 ± 0.5cB	1.1 ± 0.1bA	1.1 ± 0.1bA	4.2 ± 0.1 dB	7 ± 1fB	ND
		2008	4.9 ± 0.1fA	2.0 ± 0.02cA	3.5 ± 0.6eB	1.3 ± 0.1bA	3.0 ± 0.4dA	3.0 ± 0.1dA	ND
1672	1,8-menthadien-4-ol[b]	2007	1.8 ± 0.1bA	5.7 ± 0.5cB	20 ± 1eA	12 ± 1dA	ND	ND	ND
		2008	1.5 ± 0.06bA	4.7 ± 0.4cA	23 ± 1eA	13 ± 1dA	ND	ND	ND
1677	verbenone	2007	1.4 ± 0.2aa	ND	2.5 ± 0.1aA	1.3 ± 0.06aA	ND	ND	81 ± 4bB
		2008	4.4 ± 0.1 dB	ND	3.0 ± 0.6cA	1.4 ± 0.1bA	ND	ND	15.2 ± 0.4ea
1682	borneol	2007	4.2 ± 0.1aB	6.7 ± 0.2abB	7.6 ± 0.3bA	68 ± 3eB	16 ± 1cB	33 ± 1dA	8.7 ± 0.3bB
		2008	2.8 ± 0.1aA	3.9 ± 0.2abA	7.6 ± 0.5bcA	51 ± 3eA	10.1 ± 0.4cA	34 ± 2dA	5.2 ± 0.1abA
1684	α-terpineol	2007	54 ± 5aB	91 ± 5aB	176 ± 10bA	430 ± 10cB	570 ± 30 dB	1100 ± 50ea	176 ± 3bB
		2008	35 ± 1aA	35 ± 2aA	180 ± 10bA	250 ± 15cA	368 ± 9dA	1330 ± 50eB	14 ± 1aA
1706	carvone	2007	2.3 ± 0.1bA	3.9 ± 0.1cA	4.3 ± 0.1dA	27.8 ± 0.2eA	ND	ND	4.3 ± 0.01 dB
		2008	4.7 ± 0.1cB	5.8 ± 0.1 dB	5.9 ± 0.2 dB	27 ± 1eA	ND	ND	1.5 ± 0.01bA
1769	citronellol	2007	6.8 ± 0.1aB	9.2 ± 0.3abB	61 ± 1cA	10.4 ± 0.6bB	10.6 ± 0.1bB	12.7 ± 0.3bA	9.1 ± 0.1aB
		2008	5.8 ± 0.1aA	6.1 ± 0.1aA	97 ± 4cB	8.5 ± 0.2aA	7.2 ± 0.2aA	30 ± 0.01bB	6 ± 1aA
1794	myrtenol[b]	2007	1.9 ± 0.1aA	5.7 ± 0.4abA	25 ± 1cA	51 ± 4eB	4.1 ± 0.5aB	6.5 ± 0.3bA	37 ± 1 dB
		2008	1.5 ± 0.1aA	5.3 ± 0.4abA	30 ± 1 dB	41 ± 4ea	2.5 ± 0.1aA	7.0 ± 0.5bA	15 ± 1cA
1801	nopol	2007	2.2 ± 0.1aA	16 ± 1bB	28 ± 1cA	86 ± 6 dB	1.3 ± 0.01aA	2.5 ± 0.03aA	3.2 ± 0.4aA
		2008	1.8 ± 0.2aA	13.9 ± 0.8bA	34 ± 1cB	57 ± 5dA	1.3 ± 0.01aA	3.2 ± 0.06aB	3.2 ± 0.4aA
1810	nerol	2007	4.2 ± 0.2aA	4.4 ± 0.3aA	19 ± 1bA	7.5 ± 0.6aA	27.8 ± 0.4cB	57 ± 2ea	33 ± 1 dB
		2008	4.2 ± 0.4aA	4.7 ± 0.2aA	34 ± 1 dB	6.8 ± 0.4aA	14.0 ± 0.8bA	116 ± 1eB	19.0 ± 0.1cA
1821	isogeraniol[c]	2007	0.6 ± 0.02aA	2.7 ± 0.1abA	118 ± 4cA	4.0 ± 0.1abA	1.8 ± 0.1abB	3.0 ± 0.2abA	4.6 ± 0.4bA
		2008	0.6 ± 0.06aA	3.4 ± 0.1aB	214 ± 8bB	6.1 ± 0.1aB	1.3 ± 0.08aA	4.2 ± 0.6aB	5.7 ± 0.5aB
1859	p-cymen-8-ol[c]	2007	19 ± 2aA	1000 ± 70cA	104 ± 9bA	1710 ± 80dA	ND	ND	ND
		2008	13 ± 2aA	1300 ± 80cB	186 ± 9bB	1670 ± 90dA	ND	ND	ND
1863	geraniol	2007	17.7 ± 0.3aB	39 ± 1bA	420 ± 14eA	132 ± 1cB	172 ± 1fB	260 ± 10dA	168 ± 5fA
		2008	14 ± 1aA	41 ± 1bA	840 ± 25fB	118 ± 5cA	114 ± 1cA	425 ± 7eB	396 ± 1 dB
2012	perilla alcohol	2007	1.1 ± 0.04aB	1.8 ± 0.06aB	106 ± 6cA	239 ± 2 dB	ND	ND	13.9 ± 0.2bB
		2008	0.6 ± 0.02aA	0.8 ± 0.07aA	122 ± 6bB	133 ± 6bA	ND	ND	0.6 ± 0.001aA
2310	(E)-2,6-dimethylocta-2,7-diene-1,6-diol[d]	2007	260 ± 60bcA	183 ± 5bA	290 ± 50cA	390 ± 9 dB	730 ± 80eB	160 ± 10bA	ND
		2008	510 ± 90 dB	170 ± 10bA	260 ± 70cA	240 ± 20bA	400 ± 40cdA	530 ± 50 dB	ND
	norisoprenoids	2007	**69**	**36**	**57**	**32**	**104**	**194**	**720**
		2008	**71**	**36**	**59**	**28**	**94**	**203**	**455**
1464	theaspirane A	2007	12.9 ± 0.2cA	ND	14.4 ± 0.2cA	ND	12.7 ± 0.2bcA	16.7 ± 0.7cA	10.1 ± 0.01bA
		2008	14.4 ± 0.4 dB	ND	19.7 ± 0.2eB	ND	12.7 ± 0.2cA	35 ± 1fB	10.1 ± 0.01bA
1500	theaspirane B	2007	14 ± 1dA	4.2 ± 0.001bA	10.6 ± 0.4cB	ND	13.9 ± 0.05 dB	14 ± 2dA	4.8 ± 0.1bA
		2008	15 ± 1dA	4.2 ± 0.001bA	6.3 ± 0.4cA	ND	6.1 ± 0.4cA	29 ± 1eB	4.6 ± 0.5bcA
1810	β-damascenone	2007	7.2 ± 0.001bA	7.1 ± 0.001bA	ND	7.3 ± 0.01bA	7.1 ± 0.001bA	7.1 ± 0.2bB	7.8 ± 0.1cA
		2008	7.0 ± 0.001bA	7.0 ± 0.001bA	ND	8.1 ± 0.1 dB	7.2 ± 0.001cA	ND	7.5 ± 0.001cA
1822	dihydro-β-ionone[e]	2007	0.5 ± 0.01bA	ND	ND	ND	3.5 ± 0.1cB	3.3 ± 0.1cA	9.2 ± 0.04 dB
		2008	0.9 ± 0.1bB	ND	ND	ND	1.9 ± 0.2cA	3.9 ± 0.2eB	2.3 ± 0.1dA

