JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

J. Agric. Food Chem. **2004,** *52,* 5155–5161 **5155**

Aroma Extract Dilution Analysis of cv. Meeker (*Rubus idaeus* L.) Red Raspberries from Oregon and Washington

KEITH KLESK,[†] MICHAEL QIAN,*,[†] AND ROBERT R. MARTIN[‡]

Department of Food Science & Technology, Oregon State University, 100 Wiegand Hall, Corvallis, Oregon 97331-6602, and Horticultural Crops Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture, 3420 Northwest Orchard Avenue, Corvallis, Oregon 97330

The aromas of cultivar Meeker red raspberry from Oregon and Washington were analyzed by aroma extract dilution analysis. Seventy-five aromas were identified [some tentatively (superscript T)] by mass spectrometry and gas chromatography−retention index; 53 were common to both, and 22 have not been previously reported in red raspberry. Twenty-one compounds had an equivalent odor impact in both: 2,5-dimethyl-4-hydroxy-3-(2H)-furanone, hexanal, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one, (*E*)-*β*-3,7-dimethyl-1,3,6-octatriene[T], 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane[T], 1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one, ethanoic acid, (*Z*)-3-hexenal[T], 3-methylmercaptopropionaldehyde, (*Z*)-3-hexenol, 2,6-dimethyl-2,7-octadien-6-ol, butanoic acid, ethyl 2-methylpropanoate, (*E*)-2-hexenal, hexyl formate[T], 2,3-butanedione, heptanal[T], thiacyclopentadiene[T], cyclohexane carbaldehyde[T], (*E*)-3,7-dimethyl-2,6-octadien-1-ol[T], and 4-(*p*-hydroxyphenyl)-2-butanone. Oregon Meeker had 14 odorants with higher flavor dilution (FD) factors than Washington Meeker: 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one[T], 1-octanol, 5-isopropyl-2-methylcyclohexa-1,3-diene[T], 7-methyl-3-methylene-1,6-octadiene[T], ethyl hexanoate, 3-methylbutyl acetate[T], ethyl propanoate, 4-(4-hydroxy-3-methoxyphenyl)-2-butanone[T], 2-methylbutanoic acid, 1-octen-3-ol, ethyl cyclohexane carboxylate[T], 2-methylthiacyclopentadiene[T], (*Z*)-3-hexenyl acetate[T], and 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-ol[T]. Washington Meeker had 16 odorants with higher FD factors than Oregon Meeker: 5-ethyl-3-hydroxy-4-methyl-2-(5H)-furanone[T], dimethyl sulfide[T], 2-ethyl-4-hydroxy-5-methyl-3-(2H)-furanone[T], 1-hexanol[T], ethyl 2-methylbutanoate, 3,7-dimethyl-1,6-octadien-3-yl acetate[T], methyl hexanoate, phenyl ethanoic acid[T], neo-allo-3,7-dimethyl-1,3,6-octatriene[T], 2-nonanone[T], 2-(4-methylcyclohex-3-enyl)propan-2-ol[T], phenylmethanol[T], 5-octanolide[T], 2-phenylethanol, 1-isopropyl-4-methylenebicyclo[3.1.0]hexane[T], and 2-undecanone.

KEYWORDS: Meeker; raspberry aroma; AEDA; GC/O; GC-MS

INTRODUCTION

Raspberries have been a food staple for hundreds of years (*1*). Raspberries are a popular food because of their flavor and nutritional content, and research reporting their significant health benefits has increased their popularity. Red raspberries contain high amounts of polyphenolics and antioxidants, compounds that combat cancer, age-related mental decline, and heart and circulatory disease (*2*−*7*). Red raspberries inhibit the human inflammatory response and associated pain by inhibiting the production of COX-I and COX-II enzymes (*8*, *9*). Raspberry seed oil may have cosmeceutical applications, as the oil has a skin protection factor of 25−50 and is a rich source of vitamin E and *ω*-3-fatty acids (*10*). Red raspberries also contain ellagic acid, a plant phenol with potent anticarcinogenic and antimutagenic properties (*4*, *11*, *12*).

