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Impact of Growing Environment on Chickasaw Blackberry (*Rubus* L.) Aroma Evaluated by Gas Chromatography Olfactometry Dilution Analysis

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The aroma extract of Chickasaw blackberry (*Rubus* L.) was separated with silica gel normal phase chromatography into six fractions. Gas chromatography−olfactometry (GCO) was performed on each fraction to identify aroma active compounds. Aroma extraction dilution analysis (AEDA) was employed to characterize the aroma profile of Chickasaw blackberries from two growing regions of the United States: Oregon and Arkansas. Comparative AEDA analysis showed that the berries grown in the two regions had similar aroma compositions; however, those odorants had various aroma impacts in each region. The compounds with high flavor dilution factors in Oregon's Chickasaw were ethyl butanoate, linalool, methional, *trans,cis*-2,6-nonadienal, *cis*-1,5-octadien-3-one, and 2,5-dimethyl-4-hydroxy-3(2H)-furanone, whereas in the Chickasaw grown in Arkansas, they were ethyl butanoate, linalool, methional, ethyl 2-methylbutanoate, β-damascenone, and geraniol.

KEYWORDS: Aroma extraction dilution analysis; Chickasaw; blackberry aroma; GCO; aroma fractionation

INTRODUCTION

Blackberries (*Rubus* L.) are a popular food in North America partly due to their unique flavor. Recent studies show that blackberries contain high levels of phenolic compounds and those polyphenolic compounds in fruits may reduce the risk of chronic diseases such as coronary heart disease, cancer, and diabetes (*1*−*3*). Breeding programs, particularly those at the University of Arkansas for erect blackberries and the U.S. Department of Agriculture—Agricultural Research Service in Oregon for trailing blackberries, have been actively working to develop new cultivars that meet the needs of the expanding commercial industry, including improved fruit quality. Chickasaw is a high quality and productive cultivar that was developed by the University of Arkansas and released in 1998 (*4*). Chickasaw ripens very early and has attractive, large, firm fruit, and the fruit has a good flavor, typical for erect blackberries. Because of its positive traits, Chickasaw has become a popular cultivar for the fresh fruit market.

Although sensorial qualities, in particular aroma, can largely influence consumers' acceptance and purchase preferences, the aroma composition of blackberry has been hardly studied. Most of the early studies were focused on volatile compositions in blackberries (*5*−*9*). Recently, the aroma profiles of Thornless Evergreen and Marion trailing blackberries were investigated (*10*−*12*). Studies showed that the most important aroma compounds in Marion are 2,3-butanedione, 2-heptanol, linalool, dimethyltrisulfide, 1-penten-3-one, methional, ethyl 2-methylbutanoate, benzaldehyde, and hexanal, while the most important aroma compounds in Thornless Evergreen are 2,3-butanedione, *l*-carvone, β-pinene, methional, ethyl 2-methylpropanoate, thiophene, dimethyl disulfide, 2,5-dimethyl-4-hydroxy-3-(2H)-furanone, and 2-heptanol. Blackberries have a very wide range of aroma profiles. The aroma profiles of Thornless Evergreen and Marion blackberries would be expected to be quite different from Chickasaw as they have very different genetic backgrounds and are typically grown for different markets. The aroma profile has not been previously determined for Chickasaw or for any other erect blackberry cultivar.

Aroma compounds in fruits can be generated from fatty acids, amino acids, and carbohydrates (*13*). Different climates and sites can affect the levels of precursors and activities of related enzymes, thereby impacting flavor development. The environmental influence on flavor formation has been examined in several small fruits, including strawberry, raspberry, blueberry, and grape (*14*−*21*); however, no work has been done on blackberry. The objectives of this study were to identify the aroma compounds in Chickasaw blackberry using gas chromatography olfactometry (GCO), to compare the aroma profile in Chickasaw blackberries grown in Oregon and Arkansas by aroma extraction dilution analysis (AEDA) technique, and to elucidate the influence of growing environment on aroma quality.

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MATERIALS AND METHODS

Chemicals. 1-Methyl-4-isopropenyl-1-cyclohexene (limonene), 2-heptanone, 2,6,6-trimethylbicyclo-[3,1,1]-2-heptene (β-pinene), 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane (β-pinene), 2-nonenal, ethyl 2-methylpropanoate, and 2-undecanone were obtained from K&K Laboratories (Jamaica, NY). Ethyl butanoate, ethyl pentanoate, ethyl *trans*-2-butenoate, ethyl hexanoate, ethyl propanoate, ethyl butanoate, butyl acetate, hexyl acetate, hexyl butanoate, *cis*-3-hexenyl acetate, ethyl octanoate, ethyl 3-hydroxyhexanoate, ethyl decanoate, ethyl benzoate, methyl dodecanoate, methyl hexanoate, methyl butanoate, ethyl acetate, ethyl 2-methylbutanoate, ethyl 3-phenylpropanoate (ethyl dihydrocinnamate), ethanoic acid (acetic acid), butanoic acid, hexanoic acid, 2-methylbutanoic acid, 4-2,6,6-trimethyl-1-cyclohexen-1-yl-3-buten-2-one (β-ionone), 2-heptanol, hexanal, hepanal, octanal, nonanal, decanal, cyclohexane carbaldehyde (benzaldehyde), *trans*,*cis*-2,6-nonadienal, phenylacetaldehyde, 1-2,6,6-trimethyl-1,3-cyclohexadien-1-yl-2-buten-1-one (β-damascenone), *trans*-2-hexenal, 3,7-dimethyl-1,6-octandien-3-ol (linalool), 6,6-dimethyl-bicyclo[3.1.1]hept-2-ene-2-carboxaldehyde (myrtenal), 7-methyl-3-methylene-1,6-octadiene (myrcene), 1-isopropyl-4-methylenebicyclo[3.1.0]hexane (sabinene), β-3,7-dimethyl-1,3,6-octatriene (β-ocimene), 1-isopropyl-4-methyl-1,4-cyclohexadiene (γ-terpinene), *trans*-3,7-dimethyl-2,6-octadienal (geranial), *trans*-3,7-dimethyl-2,6-octadien-1-ol (geraniol), 3,7,11-trimethyl-1,6,10-dodecatrien-3-ol (nerolidol), 1,7,7-trimethylbicyclo[2.2.1]-2-heptanone (camphor), 2,2-dimethyl-3-methylene-bicyclo[2.2.1]heptane (camphene), 3-methylene-6-1-methylethenylcyclohexane (β-phellandrene), 1-methyl-4-1-methylethylidene-cyclohexene (α-terpinolene), 2-pentanol, 3-pentanol, 1-penten-3-ol, 3-methylbutanol, hexanol, *cis*-3-hexenol, *trans*-3-hexenol, *trans*-2-hexenol, 1-octen-3-ol, heptanol, nonanol, octanol, phenylmethanol (benzyl alcohol), 2-phenylethanol (phenethyl alcohol), 2,5-dimethyl-4-hydroxy-3(2H)-furanone (furaneol), and 2,6,10,10-tetramethyl-1-oxaspiro[4.5]dec-6-ene (theaspirane) were obtained from Aldrich Chemical Co. Inc. (Milwaukee, WI). 4-Hydroxy-decanoic acid (β-decalactone) was purchased from Pfaltz & Bauer (Waterbury, CT). Sodium chloride was obtained from Fisher Scientific (Fair Lawn, NJ). Diethyl ether, pentane, and methanol were obtained from Honeywell International Inc. (Muskegon, MI), Mallinckrodt Baker Inc. (Phillipsburg, NJ), and J. T. Baker Inc. (Phillipsburg, NJ), respectively.