Table 4. Continued

RI	compound	year	Marion	Chehalem	Santiam	Himalaya	Olallie	Logan	red raspberry (cv. Meeker)
1844	α-ionone	2007	5.2 ± 0.001aA	4.6 ± 0.001aA	5.6 ± 0.01aA	4.4 ± 0.01aB	5.7 ± 0.001aA	12.2 ± 0.4bB	185 ± 3cA
		2008	5.1 ± 0.01bA	4.8 ± 0.001bA	5.3 ± 0.6bA	ND	5.7 ± 0.001bA	10.6 ± 0.01cA	197 ± 3 dB
1908	α-ionol[e]	2007	2.3 ± 0.01bB	ND	4.2 ± 0.2bA	ND	3.8 ± 0.1bB	11.3 ± 0.8cA	124 ± 2 dB
		2008	1.9 ± 0.1bA	ND	6.3 ± 0.1cB	ND	2.7 ± 0.3bA	10.4 ± 0.5dA	27 ± 1eA
1936	β-ionone	2007	22.8 ± 0.1aa	20.3 ± 0.01aA	20.3 ± 0.1aA	20.3 ± 0.1aA	52 ± 1bA	115 ± 4cB	360 ± 20 dB
		2008	24.1 ± 0.6aB	20.3 ± 0.01aA	20.3 ± 0.01aA	20.3 ± 0.1aA	53.2 ± 0.5bA	100 ± 1cA	189 ± 2dA
1964	dihydro-β-ionol[e]	2007	0.6 ± 0.02bA	ND	1.5 ± 0.02cA	ND	3.3 ± 0.1 dB	5.3 ± 0.8eA	ND
		2008	0.6 ± 0.02bA	ND	1.5 ± 0.1cA	ND	1.6 ± 0.07cA	7.2 ± 0.2 dB	ND
2678	4-oxo-β-ionone[e]	2007	1.0 ± 0.1bB	ND	ND	ND	1.1 ± 0.04bA	1.5 ± 0.2cA	9.6 ± 0.5 dB
		2008	0.6 ± 0.07bA	ND	ND	ND	1.0 ± 0.1cA	1.3 ± 0.2dA	7.8 ± 0.4eA
2833	4-hydroxy-β-ionone[e]	2007	1.0 ± 0.1bA	ND	ND	ND	0.6 ± 0.06abA	4.7 ± 0.2cB	6.1 ± 0.7dA
		2008	1.1 ± 0.1bA	ND	ND	ND	1.0 ± 0.1bB	2.2 ± 0.1cA	6.8 ± 0.6dA
2856	3-oxo-α-ionol[e]	2007	0.6 ± 0.02bA	ND	ND	ND	ND	0.9 ± 0.09cA	1.9 ± 0.1 dB
		2008	0.4 ± 0.001bA	ND	ND	ND	ND	1.4 ± 0.1cB	1.3 ± 0.1cA
2861	4-oxo-β-ionol[e]	2007	0.9 ± 0.02bA	ND	ND	ND	ND	1.5 ± 0.1cA	1.8 ± 0.1dA
		2008	0.8 ± 0.01bA	ND	ND	ND	ND	1.3 ± 0.1cA	1.4 ± 0.1cA
	shikimic acid derivatives	**2007**	**1981**	**2010**	**1952**	**1414**	**758**	**1794**	**876**
		2008	**1084**	**2037**	**3180**	**1114**	**656**	**1962**	**1666**
1885	phenylmethanol	2007	1680 ± 20eB	1340 ± 90cA	1440 ± 60cdA	790 ± 80bA	360 ± 5aA	1630 ± 90deA	700 ± 80bA
		2008	900 ± 80bA	1500 ± 100cA	1760 ± 90cA	690 ± 50abA	340 ± 60aA	1780 ± 90cA	1510 ± 90cB
1920	2-phenylethanol	2007	180 ± 2bB	420 ± 20cA	66 ± 4aA	490 ± 70cB	177 ± 1bA	100 ± 10aA	65 ± 5aA
		2008	90 ± 4aA	360 ± 50bA	70 ± 1aA	320 ± 50bA	170 ± 10aA	90 ± 10aA	110 ± 20aB
2010	4-phenylbutan-2-ol	2007	29 ± 3cB	115 ± 9 dB	114 ± 12dA	12 ± 1bA	30 ± 4cB	2.0 ± 0.1aA	-a
		2008	18 ± 2bA	68 ± 5cA	210 ± 20 dB	13 ± 2bA	19 ± 1bA	3.8 ± 0.2aB	-a
2119	cumic alcohol	2007	ND	4.8 ± 0.4bA	5.6 ± 0.2bA	33.0 ± 0.3cB	ND	ND	68 ± 1 dB
		2008	ND	4.3 ± 0.1bA	7.2 ± 0.5cA	13 ± 1dA	ND	ND	16 ± 1eA
2303	cinnamyl alcohol	2007	30 ± 3bA	113 ± 10 dB	238 ± 5eA	58 ± 10cA	75 ± 9cB	ND	ND
		2008	23 ± 4bA	73 ± 9cA	1020 ± 20 dB	50 ± 10cA	18 ± 2bA	ND	12 ± 1bB
1755	methyl salicylate	2007	38 ± 1eB	5.0 ± 0.1bA	9.5 ± 0.4cA	ND	78.5 ± 0.5fA	13.3 ± 0.2dA	3.8 ± 0.01bA
		2008	33 ± 0.3eA	5.3 ± 0.1bA	12.7 ± 0.3cB	ND	76.0 ± 0.2fA	16.5 ± 0.2 dB	4.6 ± 0.01bB
2182	eugenol	2007	1.8 ± 0.01aB	0.9 ± 0.1aB	22 ± 1dA	5.7 ± 0.1cB	3.7 ± 0.1bB	5.7 ± 0.5cA	5.9 ± 0.4cB