The aroma of red raspberry has been studied worldwide for over 70 years. Volatile studies examined wild, hybrid, and multiple cultivars of red raspberry fresh fruit, juice, essential oils, or commercial products (*13*−*28*). Chemical and sensory studies were made on a single compound, the raspberry ketone (*13*), as well as comprehensive red raspberry volatile analyses (*14*, *17*−*28*). Two hundred thirteen volatiles have been identified in red raspberry (*28*, *29*), and 10 were suggested to be important to red raspberry aroma: 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one (α-ionone), 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (*β*-ionone), (*Z*)-3-hexenol, (*E*)-3,7-dimethyl-2,6-octadien-1-ol (geraniol), 2,6-dimethyl-2,7-octadien-6-ol (linalool), phenylmethanol (benzyl alcohol), 3-hydroxybutan-2-one (acetoin), ethanoic (acetic) and hexanoic acids, and 4-(*p*-hydroxyphenyl)-2-butanone (raspberry ketone) (*22*).

* To whom correspondence should be addressed. Tel: 541-737-9114. Fax: 541-737-1877. E-mail: michael.qian@oregonstate.edu.
[†] Oregon State University.
[‡] U.S. Department of Agriculture.

10.1021/jf0498721 CCC: $27.50
Published on Web 07/07/2004

In the United States, raspberries are grown primarily in Oregon and Washington, where the fruit has great economic importance. Ninety-seven percent of the raspberries grown in these states are the red variety, and 92% of red raspberry production are processed into a variety of food products (*30*). The red raspberry cultivar of choice in the Pacific Northwest is the Meeker. Since the early 1980s, Meeker has replaced the formerly dominant Willamette because of Meeker's superior characteristics: higher yields, good color and fruit firmness, machine harvestability, and higher sensorial quality (*31*). The demand for Meeker has stimulated research to further improve Meeker quality (*32*−*34*). The aroma analysis of Meeker red raspberry to date compared Meeker to other red varieties; no research examined the effects of geography on Meeker aroma. The purpose of this investigation was to identify, rank, and compare the odor active compounds of Oregon and Washington Meeker red raspberry using aroma extract dilution analysis (AEDA) and gas chromatography−mass spectrometry (GC-MS).

MATERIALS AND METHODS

Chemicals. The authentic aroma standards were obtained as follows: 1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one (*β*-damascenone) (Firmenich, Newark, NJ); butyl acetate, 1-methyl-4-isopropenylcyclohex-1-ene (limonene), and 2-undecanone (K&K Laboratories, Jamaica, NY); methyl hexanoate and 1-octanol (Eastman, Rochester, NY); acetic acid, *β*-ionone, butanoic acid, 2,5-dimethyl-4-hydroxy-3-(2*H*)-furanone (strawberry furanone), dimethyl disulfide, ethyl acetate, ethyl butanonate, ethyl hexanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, ethyl 2-methylpropanonate, ethyl propanoate, 4-allyl-2-methoxyphenol (eugenol), hexanal, (*E*)-2-hexenal, (*Z*)-3-hexenol, linalool, 2-methylbutanoic acid, nonanal, 1-octanol, 1-octen-3-ol, 1-octen-3-one, and 2-phenylethanol (phenethyl alcohol) (Aldrich Chemical Co. Inc., Milwaukee, WI); and 2,3-butanedione (diacetyl) and 3-methylmercaptopropionaldehyde (methional) (Sigma Chemical Co., St. Louis, MO).

Red Raspberry Samples. Meeker red raspberries from Aurora, Oregon were hand harvested from 4 year old plants in June 2003. Lynden, Washington fruit was machine harvested from 2 year old plants in July 2003. The plants were grown under standard horticultural practices, and the fruit was harvested from all sections of the entire plants. For each location, the fruit from multiple plants was pooled. Immediately after the fruit was harvested, the fruits were transported on ice to the laboratory, where they were stored at −23 °C. The samples had been frozen for 3 months when analyzed.