Blackberry Samples. Fully ripe Chickasaw blackberries were handpicked from plants growing at the Oregon State University North Willamette Research and Extension Center (OSU-NWREC; Aurora, OR) and the University of Arkansas Fruit Substation (Clarksville, AR) in July 2003. The fruits were immediately placed on ice and transported to the laboratory, where they were individually quick frozen (IQF) and stored at −23 °C. The samples from Arkansas were shipped on ice to the laboratory at Oregon State University and stored at −23 °C. The samples had been frozen for 1 month when analyzed.

Extraction of Volatile Compounds. One kilogram of IQF Chickasaw fruit from both locations was taken out of the freezer and let stand at room temperature until they were just soft enough to be blended (but still icy and cold). The berries were blended in a glass blender jar (Waring Products Division, Dynamics Corp. of America, New Hartford, CT) for a total of 90 s. Ten grams of calcium chloride was added to inhibit enzyme activity before blending. The puréed fruit was transferred to a 1 L Erlenmeyer flask covered with aluminum foil and extracted with 335 mL of freshly distilled pentane:diethyl ether (1:1 v/v) on a platform shaker (Innova 2300; New Brunswick Scientific, Edison, NJ) 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 880 mL of solvent. Volatile compounds were recovered from the organic extract by using solvent-assisted flavor evaporation (SAFE) at 50 °C under vacuum (*22*). The organic SAFE extract was dried with anhydrous Na_2SO_4, concentrated to 2 mL by solvent evaporation, and reduced to its final volume of 0.2 mL with a flow of nitrogen.

GCO. The analysis was performed using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector (FID) and an olfactometer. Samples were analyzed on a Stabilwax column [30 m × 0.32 mm i.d. cross-linked poly(ethylene glycol), 1 μm film thickness, Restek Corp., Bellefonte, PA] and a DB-5 column (30 m × 0.32 mm i.d., cross-linked phenyl-methyl polysiloxane, 1 μm film thickness, J&W Scientific, Folsom, CA). The column effluent was split 1:1 (by volume) into the FID and a heated sniffing port with a fused silica outlet splitter (Alltech Associates, Inc., Deerfield, IL). Injector and detector temperatures were 250 °C, the helium column flow rate was 2.0 mL/min at 25 °C, and the 2 μL sample was injected in the splitless mode. The oven temperature was programmed for a 2 min hold at 40 °C, then 40−100 °C at 5 °C/min, then 100−230 °C at 4 °C/min (10 min hold). Retention indices (RIs) were estimated in accordance with a modified Kovats method (*23*).

Aroma Extract Fractionation/GCO. For a better GC resolution and identification, 1 kg of Oregon Chickasaw blackberries was extracted using the same procedure as described previously. The aroma extract was concentrated to 1 mL. The concentrated sample was fractionated by adsorption chromatography on silica gel (EM Science, 35−70 mesh, 60 Å) described by Qian and Reineccius (*24*) with some modification. Eight grams of silica gel was packed into a 1.5 cm i.d. × 30 cm glass column. The column was washed with methanol and equilibrated in pentane. The sample (1 mL) was applied to the column and fractionated by eluting with 70 mL of each following solvents: pentane (fraction 1), pentane and diethyl ether (fraction 2, 95/5; fraction 3, 90/10; fraction 4, 50/50), diethyl ether (fraction 5), and methanol (fraction 6) at a flow rate of 1.5 mL/min. Each fraction was concentrated to 2 mL by solvent evaporation and reduced to its final volume of 0.2 mL with a flow of nitrogen. Fractions were analyzed by GCO at the same conditions and methods as for the AEDA analysis. The odor intensities of odorants were evaluated on a nine-point intensity scale by a trained judge. This GCO analysis was done in triplicate for each fraction.

AEDA. Two experienced panelists were used for AEDA (*25*, *26*). The aroma concentrate was diluted sequentially at 1:1 ratio. Each dilution was analyzed until the aroma could no longer be detected. Flavor dilution (FD) values were calculated based on the last dilution.

GC−Mass Spectroscopy (MS). The original concentrated samples as used for AEDA 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, DE). Volatile separation was achieved with the same Stabilwax and DB-5 columns used in the AEDA 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 AEDA analysis. Injector, detector transfer line, and ion source temperatures were 250, 280, and 230 °C, respectively. Electron impact mass spectrometric data from *m*/*z* 35−300 were collected using a scan rate of 5.27/s, with an ionization voltage of 70 eV. RIs were estimated in accordance with a modified Kovats method (*23*). Compound identifications were made by comparing mass spectral data from the Wiley 275.L (G1035) Database (Agilent) and confirmed by comparing Kovats RIs to those of the standards or RIs reported in the literature.