		2008	1.0 ± 0.01aA	0.6 ± 0.05aA	44 ± 2cB	2.5 ± 0.1aA	2.3 ± 0.1aA	8.1 ± 0.4bB	2.3 ± 0.1aA
2360	chavicol[f]	2007	5.4 ± 0.1cA	ND	6.1 ± 0.1cA	5.4 ± 0.9cB	3.2 ± 0.2bA	ND	20 ± 2 dB
		2008	4.6 ± 0.4cA	ND	5.9 ± 0.1dA	ND	2.5 ± 0.2bA	8 ± 1eA	11.0 ± 0.5fA
2364	isoeugenol	2007	ND	ND	14.3 ± 0.1dA	ND	13.2 ± 0.1bA	14.0 ± 0.1cA	13.9 ± 0.01cB
		2008	ND	12.7 ± 0.01cB	15.2 ± 0.01 dB	3.2 ± 0.1bB	13.9 ± 0.01cA	19.0 ± 0.6eB	ND
2571	methoxyeugenol[f]	2007	17 ± 3bcA	11 ± 1bA	37 ± 6eA	20 ± 3cA	18 ± 4bcA	29 ± 2dA	ND
		2008	14 ± 2bA	13 ± 2bA	35 ± 4dA	22.8 ± 0.5cA	14 ± 2bA	37 ± 4 dB	ND
	lipid derivatives	**2007**	**6141**	**3603**	**3628**	**6338**	**6707**	**5472**	**22916**
		2008	**5655**	**5324**	**6908**	**8838**	**6570**	**12854**	**14202**
	C6 compounds	**2007**	**3350**	**2211**	**1061**	**2470**	**1312**	**826**	**182**
		2008	**3330**	**3958**	**2100**	**4580**	**2620**	**1080**	**1017**
1092	hexanal	2007	550 ± 40dA	230 ± 20bcA	180 ± 30bA	210 ± 8bcA	273 ± 3cA	200 ± 30bcA	16 ± 3aA
		2008	780 ± 30bB	800 ± 90bB	420 ± 30aB	1240 ± 90cB	800 ± 30bB	390 ± 90aB	490 ± 30aB
1219	(E)-2-hexenal	2007	200 ± 30cA	140 ± 10bA	120 ± 8abA	510 ± 10dA	130 ± 20bA	90 ± 6abA	72 ± 4aA
		2008	460 ± 40aB	410 ± 60aB	490 ± 40aB	1800 ± 10bB	400 ± 40aB	300 ± 40aB	370 ± 40aB
1355	1-hexanol	2007	820 ± 90dA	440 ± 60cA	200 ± 40bA	1080 ± 60eA	247 ± 7bA	18 ± 1aA	49 ± 1aB
		2008	710 ± 90cA	570 ± 80cA	390 ± 40bB	1060 ± 90dA	400 ± 30bB	20 ± 1aA	17 ± 2aA
1379	(Z)-3-hexen-1-ol	2007	410 ± 50eB	310 ± 40dA	190 ± 40cA	ND	ND	78 ± 2bB	45 ± 5bA
		2008	240 ± 40bA	440 ± 60cA	150 ± 20bA	ND	ND	50 ± 10abA	140 ± 20bB
1400	(E)-2-hexen-1-ol	2007	1370 ± 90dA	1070 ± 90cA	340 ± 60bA	500 ± 30bA	490 ± 10bA	250 ± 50bA	ND
		2008	1140 ± 90dA	1720 ± 90eB	650 ± 50cB	480 ± 50bcA	1020 ± 40 dB	320 ± 60bA	ND
	carbonyls	**2007**	**391**	**21**	**31**	**170**	**172**	**190**	**ND**
		2008	**567**	**18**	**80**	**110**	**157**	**423**	**64**
1192	2-heptanone	2007	360 ± 50cA	3.0 ± 0.001aB	6 ± 1aA	158 ± 7bB	153 ± 1bB	160 ± 40bA	ND
		2008	540 ± 40eB	1.4 ± 0.001aA	61 ± 3bB	100 ± 20bcA	133 ± 5cA	410 ± 60 dB	32 ± 4bB
1570	2-undecanone	2007	7.0 ± 0.7bB	ND	6.2 ± 0.2bA	ND	ND	ND	ND
		2008	5.4 ± 0.1bA	ND	6.3 ± 0.1cA	ND	ND	ND	8.1 ± 0.1 dB
1477	(E,E)-2,4-heptadienal	2007	24 ± 0.001 dB	17.7 ± 0.1cA	19 ± 2cdB	12 ± 1bA	19 ± 2cdA	30 ± 4eB	ND
		2008	21.5 ± 0.5cA	16.5 ± 0.01bA	12.2 ± 0.5aA	10 ± 1aA	24 ± 3cA	13 ± 1abA	24 ± 3cB
	alcohols	**2007**	**878**	**236**	**239**	**1168**	**2201**	**286**	**83**
		2008	**672**	**262**	**560**	**1198**	**1610**	**480**	**212**
1326	2-heptanol	2007	780 ± 90cA	140 ± 50bA	76 ± 5abA	960 ± 70dA	2090 ± 10eB	240 ± 20bA	ND