Extraction of Volatile Compounds. For both the Oregon and the Washington Meeker samples (each a total of 2 kg), 500 g of frozen raspberries was thawed overnight (15 h) at 1.1 °C. The thawed berries, with icy and solid centers, were combined with 50 g of NaCl and 5 g of $CaCl_2$ in a commercial blender and blended by pulsing for a total of 3 min at high speed. Calcium chloride was added to inhibit the enzyme activity as described by Buttery et al. (*35*). To avoid strong emulsions between sample and solvent, the puréed fruit was passed through a commercial stainless steel fine mesh strainer to remove the seeds. The seed pulp was batch extracted three times with freshly distilled pentane: diethyl ether (1:1 v/v) while the seedless purée was extracted three times in a separatory funnel. The extracts were combined to yield a total volume of 300 mL. The extract volume was reduced with a flow of nitrogen to 150 mL, and nonvolatiles were removed using solvent-assisted flavor evaporation (SAFE) at 50 °C under vacuum according to the method proposed by Engel et al. (*36*). The organic SAFE extract was dried with anhydrous Na_2SO_4 and concentrated to 1 mL using a flow of nitrogen. Before gas chromatography/olfactometry (GC/O) analysis, the extract was reduced to its final volume of 0.2 mL with a flow of nitrogen.

GC/O Analysis. The analysis was performed using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector (FID) and a sniffing port. The 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). The injector and detector temperatures were 250 °C. The helium column flow rate was 2.5 mL/min, and the 2 μL sample injections were splitless. 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). The retention indices (RI) were estimated in accordance with a modified Kovats method (*37*).

AEDA. Flavor dilution (FD) factors for the odor active compounds in each Meeker sample were determined using AEDA (*38*, *39*). The concentrated samples were serially diluted with 1:1 (v/v) pentane:diethyl ether (1 + 1). GC/O with two panelists experienced in AEDA and with raspberry fruit was then performed with 2 μL injections of original samples and diluted extracts.

GC-MS Analysis. Analysis of the original concentrated AEDA samples was performed using an Agilent 6890 gas chromatograph equipped with an Agilent 5973 Mass Selective Detector (MSD). 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 two fused silica capillary columns used in the GC/O analysis. The helium column flow rate was 2.5 mL/min, and the 2 μL sample injections were splitless. The oven temperature was programmed as for the GC/O 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 at 5.27 scans/s, at an ionization voltage of 70 eV. The RIs were estimated in accordance with a modified Kovats method (*37*). Compound identifications were made by comparing aromas with authentic standards and Kovats RIs, RIs reported in the literature, and/or mass spectral data from the Wiley 275.L (G1035) Database (Agilent Technologies, Inc.).

Supplemental AEDA of the Raspberry Ketone. The complexities of the samples' volatile profiles precluded AEDA evaluation of 4-(*p*-hydroxyphenyl)-2-butanone (raspberry ketone) on the Stabilwax column, as the GC temperature program required did not elute the compound before completion of the GC/O run. Therefore, AEDA runs were performed to evaluate only the raspberry ketone. An HP-Wax column [30 m × 0.25 mm i.d. cross-linked poly(ethylene glycol), 0.5 μm film thickness, Agilent] was installed in the GC-MS equipment previously mentioned. The column effluent was split 1:1 (by volume) into the MSD and a heated sniffing port with a fused silica outlet splitter (Alltech Associates, Inc.). The helium column flow rate was 2.5 mL/min, and the 2 μL sample injections were splitless. Instrumental conditions were identical to those used in the GC-MS analysis previously described, except that the oven temperature was programmed for a 2 min hold at 40 °C, then 40−210 °C at 12 °C/min, then 210−230 °C at 2 °C/min (15 min hold). AEDA was performed on both Meeker samples as previously discussed.