RESULTS AND DISCUSSION

Aroma Fractionation of Oregon Chickasaw Blackberries. The aroma extract of Chickasaw blackberries is very complex. To increase the resolution of GC and facilitate the identification of aroma compounds, silica gel normal phase chromatography was applied on the aroma extract of the Oregon samples. Six fractions were obtained, and GCO and GC-MS were performed on each fraction. In the GCO experiment, one experienced judge was chosen to evaluate the intensity of odorants from each fraction on a 0−9 scale. Although this GCO experiment cannot provide a quantitative estimation of their odor intensity due to limited panelists, it can provide information about the aroma quality of the compounds, as well as positive mass spectrometry identification. The results of fractionation were summarized in **Table 1**.

A total of eighty-four compounds were isolated and identified from the six fractions, including nineteen esters, eighteen

Table 1. Odor Active Compounds in Aroma Fractions for Oregon-Grown Chickasaw Blackberries

RI on				odor intensity						identification
Stabilwax	DB-5	odorant	odor quality	Fr 1[a]	Fr 2	Fr 3	Fr 4	Fr 5	Fr 6	basis[b]
938	718	dimethyl sulfide[d]	sulfur, cabbage-like			4				odor, RI
965	725	ethyl propanoate	fruity		3	5				MS, odor, RI
965	754	ethyl 2-methylpropanoate	fruity		4					MS, odor, RI
989	728	methyl butanoate	fruity, sweet		2	3				MS, odor, RI
1023	932	2,6,6-trimethylbicyclo[3,1,1]-eptene (α-pinene)	resinous	4						MS, odor, RI
1042	803	ethyl butanoate	fruity, apple-like		5	8				MS, odor, RI
1051	848	ethyl 2-methylbutanoate	fruity, sweet		3					MS, odor, RI
1061	946	2,2-dimethyl-3-methylene-bicyclo-[2.2.1]heptane (camphene)	green, terpene-like	5						MS, odor, RI
1074	814	butyl acetate	fruity, juicy		3	5				MS, odor, RI
1088	800	hexanal	green, grassy			5	4			MS, odor, RI
1106	932	6,6-dimethyl-2-methylenebicyclo-[3.1.1]heptane (β-pinene)	woody, resinous	4						MS, odor, RI
1110		3-pentanol	green				2			MS, odor, RI
1122	718	2-pentanol	cut grass, green				2			MS, odor, RI
1139	903	ethyl pentanoate	fruity		3					MS, odor, RI
1167	844	ethyl *trans*-2-butenoate	fruity, green			4∼5				MS, odor, RI
1168	991	7-methyl-3-methylene-1,6-octadiene (myrcene)	resinous, balsamic	5						MS, odor, RI
1169	680	1-penten-3-ol	green				4			MS, odor, RI
1186		2-methylthiophene[d]	french fries, cooked potato			7				odor, RIL[c](*11*)
1189	924	methyl hexanoate	fruity, sweet		4					MS, odor, RI
1190	902	heptanal	oily, fatty			3	2			MS, odor, RI
1198	1023	3-methylene-6-(1-methylethenyl)-cyclohexane (β-phellandrene)	mint, herbaceous	2						MS, odor, RI
1198	892	2-heptanone	floral, fruity			4	2			MS, odor, RI
1199	1028	1-methyl-4-isopropenyl-1-cyclohexene (limonene)	piney, herbaceous	4						MS, odor, RI
1213	1027	1-isopropyl-4-methylenebicyclo-[3.1.0]hexane (sabinene)	green, fatty, woody	2						MS, odor, RI
1218	786	3-methylbutanol	green, pungent				2			MS, odor, RI
1221	851	*trans*-2-hexenal	green, leafy				5			MS, odor, RI
1240	1001	ethyl hexanoate	apple-like, fruity, sweet		2	5				MS, odor, RI
1240	1038	*trans*-β-3,7-dimethyl-1,3,6-octatriene (*trans*-β-ocimene)	woody	2						MS, odor, RI
1247	1057	1-isopropyl-4-methyl-1,4-cyclohexadiene (γ-terpinene)	woody, oil, barney	5						MS, odor, RI
1278	1086	1-methyl-4-(1-methylethylidene)-cyclohexene (α-terpinolene)	woody, herbaceous		2					MS, odor, RI
1294	1003	octanal	floral, fruity, fatty			5				MS, odor, RI
1317	1008	*cis*-3-hexenyl acetate	green, grass		4					MS, odor, RI
1331	905	2-heptanol	mushroom				2			MS, odor, RI
1364	875	hexanol	fruity				3			MS, odor, RI
1374	853	*trans*-3-hexenol	green				2			MS, odor, RI
1395	986	*cis*-1,5-octadien-3-one[d]	piney, green				8			odor, RIL (*28*)
1398	1105	nonanal	floral, citrus			4				MS, odor, RI
1414	1192	hexyl butanoate	fruity,melon-like		2∼3	4				MS, odor, RI
1417	868	*trans*-2-hexenol	walnut, green				5			MS, odor, RI
1440	1200	ethyl octanoate	fruity, fatty, apricot		2∼3					MS, odor, RI
1462	985	1-octen-3-ol	fatty, mushroom				5			MS, odor, RI
1465		3-isopropyl-2-methoxy-pyrazine[d]	beany, vegetable			3				odor, RIL (*29*)
1476	716	ethanoic acid (acetic acid)	acid, sour						6	MS, odor, RI
1480	977	heptanol	green, fruity				2			MS, odor, RI
1500	1298	2,6,10,10-tetramethyl-1-oxaspiro-[4.5]dec-6-ene (theaspirane B)	fruity, floral		3					MS, odor, RI
1503	1206	decanal	soapy, citrus			3	5			MS, odor, RI
1509	1141	1,7,7-trimethylbicyclo[2.2.1]-2-heptanone (camphor)	soapy, fatty				2			MS, odor, RI
1527	958	cyclohexane carbaldehyde (benzaldehyde)	berry, fruity			2				MS, odor, RI
1540	964	ethyl 3-hydroxybutanoate	fruity				2∼3			MS, odor, RIL (*30*)
1560	1102	3,7-dimethyl-1,6-octandien-3-ol (linalool)	floral			7	6			MS, odor, RI
1570		*trans*-2-nonenal	green, fruity				2			MS, odor, RIL (*31*)
1570	1150	*trans,cis*-2,6 nonadienal[d]	cucumber, green			5	3			odor, RI
1591		undecanal	fresh floral fruity			4∼5				MS, odor, RIL (*32*)
1601	1295	2-undecanone	floral, fruity			4∼5				MS, odor, RI
1619	1195	6,6-dimethyl-bicyclo[3.1.1]hept-2-ene-2-carboxaldehyde (myrtenal)	spicy, cinnamon				4			MS, odor, RI