Table 4. Continued

RI	compound	year	Marion	Chehalem	Santiam	Himalaya	Olallie	Logan	red raspberry (cv. Meeker)
		2008	610 ± 90cA	170 ± 40bA	260 ± 40bB	1060 ± 90dA	1510 ± 70eA	410 ± 90bcB	ND
1446	1-octen-3-ol	2007	8.0 ± 0.6eB	5.6 ± 0.6dA	4.4 ± 0.4cA	7.6 ± 0.1eA	4.8 ± 0.4cdA	3.4 ± 0.1bA	2.2 ± 0.1aA
		2008	5 ± 1bA	5.6 ± 0.2bA	12 ± 1dB	7.3 ± 0.5cA	11.1 ± 0.2dB	4.4 ± 0.6abA	4.1 ± 0.1aB
1452	heptanol	2007	15 ± 1bB	22 ± 2cA	24 ± 3cA	24 ± 2cA	9.2 ± 0.5bB	13 ± 2bA	2.8 ± 0.2aA
		2008	10 ± 1bA	24 ± 2cA	34 ± 2eB	23 ± 2dA	6.1 ± 0.1abA	18 ± 3cB	4.0 ± 0.2aB
1461	6-methyl-5-hepten-2-ol	2007	34 ± 5aB	37 ± 4aA	110 ± 10cA	20 ± 2aA	78 ± 1bA	20 ± 3aA	78 ± 3bA
		2008	22 ± 4aA	43 ± 5bA	94 ± 6dA	19 ± 2aA	76 ± 4cA	32 ± 6abB	191 ± 7eB
1543	octanol	2007	41 ± 6fB	32 ± 2eB	25 ± 3dA	157 ± 1gB	19 ± 3cB	10 ± 1bA	-aA
		2008	25 ± 4aA	19 ± 1aA	160 ± 20cB	89 ± 5bA	7 ± 1aA	15.2 ± 0.1aB	13 ± 1aB
	acids	2007	**1424**	**1115**	**2076**	**2468**	**2840**	**4012**	**15410**
		2008	**759**	**1040**	**3816**	**2890**	**1982**	**10610**	**9540**
1607	butanoic acid	2007	310 ± 3aA	240 ± 30aA	390 ± 10abA	290 ± 20aB	540 ± 30cB	440 ± 20bA	3530 ± 50dB
		2008	298 ± 8aA	225 ± 6aA	790 ± 10cB	237 ± 9aA	452 ± 8bA	1560 ± 80dB	1390 ± 50dA
1655	2-methylbutanoic acid	2007	335 ± 6bcB	430 ± 20cA	216 ± 3abA	1330 ± 90dA	210 ± 6abA	172 ± 2aA	440 ± 40cA
		2008	270 ± 20abA	490 ± 50abA	226 ± 7abA	2100 ± 20cB	220 ± 20abA	200 ± 10aB	600 ± 40bB
1856	hexanoic acid	2007	660 ± 90abB	330 ± 60aA	830 ± 80abA	810 ± 90abB	1840 ± 90bB	3320 ± 90cA	10700 ± 900dB
		2008	109 ± 9aA	260 ± 40aA	2040 ± 90bB	533 ± 3abA	1140 ± 30bA	8460 ± 20cB	6750 ± 90cA
2080	octanoic acid	2007	119 ± 5aB	115 ± 9aB	640 ± 20cA	38 ± 3aB	250 ± 10bB	80 ± 10aA	740 ± 80dA
		2008	82 ± 3abA	65 ± 2aA	760 ± 70dA	20 ± 1aA	170 ± 20bA	390 ± 70cB	1340 ± 90eB
	esters	2007	**71**	**10**	**59**	**2**	**105**	**45**	**118**
		2008	**305**	**36**	**169**	**5**	**152**	**91**	**15**
1043	ethyl butanoate	2007	ND	ND	ND	ND	17.7 ± 0.2bB	ND	ND
		2008	ND	ND	ND	ND	8.0 ± 0.5bA	ND	ND
1197	methyl hexanoate	2007	ND	ND	1.8 ± 0.3bA	ND	7.8 ± 0.4cB	9.4 ± 0.6cB	44 ± 2dB
		2008	ND	ND	1.6 ± 0.3bA	ND	3.4 ± 0.2cA	ND	1.3 ± 0.2bA
1244	ethyl hexanoate	2007	10 ± 1bB	4.3 ± 0.1abB	22 ± 2cA	2.0 ± 0.1aA	46 ± 1dB	28 ± 1cA	70 ± 5eB
		2008	2.9 ± 0.1aA	1.6 ± 0.1aA	30 ± 1cB	5.3 ± 0.4aB	16.5 ± 0.6bA	32 ± 4cA	13 ± 1bA
1274	hexyl acetate	2007	23 ± 2cA	ND	10 ± 1bA	ND	8.6 ± 0.2bA	ND	1.4 ± 0.2aB
		2008	96 ± 4dB	5.1 ± 0.5aB	30 ± 1cB	ND	24 ± 1bB	ND	ND
1314	(*Z*)-3-hexenyl acetate	2007	4.3 ± 0.9dA	1.3 ± 0.1bA	2.4 ± 0.7bcA	ND	ND	2.2 ± 0.2bA	2.7 ± 0.2cB
		2008	49 ± 2dB	9.2 ± 0.8bB	12.7 ± 0.5cB	ND	ND	15 ± 2cB	1.1 ± 0.1aA
1330	(*E*)-2-hexenyl acetate	2007	34 ± 1dA	4.8 ± 0.6bA	23 ± 2cA	ND	25.3 ± 0.6cA	5.1 ± 0.8bA	ND
		2008	157 ± 20dB	20 ± 4bB	95 ± 4cB	ND	100 ± 2cB	44 ± 6bB	ND
	lactones	2007	**27**	**10**	**162**	**60**	**76**	**113**	**7123**
		2008	**22**	**10**	**183**	**55**	**49**	**170**	**3354**
1912	γ-octalactone	2007	3.8 ± 0.01abA	3.2 ± 0.01aA	5.7 ± 0.1cA	4.7 ± 0.01bcA	9.0 ± 0.2dB	4.1 ± 0.01abA	51 ± 1eB
		2008	3.7 ± 0.1bA	3.0 ± 0.001aA	7.7 ± 0.1eB	5.1 ± 0.1dA	8.0 ± 0.001eA	4.6 ± 0.001cA	38.0 ± 0.4fA
1967	δ-octalactone	2007	4.1 ± 0.4aA	ND	63 ± 2cA	ND	1.8 ± 0.2aA	25.3 ± 0.4bA	1780 ± 30dB
		2008	3.9 ± 0.2aA	ND	82 ± 3cB	ND	1.3 ± 0.2aA	72 ± 3bB	1010 ± 6dA
1998	γ-nonalactone	2007	ND	ND	ND	ND	ND	ND	10 ± 1bA
		2008	ND	ND	ND	ND	ND	ND	16.5 ± 0.4bB
2022	δ-nonalactone	2007	3.5 ± 0.2abB	2.9 ± 0.1aB	4.1 ± 0.2abA	4.4 ± 0.01bA	4.6 ± 0.2bB	4.4 ± 0.2bA	29 ± 2cA
		2008	2.8 ± 0.04abA	2.3 ± 0.05aA	3.7 ± 0.2bA	5.6 ± 0.4cB	3.9 ± 0.02bA	3.5 ± 0.5bA	26.6 ± 0.6dA
2031	γ-decalactone	2007	4.2 ± 0.1bcB	1.8 ± 0.04aA	5.8 ± 0.4cA	42 ± 2eA	52 ± 1fB	3.2 ± 0.1abB	12 ± 1dA
		2008	3.7 ± 0.1bA	1.8 ± 0.1aA	6.3 ± 0.1cA	38 ± 1fA	30 ± 2eA	1.9 ± 0.1aA	12.2 ± 0.4dA
2079	δ-decalactone	2007	7.8 ± 0.1bB	1.0 ± 0.1aA	82 ± 2cA	7.7 ± 0.2bB	8.0 ± 0.4bB	75 ± 3cA	5240 ± 90dB
		2008	6.8 ± 0.1aA	2.2 ± 0.1aB	81 ± 4bA	4.7 ± 0.1aA	4.6 ± 0.4aA	87 ± 4bB	2250 ± 30cA
2142	δ-dodecalactone	2007	3.5 ± 0.2cB	1.3 ± 0.001bB	1.5 ± 0.001bA	1.5 ± 0.1bA	1.0 ± 0.001abA	0.8 ± 0.001aA	0.8 ± 0.001aA
		2008	1.5 ± 0.001bA	0.6 ± 0.001aA	2.5 ± 0.001dB	1.9 ± 0.1cB	0.8 ± 0.001aA	0.6 ± 0.001aA	0.8 ± 0.001aA
	furanones	2007	**3888**	**230**	**740**	**4121**	**2767**	**230**	**710**
		2008	**3593**	**240**	**810**	**4018**	**2432**	**240**	**730**
1567	mesifurane	2007	38 ± 2bB	ND	ND	81 ± 1cA	26.6 ± 0.4bB	ND	ND
		2008	22.8 ± 0.6bA	ND	ND	208 ± 9cB	21.5 ± 0.4bA	ND	ND
2060	Furaneol	2007	3850 ± 30dB	230 ± 20aA	740 ± 10bA	4040 ± 20dB	2740 ± 20cB	230 ± 2aA	710 ± 30bA
		2008	3570 ± 3dA	240 ± 20aA	810 ± 20bA	3810 ± 50dA	2410 ± 50cA	240 ± 5aA	730 ± 10bA