RESULTS AND DISCUSSION

Tables 1 and **2** list Oregon and Washington Meeker red raspberry volatiles separated with polar and nonpolar columns. On the polar column, a total of 59 aroma compounds were detected, with 53 of them identified. On the nonpolar column, 53 aromas were detected, and 48 of them were identified. Among these identified aromas, 27 were detected on the polar column only, while 22 were detected on the nonpolar column only. Combined data (**Table 3**) show that 75 odor active volatiles were detected, and 53 were common to both cultivars. Oregon Meeker contained 61 of 75 volatiles, and Washington Meeker contained 67 of 75 volatiles. Twenty-two of the 75 have not been previously reported in red raspberry (*28*, *29*). This relatively large number of new volatiles is probably due to the extraction and analytical methods used.

A FD factor is a relative measure; it is the ratio of an odorant's concentration in an initial GC/O extract to its concentration in

Table 1. AEDA of Oregon and Washington Red Raspberry cv. Meeker (Stabilwax Column)

RI	compound[a]	aroma descriptors this study	ID basis[b]		FD factors	
			OR	WA	OR	WA
904	ethyl acetate	sweet, berry	ND	MS, RI		4
924	ethyl propanoate*	sweet, floral, cherry	ND	RI		4
982	propyl acetate*[T]	sweet, fruity	RIL	ND	1	
999	2,3-butanedione (diacetyl)	buttery	RI	ND	1	
1034	thiacyclopentadiene (thiophene)*[T]	sulfury, garlic bologna	RIL	RIL	1	32
1034	unknown	fruity, berry, woody			32	
1047	ethyl butanoate	juicy, fruity, wine-like	RI	MS, RI	2	16
1052	ethyl 2-methylbutanoate	fruity, sweet, berry	RI	RI	2	128
1080	butyl acetate*	grassy, berry, sweet, fruity	RI	ND	4	
1103	hexanal	green, fruity, cut grass	MS, RI	MS, RI	256	16
1125	6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane (β-pinene)[T]	cut grass, piney, pungent	MS, RIL	ND	1	
1125	3-methylbutyl acetate*[T]	floral, fruity, sweet	RIL	RIL	128	16
1143	unknown	green, fruity,,juicy, sweet			64	
1160	(*Z*)-3-hexenal[T]	grassy, brassy, resin	MS, RIL	MS, RIL	128	256
1165	ethyl 2-butenoate*[T]	green, apple, sweet, fruity	RIL	ND	8	
1184	5-isopropyl-2-methylcyclohexa-1,3-diene (α-phellandrene)[T]	green, cut grass	MS, RIL	MS, RIL	2048	1
1204	methyl hexanoate	sweet, berry, fruity, green	ND	RI		128
1219	1-methyl-4-isopropenylcyclohex-1-ene (limonene)	floral, green, sweet	MS, RI	MS, RI	2	1
1231	1-isopropyl-4-methylenebicyclo[3.1.0]hexane (sabinene)[T]	green, pungent, green leaf	MS, RIL	MS, RIL	2	16
1244	(*E*)-2-hexenal	floral, fruity, sweet	MS, RI	ND	32	
1251	ethyl hexanoate	fruity, floral, sweet, juicy	MS, RI	MS, RI	128	32
1267	1-isopropyl-4-methyl-1,4-cyclohexadiene (γ-terpinene)[T]	musty, barn-like	MS, RIL	ND	4	
1317	1-octen-3-one	mushroom	RI	RI	2	2
1338	(*Z*)-3-hexenyl acetate[T]	berry, sweet, fruity, green	RIL	MS, RIL	16	4
1371	hexyl formate*[T]	sweet, berry, fruity, woody	RIL	MS, RIL	64	64
1371	1-hexanol[T]	floral, sweet, watermelon	ND	MS, RIL		4
1406	(*Z*)-3-hexenol	pungent, piney, green, resin	MS, RI	MS, RI	64	128