Table 1 (Continued)

RI on				odor intensity						identification
Stabilwax	DB-5	odorant	odor quality	Fr 1[a]	Fr 2	Fr 3	Fr 4	Fr 5	Fr 6	basis[b]
1621		1-methyl-4-isopropyl-1-cyclohexen-4-ol (4-terpineol)	floral, herbal				3			MS, odor, RIL (*33*)
1645	1397	ethyl decanoate	fruity			4				MS, odor, RI
1648	815	butanoic acid	sour, rancid						3	MS, odor, RI
1649	1043	phenylacetaldehyde	lilac, floral				4			MS, odor, RI
1663	1170	ethyl cyclohexane carboxylate (ethyl benzoate)	fruity, tea		4					MS, odor, RI
1672	1185	nonanol	fatty, green, oily, floral				3∼4			MS, odor, RI
1690	1129	ethyl 3-hydroxyhexanoate	floral, fruity				2			MS, odor, RI
1700	876	2/3-methylbutanoic acid	cheesy, sour						3	MS, odor, RI
1729	1271	*trans*-3,7-dimethyl-2,6-octadienal (geranial)	tea, mint, citrus			3∼4				MS, odor, RI
1804	1526	methyl dodecanoate	sweet, floral		2					MS, odor, RI
1819	1383	1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one (β-damascenone)	berry, sweet, floral			5				MS, odor, RI
1862	1269	*trans*-3,7-dimethyl-2,6-octadien-1-ol (geraniol)	rosy-like, floral				4			MS, odor, RI
1866	1006	hexanoic acid	sour, acid., rancid						3	MS, odor, RI
1890		phenylmethanol (benzyl alcohol)	watermelon fruity floral				3			MS, odor, RI
1936	1136	2-phenylethanol (phenethyl alcohol)	rosy				4			MS, odor, RI
1986	1486	4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (β-ionone)	dry fruit, floral				2			MS, odor, RI
2012	1550	3,7,11-trimethyl-1,6,10-dodecatrien-3-ol (nerolidol)	woody, floral				5			MS, odor, RI
2064		2,5-dimethyl-4-hydroxy-3(2H)-furanone (furaneol)	caramel, cooked sugar					3	8	MS, odor, RI
2100		2-ethyl-4-hydroxy-5-methyl-3(2H)-furanone (homofuraneol)[d]	sweet, caramel					2	8	odor, RIL (*34*)
2149	1472	5-hexyldihydro-2[3H]-furanone (γ-decalactone)	candy, sweet					5		MS, odor, RI
	858	*cis*-3-hexenol	cut grass				4			MS, odor, RI
	1049	ethyl *trans*-2-hexenoate	sweet, green, vegetable			5				MS, odor, RI
	1066	5-ethyldihydro-2[3H]-furanone (γ-hexalactone)	sweet, fruity					6		MS, odor, RIL (*35*)
	1080	octanol	soapy, fatty				3∼4			MS, odor, RI
	1242	6,6-dimethyl-2-oxymethlybicyclo-[1.1.3]hept-2-ene (myrtenol)	woody, balsamic				4			MS, odor, RI
	1257	4-octanolide (γ-octalactone)	coconut					3∼4		MS, odor, RI
	1295	5-octanolide (δ-octalactone)	fruity, sweet					3		MS, odor, RIL (*36*)
	1369	*trans*-2-undecenal	fatty, waxy, green			2				MS, odor, RIL (*37*)
	1559	1,2,3-trimethoxy-5-allylbenzene (elemicin)	sweet, woody		2					MS, odor, RIL (*38*)

[a] Fraction. [b] MS, mass spectral data; RIL, retention index from literature; RI, retention index from standards. [c] Retention index from the literature. [d] Tentative identification.

terpenes and terpenoids, fifteen alcohols, thirteen aldehydes, four ketones, four acids, four lactones, two furans, two sulfur-containing compounds, one pyrazine, and two miscellaneous compounds. The highest recoveries for terpenes were achieved in fraction 1 eluted with pentane, but terpenoids were found in fractions 2, 3, and 4, which are the more polar fractions (pentane/diethyl ether, 95:5v, 90:10v, and 50:50v). Except for ethyl 3-hydroxybutanoate and ethyl 3-hydroxyhexanoate, which were found in fraction 4, esters were mostly recovered in fractions 2 and 3. Aldehydes and ketones were generally found in fractions 3 and 4. In general, alcohols were eluted in fraction 5 with diethyl ether. Acids and furans were mostly recovered in polar fraction 6 with methanol.