[a] Letters (a–g) within rows indicate the significant difference of the compounds among the cultivars by ANOVA with a Tukey test at $p = 0.05$. Letters (A, B) between years indicate significant difference between years by *t* test. ND, not detected. RI, retention index. [b] The concentration was estimated by the compound of 4-terpineol in SBSE method. [c] The concentration was estimated by the compound geraniol in SBSE method. [d] The concentration was estimated by the compound isoeugenol in SPE method. [e] The concentration was estimated by the compound β-ionone in SBSE method. [f] The concentration was estimated by the compound isoeugenol in SBSE method.

for other terpene compounds. Some compounds have a low degree of heritability, and they are easily lost during the breeding process (*5*).

(*ii*) *Norisoprenoids*. 'Marion' contained the whole spectrum of norisoprenoids, with a middle range concentration. However, the concentration for each individual compound was low.

Article

J. Agric. Food Chem., Vol. 58, No. 3, 2010 **1867**

The cultivars from the maternal side of the pedigree including 'Chehalem', 'Santiam', and 'Himalaya' had very limited amounts of norisoprenoids, whereas the cultivars representing the paternal side including 'Olallie', 'Logan', and especially 'Meeker' had significantly higher ($p < 0.001$) norisoprenoid contents. The total concentration of norisoprenoids in 'Meeker' was >10 times the amount in 'Marion'.

Norisoprenoids are important aroma-contributing compounds in 'Marion' blackberry and raspberry (*13, 14*). The genotypes in the paternal side of 'Marion' pedigree all had high levels of β-ionone. 'Meeker' had extremely high α-ionone and β-ionone contents. 'Logan' had much less β-ionone than 'Meeker' raspberry. Between 'Logan' and 'Olallie', about a 50% decrease was observed for β-ionone. However, the concentration of β-ionone in 'Marion' as well as in the cultivars from the maternal side of the pedigree was at similarly low level. Similarly, a 50% decrease was observed for α-ionone between 'Logan' and 'Olallie'. The level of α-ionone in 'Marion' was very similar to that in 'Chehalem' and 'Olallie'. Except for 'Santiam', the concentration of β-damascenone was similar for all genotypes in 'Marion's pedigree. β-Damascenone has a floral, rosy aroma, whereas α-ionone and β-ionone have typical raspberry notes.

(*iii*) *Shikimic Acid Derivatives.* Two types of compounds were in this group: benzyl alcohols and volatile phenols. The sensorial contribution of shikimic acid derivatives to berry fruit is probably very small, because many of these compounds had low concentrations and high sensory thresholds. Phenylmethanol could contribute floral, rosy, aroma notes to the berry aroma. In 'Marion's pedigree, 'Marion' had a moderate level of phenylmethanol content, 'Chehalem', 'Santiam', and 'Logan' had high levels of phenylmethanol, and 'Himalaya' and 'Olallie' had low levels of phenylmethanol.