On the basis of their odor intensity, ethyl butanoate, linalool, *cis*-1,5-octadien-3-one, 2-methylthiophene, 2,5-dimethyl-4-hydroxy-3(2H)-furanone, and 2-ethyl-4-hydroxy-5-methyl-3(2H)-furanone (odor intensity = 8, 7, 8, 7, 8, and 8, respectively) were detected as the most potent aroma compounds in the Oregon sample. Besides, ethyl propanoate, butyl acetate, ethyl *trans*-2-butenoate, ethyl hexanoate, ethyl *trans*-2-hexenoate, camphene, myrcene, γ-terpinene, hexanal, *trans*-2-hexenal, decanal, undecanal, *trans*,*cis*-2,6-nonadienal, 2-undecanone, β-damascenone, *trans*-2-hexenol, 1-octen-3-ol, γ-decalactone, and γ-hexalactone also are important odorants to Oregon Chickasaw blackberry flavor with an odor intensity around 5. Although the odor intensities of those odorants are not conclusive, it is very likely that those aroma compounds could be important to Chickasaw aroma.

Comparative AEDA of Chickasaw Blackberries from Oregon and Arkansas States. Although the two samples selected for this study were from the same blackberry cultivar, the two climates during fruit ripening were quite different. During June and July in Clarksville, Arkansas, the temperatures during the day (mean July max = 33.6 °C) and night (mean July min = 20.1 °C) are warm, the relative humidity is generally very high, there can be substantial precipitation (mean July cumulative precipitation = 73.7 mm), and while the sunlight can be quite intense, there is much greater cloud cover than in Oregon. In contrast, during July at the OSU-NWREC in Oregon, the temperatures are moderate during the day (mean July max = 26.8 °C), cool at night (mean July min = 11.7 °C), the relative humidity is very low, there is very little precipitation (mean

July cumulative precipitation = 16.5 mm), and the days are very clear and sunny. Because of the difference in growing environment, the fruits developed distinctive aromas. In preliminary sensory evaluations (seven expert panelists), berries from Oregon were characterized as having cut grass, green, fruity, citrus, and watermelon aromas. However, Arkansas berries were judged to be less green and fruity but described as having cinnamon, piney, floral, sweet, and caramel smelling aromas.

The odor active volatiles in the samples from the two regions were analyzed by AEDA (*25*, *26*). When the data from polar (**Table 2**) and nonpolar columns (**Table 3**) are combined, a total of 87 odorants were detected in the FD range of 2−2048, 77 of which could be identified. Sixty-five odorants were identified in Oregon samples, while 68 were identified in the Arkansas sample. Of these, 56 were common to both.

Judging by FD factors, esters were found to be the most important chemical class in Chickasaw blackberries from both states; they were responsible for intense fruity and floral notes in the fruit samples. A total of 20 odor active esters were detected; all of the 20 esters were found in Oregon samples and 16 in Arkansas samples. Thirteen of these esters were considered to be important odorants with high FD factors ranging from 64 to 2048. Of these, ethyl butanoate, ethyl 2-methylbutanoate, ethyl 2-methylpropanoate, methyl hexanoate, and ethyl *trans*-2-hexenoate (FD = 2048, 64, 512, 128, and 128, respectively, in Oregon fruit; FD = 2048, 2048, 512, 256, and 64, respectively, in Arkansas fruit) were found in both. With the exception of ethyl 2-methylbutanoate, the other four esters were considered to contribute equally (FD factors ± one dilution are considered equivalent) to the aroma profile in the berry samples from both states. Ethyl butanoate was found to be the most important volatile in both samples (FD = 2048 in both), and it actively contributes to the desirable fruity flavor of blackberries due to its small molecular weight and high volatility. Apart from ethyl butanoate, six more esters, ethyl propanoate, methyl butanoate, butyl acetate, ethyl hexanoate, hexyl acetate, and ethyl dihydrocinnamate, show high FD factors in Oregon berry samples, while two more esters, *cis*-3-hexenyl acetate and ethyl benzoate, show high FD factors in Arkansas samples. Comparing the numbers and the magnitude of FD factors of these odorants in the two samples, the esters in Oregon might play a bigger role than in Arkansas for the overall aroma, which was supported by the sensory evaluation.

There were eighteen odor active terpenes and terpenoids detected in both berries. Eight of them show high FD factors. Linalool (FD = 2048 in both), geraniol (FD = 256 in Oregon, FD = 2048 in Arkansas), and α-pinene (FD= 512 in Oregon, FD = 256 in Arkansas) were the most potent odorants in both samples. Linalool and geraniol, characterized as a floral, rose-like odor, could be related to the floral notes of Chickasaw blackberries, whereas α-pinene might be associated with the piney, woody, and resinous smell. Additionally, limonene and citronellol (FD = 512 and 256) show high FD factors in Oregon, while γ-terpinene, γ-cadinene, and *allo*-ocimene (FD = 256, 256, and 512, respectively) show high FD factors in Arkansas. Among these five compounds, while citronellol is sweet and fruity smelling, the other terpenes were described as having piney, minty, and woody notes. The fact that Arkansas has more potent piney smelling compounds is in good agreement with the results from sensory evaluation, which suggested that Chickasaw from Arkansas had stronger piney and woody notes than those from Oregon.

A total of nine aldehydes were identified in berry samples from the two locations. All of the six aldehydes found in Oregon fruit were also identified in Arkansas fruit. Furthermore, Arkansas has three more odor active aldehydes than Oregon. Seven aldehydes were reported having high FD factors. Hexanal, *trans*,*cis*-2,6-nonadienal, and benzaldehyde (FD = 516, 1024, and 256, respectively, in Oregon; FD = 16, 64, and 8, respectively, in Arkansas) showed higher FD factors in Oregon, while heptanal and *trans*-2-hexenal (FD = 16 and 16 in Oregon; FD = 64 and 512 in Arkansas) had higher FD factors in Arkansas. Additionally, the Arkansas samples had two more potent aldehydes that were not present in Oregon samples, nonanal and vanillin (FD = 128 and 256).

There were seven odor active ketones detected; of these, four had a FD factor exceeding 64. All four of these ketones were found in the Oregon samples, but only two were found in the berries grown in Arkansas. *cis*-1,5-Octadien-3-one (FD = 2048 in Oregon, FD = 256 in Arkansas) was the most important ketone that showed high FD factors in both berries. β-Damascenone, with a rose-like, sweet, berry odor, also has high FD factors (FD = 64 in Oregon, FD = 1024 in Arkansas) in samples from both locations, but it shows a significantly higher aroma impact in Arkansas than in Oregon. Additionally, 2-undecanone and 2,3-butanedione (FD = 128 and 512) also showed high FD factors in Oregon.

Eight alcohols, including six aliphatic and two aromatic alcohols, were perceived in two aroma extracts, while only aromatic alcohols were detected as having high FD factors. Benzyl alcohol and phenethyl alcohol, both exhibiting floral, rose-like aromas, were detected. Phenethyl alcohol had a higher FD factor in the Oregon grown fruit (128, FD = 8 in Arkansas), while benzyl alcohol had a higher FD factor in those from Arkansas (256, FD = 8 in Oregon). The aroma of other aliphatic alcohols was generally described as grass, green, and waxy.

Four odor active short chain fatty acids were found in berries from both regions. Generally, acids were not considered as impact aroma compounds due to their high odor threshold and it is not easy to detect their acid, cheesy smell except when they are present in large quantities. The highest FD factors in acids were given to acetic and 2/3-methylbutanoic acids; both were 128 in the berries from the two states. Butanoic acid was also present in the Arkansas sample and had a high FD factor of 128.

Two sulfur-containing compounds, methional, which has cooked potato notes, and the cabbage-like dimethyl sulfide, were detected. Both compounds have been detected as odor active compounds in Marion and Thornless Evergreen blackberries recently (*10*, *11*). In this study, AEDA also revealed that methional was one of the most important odorant for Chickasaw berries, with a FD factor of 2048 in samples from both locations. Methional is well-known to be generated from the Strecker degradation of amino acid methionine, while dimethyl sulfide was formed from the further degradation of methional. With an odor threshold of 0.2 ppb in water (*27*), methional might strongly influence the blackberry aroma. However, in the sensory evaluation of berry samples from the two locations, no descriptions related to cooked potato were given by the panelists.

There were two furans, 2,5-dimethyl-4-hydroxy-3(2H)-furanone (furaneol) and 2-ethyl-4-hydroxy-5-methyl-3(2H)-furanone (homofuraneol), and two lactones, δ-decalactone and γ-decalactone, identified in samples from both states. 2,5-Dimethyl-4-hydroxy-3(2H)-furanone was characterized as a key aroma compound in both berry samples (FD = 2048 in Oregon, FD = 512 in Arkansas), exhibiting an intensely sweet, caramel, and

Table 2. AEDA of Oregon- and Arkansas-Grown Chickasaw Blackberries (Stabilwax Column)

RI	compound	descriptors	FD factors OR	FD factors AR	identification basis[a]
874	ethyl acetate	fruity	8	2	MS, odor, RI
898	dimethyl sulfide[c]	cabbage, sulfur	4	8	odor, RI
955	ethyl propanoate	fruity	16	16	MS, odor, RI
966	ethyl 2-methylpropanoate	fruity	32	16	MS, odor, RI
976	2,3-butanedione (diacetyl)[c]	buttery	16	16	odor, RI
995	methyl butanoate	fruity	512		MS, odor, RI
1038	2,6,6-trimethylbicyclo[3,1,1]-2-heptene (α-pinene)	piney, resinous	4	8	MS, odor, RI
1056	ethyl butanoate	fruity, apple	2048	512	MS, odor, RI
1070	ethyl 2-methylbutanoate	fruity, sweet	32	32	MS, odor, RI
1075	butyl acetate	fruity, juicy	8		MS, odor, RI
1098	hexanal	green	128	16	MS, odor, RI
1125	6,6-dimethyl-2-methylenebicyclo-[3.1.1]heptane (β-pinene)	woody, resinous	2	8	MS, odor, RI
1161	ethyl pentanoate	fruity	32		MS, odor, RI
1176	1-penten-3-ol	green, pungent	32		MS, odor, RI
1181	7-methyl-3-methylene-1,6-octadiene (myrcene)	balsamic, plastic	8	8	MS, odor, RI
1193	2-heptanone	fruity, banana		16	MS, odor, RI
1208	methyl hexanoate	fruity, apple	128	256	MS, odor, RI
1213	heptanal	oily, fatty		4	MS, odor, RI
1226	1-methyl-4-isopropenyl-1-cyclohexene (limonene)	piney, herbaceous	128	32	MS, odor, RI
1237	3-methylbutanol	pungent, green	16	-	MS, odor, RI
1248	*trans*-2-hexenal	green, leaf	16	512	MS, odor, RI
1258	ethyl hexanoate	apple, fruit	32	16	MS, odor, RI
1269	1-isopropyl-4-methyl-1,4-cyclo-hexadiene (γ-terpinene)	oily, woody	4	256	MS, odor, RI
1319	octanal	citrus-like, fruity	32	8	MS, odor, RI
1338	*cis*-3-hexenyl acetate	green, grass	32	256	MS, odor, RI
1344	2-heptanol	woody vegetal	4		MS, odor, RI
1408	*cis*-1,5-octadien-3-one[c]	green, grassy	1024	512	odor, RIL (*28*)
1441	hexyl butanoate	apple peel	16	8	MS, odor, RI
1464	ethyl octanoate	fruity, apricot	16	8	MS, odor, RI
1475	3-isopropyl-2-methoxypyrazine[c]	earthy, beany	2		odor, RIL[b] (*29*)
1486	ethanoic acid (acetic acid)	acid, sour	64	128	MS, odor, RI
1499	3-methylmercaptopropion-aldehyde (methional)[c]	cooked potato	2048	2048	odor, RI
1540	2,6,10,10-tetramethyl-1-oxaspiro-[4.5]dec-6-ene (theaspirane B)	floral	16	8	MS, odor, RI
1578	3,7-dimethyl-1,6-octandien-3-ol (linalool)	floral, citrus	2048	2048	MS, odor, RI
1601	2-undecanone	sweet, fruity	128	32	MS, odor, RI
1608	*trans,cis*-2,6-nonadienal[c]	cucumber	128	64	odor, RI
1641	unknown	floral, fruit, watermelon	128		
1645	1-methyl-4-isopropyl-1-cyclohexen-4-ol (4-terpineol)	earthy, woody		8	MS, odor, RIL (*33*)
1663	butanoic acid	rancid, acid	16	256	MS, odor, RI
1706	2/3-methylbutanoic acid	cheesy, sour	128	128	MS, odor, RI
1725	*trans*-3,7-dimethyl-2,6-octadienal (geranial)	sweet, floral		8	MS, odor, RI
1745	(*R*)-5-isopropenyl-2-methyl-2-cyclo-hexenone (*l*-carvone)	herbaceous, mint	8	8	MS, odor, RI
1788	(1S-(1α,4α,4α,6α,8β))-decahydro-4-isopropyl-1,6-dimethyl-naphthalene (γ-cadinene)	woody	16	256	MS, odor, RI
1803	3,7-dimethyl-6-octen-1-ol (citronellol)	green, cucumber	32	16	MS, odor, RI
1817	*cis*-3,7-dimethyl-2,6-octadien-1-ol (nerol)	floral, rose		4	MS, odor, RI
1846	unknown	Chinese medicine, herbaceous		2	
1850	1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one (β-damascenone)	rose, floral, sweet	32	128	MS, odor, RI
1879	*trans*-3,7-dimethyl-2,6-octadien-1-ol (geraniol)	sweet, rose, candy		8	MS, odor, RI
1884	hexanoic acid	sour	8	2	MS, odor, RI
1915	phenylmethanol (benzyl alcohol)	floral	8	256	MS, odor, RI
1961	2-phenylethanol (phenethyl alcohol)	rosy	16	4	MS, odor, RI
1967	4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one(β-ionone)	dry fruit, berry	4	4	MS, odor, RI
1995	unknown	rosy, floral		32	
2045	3,7,11-trimethyl-1,6,10-dodecatrien-3-ol (nerolidol)	floral, woody		16	MS, odor, RI
2063	2,5-dimethyl-4-hydroxy-3(2H)-furanone (furaneol)	sweet, caramel	2048	32	MS, odor, RI
2086	2-ethyl-4-hydroxy-5-methyl-3(2H)-furanone (homofuraneol)[c]	sweet, berry	32	8	odor, RIL (*34*)
2187	4-allyl-2-methoxyphenol (eugenol)	clove, honey		4	MS, odor, RI
2218	5-decanolide (δ-decalactone)[c]	coconut, peach, dairy	128	8	odor, RIL (*37*)
2264	unknown	herbaceous, woody	128	2	