(*iv*) *Lipid Derivatives.* Lipid derivatives were the most abundant volatile compounds in the genotypes representing 'Marion's pedigree. Thirty compounds were quantified, belonging to C6 compounds, carbonyls, alcohols, acids, esters, and lactones.

C6 compounds such as hexanal, (*E*)-2-hexenal, and (*Z*)-3-hexen-1-ol contribute to a green, fresh fruit aroma. The concentration of these compounds strongly depends on fruit ripening stage. The same occurs with other carbonyl compounds. Although 'Himalaya' and 'Olallie' had no detectable level of (*Z*)-3-hexen-1-ol, it was reported that it was highly heritable and contributes to the aroma of fresh strawberry (*6*).

Five alcohol compounds were analyzed, and the major alcohol compound was 2-heptanol. 2-Heptanol is one of the very important aroma compounds in blackberries that contribute to fruity flavor. The concentration of 2-heptanol in 'Marion' was between that of its parents, 'Chehalem' and 'Olallie'.

Acids were found in all cultivars in the 'Marion' pedigree. 'Marion' had the lowest acid content, alongside its parent, 'Chehalem'. All other cultivars contained much higher acid, especially 'Meeker'. The high acid content in 'Meeker' was in agreement with a literature report (*13*).

Esters are important aroma compounds in fruit, responsible for the fruity impressions. Overall, the amount of esters was small in the genotypes representing 'Marion's pedigree, especially in 'Himalaya'. Only ethyl hexanoate was identified in 'Himalaya'. 'Chehalem' contained only a trace amount of esters. Esters such as ethyl hexanoate and hexyl acetate were important to 'Marion' flavor. The concentration of ethyl hexanoate in 'Marion' was between that of its parents, 'Chehalem' and 'Olallie'. However, 'Marion' had the highest level of hexyl acetate. In strawberry, ethyl hexanoate levels in the offspring often were much greater than that in either parent when the parents had very low levels, whereas for hexyl acetate, the levels of the offspring ranged

around those of the parents, with some offspring having much lower and some much higher levels than the parents (*5*).

Lactones can contribute to fruity, peach aromas. However, the aroma contribution from lactones to 'Marion' was small and probably only served as background odor. 'Marion' only had trace amounts of lactones, similar to its parent 'Chehalem'. All other cultivars contained much higher lactones. 'Meeker' had extremely high lactone constituents, especially δ-octalactone and δ-decalactone, in agreement with a previous study (*13*). γ-Nonalactone was identified in only 'Meeker'. The concentration of lactones in 'Marion' was between that of its parents.

(*v*) *Furanones.* Furaneol and mesifurane were quantified in this study. All cultivars contained Furaneol; however, 'Marion', 'Himalaya', and 'Olallie' had much higher amounts of Furaneol than other cultivars. Of the three cultivars with high Furaneol concentrations, 'Himalaya' had the highest amount. Mesifurane was found only in the cultivars 'Marion', 'Himalaya', and 'Olallie'.

Furaneol has a sweet, caramel, and burnt sugar flavor, whereas mesifurane imparts sweet, cherry-like, and herbal notes. Furaneol is one of the most important compounds in 'Marion' flavor (*8, 14*). Interestingly, the concentration of furaneol was higher in 'Marion' than in its parents, 'Chehalem' and 'Olallie'.

Chiral Anaysis. There has been great interest in the determination of the enantiomeric composition of chiral compounds in foodstuffs (*16*) because different enantiomeric compounds may have different sensory thresholds and attributes (*17, 18*). Many aroma compounds in nature have a chiral center and can exist as enantiomeric forms. Generally, because enzymes in the plant metabolism are often stereospecific, the resulting secondary metabolites may have an enantiomer dominance. Different cultivars may have different enzyme systems and thus will affect the enantiomeric ratio of aroma compounds (*11, 19*). Study on the enantiomeric ratio of odor-active compounds in blackberries is very limited; only the stereodifferentiation of 2-heptanol, 6-methyl-5-hepten-2-ol, and linalool oxide has been reported (*20, 21*).

In this study, 11 pairs of chiral isomers were separated under experimental conditions in the cultivars representing 'Marion's pedigree (**Table 5**). Seasonal variation was observed. However, the trends for each individual enantiomeric compound in each cultivar were consistent from year to year. The genotypes in 'Marion's pedigree showed large variability for chiral isomers.

Most of the compounds demonstrated a much higher percentage of one isomer over another, particularly δ-octalactone, δ-decalactone, 6-methyl-5-hepten-2-ol, and α-ionone. δ-Octalactone and δ-decalactone had a strong enantiomeric excess of the (*S*)-form over the (*R*)-form, in >80% for most of cultivars. δ-Decalactone provides a peachy/apricot-like olfactory impression and occurs in its (*S*)-form in the fruits(*19*). 2-Heptanol also occurred in enantiomeric excess of the (*S*)-form over the (*R*)-form for most of the cultivars, except for 'Chehalem'. 'Chehalem' had a (*R*)-form preference. This result contradicted a literature report that 2-heptanol occurred enantiomerically pure in unrelated blackberry species (*R. laciniatus* and *R. glaucus*) (*20, 22*). Linalool also existed in enantiomeric excess of the (*S*)-form over the (*R*)-form for most of cultivars. However, in 'Chehalem' and 'Himalaya' it existed in a racemic mixture. It is interesting to observe that a high (*S*)-linalool in 'Olallie' and a racemic (*S*)/(*R*)-linalool in 'Chehalem' resulted in an increased (*S*)-linalool in 'Marion'. The enantiomeric distribution of linalool in nature varies. Linalool is nearly a racemic mixture in raspberry(*11*) and passion fruit (*17*), but occurs as the almost pure (*S*)-isomer in orange juice (*23*). 2-Methylbutanoic acid was also in (*S*)-isomer form in excess of

1868 *J. Agric. Food Chem.,* Vol. 58, No. 3, 2010

Du et al.