[a] MS, mass spectral data; RIL, retention index from literature; RI, retention index from standards. [b] Retention index from the literature. [c] Tentative identification.

Table 3. AEDA of Oregon- and Arkansas-Grown Chickasaw Blackberries (DB-5 Column)

RI	compound	aroma descriptors	FD factors OR	FD factors AR	identification basis[a]
709	2,3-butanedione (diacetyl)[c]	buttery	512	8	odor, RI
716	ethanoic acid (acetic acid)	sour, vinegar	128	32	MS, odor, RI
725	dimethyl sulfide[c]	cabbage-like		8	odor, RI
730	2-pentanol	pungent, plastic, green	2		MS, odor, RI
744	ethyl propanoate	fruity	128		MS, odor, RI
754	methyl butanoate	sweet, fruity	16	4	MS, odor, RI
779	ethyl 2-methylpropanoate	fruity	512	512	MS, odor, RI
800	hexanal	green, grassy	512	16	MS, odor, RI
807	ethyl butanoate	fruity, apple	1024	2048	MS, odor, RI
814	butyl acetate	fruity	64		MS, odor, RI
817	butanoic acid	sour, rancid, pungent	32	128	MS, odor, RI
823	unknown	rubbery, buttery		8	
854	ethyl 2-methylbutanoate	fruity, apple	64	2048	MS, odor, RI
870	2/3-methylbutanoic acid	pungent, cheesy, sour	64	8	MS, odor, RI
882	*cis*-3-hexenol	green, grassy		8	MS, odor, RI
899	heptanal	oily, fatty	16	64	MS, odor, RI
907	3-methylmercaptopropionaldehyde (methional)[c]	cooked potato	2048	2048	odor, RI
944	2,6,6-trimethylbicyclo-[3,1,1]-2-heptene (α-pinene)	piney, woody, resinous	512	256	MS, odor, RI
963	cyclohexane carbaldehyde (benzaldehyde)	fruity,cherry	256	8	MS, odor, RI
982	*cis*-1,5-octadien-3-one	green, resinous	2048	256	odor, RIL[b] (*28*)
1003	ethyl hexanoate	fruity, sweet, pineapple	512	32	MS, odor, RI
1009	unknown	hay, dry woody		4	
1019	3-methylene-6-(1-methylethenyl)-cyclohexane (β-phellandrene)	mint, cool		8	MS, odor, RI
1022	hexyl acetate	sweet, fruity	256		MS, odor, RI
1022	phenylacetaldehyde	lilac, floral		4	MS, odor, RI
1027	1-methyl-4-isopropyl-benzene (*p*-cymene)	pungent, solvent	16		MS, odor, RI
1039	unknown	fruity, sour,		4	
1047	1-methyl-4-isopropenyl-1-cyclohexene (limonene)	piney, herbaceous, mint	512	8	MS, odor, RI
1052	ethyl *trans*-2-hexenoate	green, fruity	128	64	MS, odor, RI
1062	2,5-dimethyl-4-hydroxy-3(2H)-furanone (furaneol)	sweet, strawberry	512	512	MS, odor, RI
1084	2-ethyl-4-hydroxy-5-methyl-3(2H)-furanone (homofuraneol)[c]	sweet, candy, caramel	128	8	odor, RIL (*34*)
1099	1-methyl-4-(1-methylethylidene)-cyclohexene (α-terpinolene)	woody, earthy, herbaceous		8	MS, odor, RI
1106	3,7-dimethyl-1,6-octandien-3-ol (linalool)	floral, citrus	2048	2048	MS, odor, RI
1068	octanol	waxy, fatty		8	MS, odor, RI
1112	nonanal	floral		128	MS, odor, RI
1121	*allo*-3,7-dimethyl-1,3,6-octatriene (*allo*-ocimene)	Chinese medicine, herbaceous		512	MS, odor, RI
1140	2-phenylethanol (phenethyl alcohol)	rose	128	8	MS, odor, RI
1157	ethyl 3-hydroxyhexanoate	fruity	4	8	MS, odor, RI
1164	*trans,cis*-2,6-nonadienal[c]	cucumber, green	1024	16	odor, RI
1174	ethyl cyclohexane carboxylate (ethyl benzoate)	fruity, musty, tea	32	32	MS, odor, RI
1180	1-methyl-4-acetyl benzene (*p*-methylacetophenone)[c]	sweet, hot candy	8	2	odor, RIL (*11*)
1189	1-methyl-4-isopropyl-1-cyclohexen-4-ol (4-terpineol)	woody, earthy, musty	2	4	MS, odor, RIL (*33*)
1214	6,6-dimethyl-2-oxymethlybicyclo[1.1.3]-hept-2-ene (myrtenol)	medicinal, woody	16	8	MS, odor, RI
1237	3,7-dimethyl-6-octen-1-ol (citronellol)[c]	fruity	256	2	odor, RI
1246	(*R*)-5-isopropenyl-2-methyl-2-cyclohexenone (*l*-carvone)	herbaceous, caraway	16	4	MS, odor, RI
1275	*trans*-3,7-dimethyl-2,6-octadien-1-ol (geraniol)	rose	256	2048	MS, odor, RI
1315	2-undecanone	rose, iris	64	4	MS, odor, RI
1324	unknown	herbaceous, floral		16	
1360	ethyl 3-phenylpropanoate (ethyl dihydrocinnamate)	floral	64	8	MS, odor, RI
1394	1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one (β-damascenone)	rose, floral, berry, sweet	64	1024	MS, odor, RI
1405	ethyl decanoate	fruity	2		MS, odor, RI
1411	3-methoxy-4-hydroxy-cyclohexane carbaldehyde (3-methoxy-4-hydroxybenzaldehyde, vanillin)	vanilla		256	MS, odor, RIL (*37*)
1470	5-hexyldihydro-2[3H]-furanone (γ-decalactone)	coconut	16	64	MS, odor, RI
1493	4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (β-ionone)	dry fruit	8	16	MS, odor, RI
1504	5-decanolide (δ-decalactone)[c]	peach	16	64	MS, odor, RIL (*37*)
1565	1,2,3-trimethoxy-5-allylbenzene (elemicin)	spicy, woody, sweet	4	2	MS, odor, RIL (*38*)
1751	benzyl benzene carboxylate (benzyl benzoate)	balsamic	4	8	MS, odor, RIL (*39*)
1892	unknown	sweet, woody, caramel	4	8	
1926	unknown	floral, wine, perfume		16	

[a] MS, mass spectral data; RIL, retention index from literature; RI, retention index from standards. [b] Retention index from the literature. [c] Tentative identification.

strawberry-like aroma note to fruits. In Oregon-grown Chickasaw, 2-ethyl-4-hydroxy-5-methyl-3(2H)-furanone rendered additional sweet, caramel notes (FD= 128), but it was not considered as an important odorant in Arkansas-grown fruit (FD = 8). The FD factors of δ-decalactone were close in the two samples (FD = 128 in Oregon, FD = 64 in Arkansas), while γ-decalactone showed somewhat higher FD factors in Arkansas (FD = 64, FD = 16 in Oregon).

Four other compounds were identified in berry samples from the two locations: 3-isopropyl-2-methoxypyrazine, eugenol, elemicin, and theaspirane B. Because none of these showed a FD factor higher than 16, they were not considered as important odorants. Some unknown compounds also showed up on two stationary phase columns. They could not be identified as they appeared in a very small quantity and coeluted with other compounds.

When comparing the numbers of odor active volatiles in each chemical class, the aroma compositions of the Chickasaw samples from two locations were quite similar. However, these odorants show various aroma impacts in the samples from the two regions. On the basis of FD factors (FD $\geq$ 1024), the aroma of Chickasaw grown in Oregon can be primarily attributed to six compounds: ethyl butanoate, linalool, methional, *trans,cis*-2,6-nonadienal, *cis*-1,5-octadien-3-one, and 2,5-dimethyl-4-hydroxy-3(2H)-furanone. Additionally, ethyl 2-methylpropanoate, methyl butanoate, ethyl hexanoate, 2,3-butanedione, α-pinene, limonene, and hexanal are also important volatiles in the Oregon-grown fruit (FD $\geq$ 512). In the samples from Arkansas, the most potent aromas were ethyl butanoate, linalool, methional, ethyl 2-methylbutanoate, β-damascenone, and geraniol. Furthermore, ethyl 2-methylpropanoate, *allo*-ocimene, *trans*-2-hexenal, and 2,5-dimethyl-4-hydroxy-3(2H)-furanone were detected as potent aroma compounds in Chickasaw grown in Arkansas (FD $\geq$ 512).

In conclusion, these results showed that flavor formation in Chickasaw blackberries was strongly influenced by their growing environment. The most potent aroma compounds in Oregon-grown Chickasaw are ethyl butanoate (fruity, apple-like), linalool (floral, perfume), methional (cooked potato), *trans,cis*-2,6-nonadienal (green, cucumber), *cis*-1,5-octadien-3-one (green, grass), and 2,5-dimethyl-4-hydroxy-3(2H)-furanone (sweet, strawberry-like), while in Arkansas-grown Chickasaw, they are ethyl butanoate, linalool, methional, ethyl 2-methylbutanoate (fruity), β-damascenone (rose-like, berry), and geraniol (sweet, rose-like). Although AEDA is a widely used screening method to identify the important odorants, there are many variations associated with human olfactometry. To further explain and identify the difference between samples of the same genotype grown in two different regions, quantitative studies are required.

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