Table 5. Isomeric Ratio of Some Chiral Compounds in Berries from the Genotypes Representing 'Marion' Blackberry's Pedigree

compound	year	Marion	Chehalem	Santiam	Himalaya	Ollallie	Logan	Meeker
heptan-2-ol (*S*/*R*)	2007	62.0/38.0	43.6/56.4	67.1/32.9	77.0/23.0	51.6/48.4	100/0	68.3/31.7
	2008	63.2/36.8	38.5/61.5	85.0/15.0	71.4/28.6	59.4/40.6	92.1/7.9	66.4/33.6
linalool (*S*/*R*)	2007	80.2/19.8	49.8/50.2	74.7/25.3	48.9/51.1	92.4/7.6	80.7/19.3	69.3/30.7
	2008	87.2/12.8	50.5/49.5	70.5/29.5	46.9/53.1	92.9/7.1	84.6/15.4	76.5/23.5
2-methylbutanoic acid (*S*/*R*)	2007	83.5/16.5	82.8/17.2	62.0/38.0	77.9/22.1	64.9/35.1	64.1/35.9	78.0/22.0
	2008	79.2/20.8	83.8/16.2	61.4/38.6	82.5/17.5	64.8/35.2	61.1/38.9	72.8/27.2
δ-octalactone (*S*/*R*)	2007	82.0/18.0	−/−	95.3/4.7	−/−	92.0/8.0	89.6/10.4	96.6/3.4
	2008	89.6/10.4	−/−	95.6/4.4	−/−	83.7/16.3	92.8/7.2	94.6/5.4
δ-decalactone (*S*/*R*)	2007	94.1/5.9	100/0	99.2/0.8	88.2/11.8	92.6/7.4	98.2/1.8	92.8/7.2
	2008	85.7/14.3	100/0	99.0/1.0	90.2/9.8	91.4/8.6	98.7/1.3	99.5/0.5
6-methyl-5-hepten-2-ol (*S*/*R*)	2007	4.7/95.3	2.7/97.3	2.1/97.9	0/100	8.8/91.2	8.3/91.7	9.0/91.0
	2008	3.3/96.7	1.4/98.6	3.5/96.5	0/100	11.0/89.0	3.8/96.2	5.0/95.0
α-ionone (*S*/*R*)	2007	0/100	0/100	0/100	0/100	0/100	0/100	0.3/99.7
	2008	0/100	0/100	0/100	0/100	0/100	0/100	0.1/99.9
terpinen-4-ol (*S*/*R*)	2007	19.2/80.8	15.0/85.0	17.1/82.9	13.3/86.7	39.5/60.5	31.6/68.4	14.2/85.8
	2008	18.8/81.2	16.2/83.8	17.5/82.5	14.8/85.2	43.7/56.3	33.5/66.5	16.8/83.2
limonene (*S*/*R*)	2007	57.6/42.4	46.4/53.6	60.6/39.4	61.0/39.0	57.5/42.5	59.0/41.0	46.5/53.5
	2008	58.4/41.6	45.6/54.4	54.7/45.3	58.5/41.5	59.2/40.8	57.8/42.2	40.1/59.9
α-terpinenol (*S*/*R*)	2007	58.7/41.3	38.8/61.2	44.9/55.1	49.7/50.3	59.6/40.4	57.8/42.2	78.4/21.6
	2008	58.6/41.4	35.6/64.4	42.1/57.9	45.7/54.3	59.1/40.9	54.8/45.2	65.8/34.2
Furaneol (1)/(2)[a]	2007	47.2/52.8	47.2/52.8	47.1/52.9	48.0/52.0	47.9/52.1	50.6/49.4	47.5/52.5
	2008	47.5/52.5	46.9/53.1	47.4/52.6	48.0/52.0	46.9/53.1	49.4/50.6	46.8/53.2

[a] Isomeric configuration is not identified.

the (*R*)-form. 2-Methylbutanoic acid is biosynthetically linked with L-isoleucin, so that the (*S*)-configuration in fruits is to be expected.

(*R*)-6-Methyl-5-hepten-2-ol was predominant in the (*R*)-form; α-ionone was almost pure enantiomer in all of the cultivars, which was in agreement with previous reports in blackberry (*20*) and raspberries (*19*). Terpinen-4-ol also occurred in the major isomer of (*R*)-form. Terpinen-4-ol has been reported predominantly in the (*R*)-form in Andes berry (*22*); however, the (*S*)-isomer exists in raspberry (*11*) and passion fruit (*17*). Limonene had a weak chiral isomeric preference of the (*S*)-form in most of the cultivars. It has been reported that the major isomer of limonene in Valencia late oranges is the (*R*)-form (*23*). However, varying tendency toward the racemization of limonene has been reported for lavender oils, depending upon the method of analysis (*24*). α-Terpinenol was in a racemic mixture. Naturally occurring racemates of α-terpinenol have been reported in yellow passion fruit (*17*).

The isomeric form of Furaneol could not be confirmed in this study because of the absence of authentic standards. It is reported that the (*R*)-isomer has a stronger sugary, jammy, and sweet aroma than the (*S*)-isomer (*25*). In this study, Furaneol was in a racemic form; however, the racemates of Furaneol cannot be confirmed in berry samples because the unique keto−enol tautomeric feature in the molecular structure can cause their racemization (*25*).

In conclusion, the volatile compounds in 'Marion's pedigree were diverse, and some trends in volatile levels among parental and offspring genotypes were observed. For most of the compounds, the concentrations of volatile compounds in progenies were intermediate to the levels of their parents. However, in some cases, such as Furaneol in 'Marion', the concentration in the progeny exceeded that in its parents. Each cultivar in 'Marion's pedigree had its unique chiral isomeric distribution.

LITERATURE CITED

(1) Finn, C. E.; Strik, B. C.; Lawrence, F. J. 'Marion' trailing blackberry. *Fruit Var. J.* **1997**, *51*, 130–133.

(2) Pyysalo, T. Identification of volatile compounds in hybrids between raspberry (*Rubus idaeus*, L.) and arctic bramble (*Rubus arcticus*, L.). *Z. Lebensm. Unters. Forsch.* **1976**, *162*, 263–272.

(3) Hirvi, T.; Honkanen, E. The volatiles of two new strawberry cultivars, 'Annelie' and 'Pioneer', obtained by backcrossing of cultivated strawberries with wild strawberries, *Fragaria vesca*, Rügen and *Fragaria virginiana*. *Z. Lebensm. Unters. Forsch.* **1982**, *175*, 113–116.

(4) Hirvi, T.; Honkanen, E. The aroma of some hybrids between high-bush blueberry (*Vaccinium corymbosum*, L.) and bog blueberry (*Vaccinium uliginosum*, L.). *Z. Lebensm. Unters. Forsch.* **1983**, *176*, 346–349.

(5) Olbricht, K.; Grafe, C.; Weiss, K.; Ulrich, D. Inheritance of aroma compounds in a model population of *Fragaria × ananassa* Duch. *Plant Breed.* **2008**, *127*, 87–93.

(6) Carrasco, B.; Hancock, J. F.; Beaudry, R. M.; Retamales, J. B. Chemical composition and inheritance patterns of aroma in *Fragaria × ananassa* and *Fragaria virginiana* progenies. *HortScience* **2005**, *40*, 1649–1650.

(7) Kerler, J.; Jagers, P.; Bouter, N.; Weenen, H.; Bruijnje, A.; Glasius, M.; Duineveld, K.; Heij, H.; Meulenbroek, B. Strawberry derived flavor via plant breeding. In *Frontiers of Flavour Science*, Proceedings of the Weurman Flavour Research Symposium, 9th, Freising, Germany, June 22-25, 1999; Schieberle, P., Engel, K. H., Eds; Deutsche Forschung. Lebensmittel: Garching, Germany, 2000; pp 370−374.

(8) Du, X.; Qian, M. C. Quantification of 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone using solid-phase extraction and direct microvial insert thermal desorption gas chromatography-mass spectrometry. *J. Chromatogr., A* **2008**, *1208*, 197–201.

(9) Perkins-Veazie, P.; Clark, J. R.; Huber, D. J.; Baldwin, E. A. Ripening physiology in 'Navaho' thornless blackberries: color, respiration, ethylene production, softening, and compositional changes. *J. Am. Soc. Hortic. Sci.* **2000**, *125*, 357–363.

(10) Moore, P. P.; Burrows, C.; Fellman, J.; Mattinson, D. S. Genotype × environment variation in raspberry fruit aroma volatiles. *Acta Hortic.* **2002**, *585*, 511–516.

(11) Malowicki, S. M. A.; Martin, R.; Qian, M. C. Volatile composition in raspberry cultivars grown in the Pacific Northwest determined by stir bar sorptive extraction−gas chromatography−mass spectrometry. *J. Agric. Food Chem.* **2008**, *56*, 4128–4133.

(12) Qian, M.; Wang, Y. Seasonal variation of volatile composition and odor activity value of 'Marion' (*Rubus* spp. *hyb.*) and 'Thornless Evergreen' (*R. laciniatus* L.) blackberries. *J. Food Sci.* **2004**, *70*, C13–C20.

(13) Klesk, K.; Qian, M.; Martin, R. R. Aroma extract dilution analysis of cv. Meeker (*Rubus idaeus* L.) red raspberries from Oregon and Washington. *J. Agric. Food Chem.* **2004**, *52*, 5155–5161.

Article

J. Agric. Food Chem., Vol. 58, No. 3, 2010   **1869**

(14) Klesk, K.; Qian, M. Aroma extract dilution analysis of cv. Marion (*Rubus* spp. hy*b*) and cv. Evergreen (*R. laciniatus* L.) blackberries. *J. Agric. Food Chem.* **2003**, *51*, 3436–3441.

(15) Du, X.; Finn, C. E.; Qian, M. C. Volatile composition and odour-activity value of thornless 'Black Diamond'and 'Marion'blackberries. *Food Chem.* **2010**, *119*, 1127–1134.

(16) Armstrong, D. W.; Chang, C.-D.; Li, W. Y. Relevance of enantiomeric separations in food and beverage analyses. *J. Agric. Food Chem.* **1990**, *38*, 1674–1677.

(17) Werkhoff, P.; Guntert, M.; Krammer, G.; Sommer, H.; Kaulen, J. Vacuum headspace method in aroma research: flavor chemistry of yellow passion fruits. *J. Agric. Food Chem.* **1998**, *46*, 1076–1093.

(18) Minh Tu, N. T.; Onishi, Y.; Choi, H.-S.; Kondo, Y. Characteristic odor components of *Citrus sphaerocarpa* Tanaka (Kabosu) cold-pressed peel oil. *J. Agric. Food Chem.* **2002**, *50*, 2908–2913.

(19) Casabianca, H.; Graff, J. B. Enantiomeric and isotopic analysis of flavor compounds of some raspberry cultivars. *J. Chromatogr., A* **1994**, *684*, 360–5.

(20) Humpf, H. U.; Schreier, P. Bound aroma compounds from the fruit and the leaves of blackberry (*Rubus laciniata* L.). *J. Agric. Food Chem.* **1991**, *39*, 1830–1832.

(21) Greule, M.; Mosandl, A. Heptan-2-ol and *trans*-linalool oxide (fur.) as inherent indicators of natural blackberry flavors using enantio-selective and multielement-MDGC-IRMS analysis. *Eur. Food Res. Technol.* **2008**, *226*, 1001–1006.

(22) Morales, A. L.; Albarracin, D.; Rodriguez, J.; Duque, C. Volatile constituents from Andes berry (*Rubus glaucus* Benth). *J. High Resolut. Chromatogr.* **1996**, *19*, 585–587.

(23) Hinterholzer, A.; Schieberle, P. Identification of the most odour-active volatiles in fresh, hand-extracted juice of Valencia late oranges by odour dilution techniques. *Flavour Fragrance J.* **1998**, *13*, 49–55.

(24) Weinreich, B.; Nitz, S. Influences of processing on the enantiomeric distribution of chiral flavour compounds. Part A. linalyl acetate and terpene alcohols. *Chem. Mikrobiol. Technol. Lebensm.* **1992**, *14*, 117–124.

(25) Yaguchi, Y.; Nakahashi, A.; Miura, N.; Sugimoto, D.; Monde, K.; Emura, M. Stereochemical study of chiral tautomeric flavorous furanones by vibrational circular dichroism. *Org. Lett.* **2008**, *10*, 4883–4885.