1413	2-nonanone[T]	sweet, woody, berry, fruity	ND	MS, RIL		64
1444	ethyl octanoate*[T]	fruity	RIL	ND	4	
1461	ethanoic acid (acetic acid)	pungent, sour, vinegar	MS, RI	MS, RI	256	256
1485	3-methylmercaptopropionaldehyde (methional)*	baked potato, french fries	RI	RI	16	8
1520	unknown	floral, woody			64	128
1535	2-nonanol*[T]	green, watermelon	MS, RIL	MS, RIL	8	8
1564	2,6-dimethyl-2,7-octadien-6-ol (linalool)	floral, citrus, grassy	RI	RI	1	8
1576	1-octanol	tart raspberry, herbal, floral	MS, RI	MS, RI	2048	128
1609	(*E*)-α-2,6-dimethyl-6-(4-methylpent-3-enyl)bicyclo[3.1.1]-hept-2-ene ((*E*)-α-bergamotene)*[T]	cucumber, sweet	ND	RIL		8
1623	2-undecanone	floral, green, citrus	MS, RI	MS, RI	4	16
1650	butanoic acid	sour, pungent, cheesy	MS, RI	MS, RI	64	32
1652	unknown	sweet, berry, fruity, woody	ND			128
1703	2-methylbutanoic acid	pungent, sour, cheesy	RI	RI	16	8
1751	4-ethylbutanolide (γ-hexalactone)*[T]	sweet, berry, caramel	ND	MS		2
1759	unknown	fruity, herbal, tea, floral		ND	32	
1826	unknown	fruity, woody, sweet	ND			32
1852	1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one (β-damascenone)	sweet, perfume, floral fruity	RI	RI	512	512
1869	(*E*)-3,7-dimethyl-2,6-octadien-1-ol (geraniol)[T]	sweet, fruity, floral, green	RIL	MS, RIL	4	16
1889	4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one (α-ionone)[T]	rose, floral, sweet, perfume	MS, RIL	MS, RIL	2048	8
1898	phenylmethanol (benzyl alcohol)[T]	floral, perfume, raspberry	MS, RIL	MS, RIL	2	16
1923	4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-ol (α-ionol)*[T]	hot tea, lemon-sweet, violet	MS	MS	16	4
1948	2-phenylethanol (phenylethyl alcohol)	hot tea, floral	ND	RI		2
1975	4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (β-ionone)[T]	floral, perfume, raspberry	MS, RI	MS, RI	2048	2048
1991	4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-butan-2-ol (dihydro-β-ionol)*[T]	perfume, juicy fruit	MS	MS	1	2
2014	5-octanolide (δ-octalactone)[T]	sweet	ND	MS		16
2056	2,5-dimethyl-4-hydroxy-3-(2H)-furanone (strawberry furanone)	cooked strawberry	MS, RI	MS, RI	2048	1024
2067	2-ethyl-4-hydroxy-5-methyl-3-(2H)-furanone*[T]	cooked raspberry	ND	RIL		1024
2223	4,5-dimethyl-3-hydroxy-2-(5H)-furanone (sotolon)[T]	sweet, floral, cooked bramble	RIL	RIL	2	2
2243	5-decanolide (δ-decalactone)[T]	buttery caramel, floral	MS	ND	4	
2244	5-ethyl-3-hydroxy-4-methyl-2-(5H)-furanone (maple furanone)*[T]	floral, sweet, raspberry	RIL	RIL	128	2048
2514	4-oxo-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (4-oxo-β-ionone)*[T]	sweet, fruity, berry	MS	ND	4	
3000	4-(*p*-hydroxyphenyl)-2-butanone[TW] (raspberry ketone)	fruity, raspberry, woody	MS, RIL	MS, RIL	4	8

[a] *, not previously reported in red raspberry; T, tentative identification; W, HP-Wax RI. [b] MS, mass spectral data; RIL, retention index (literature); RI, retention index (standards); ND, not detected.

Table 2. AEDA of Oregon and Washington Red Raspberry cv. Meeker (DB-5 Column)

RI	compound[a]	aroma descriptors this study	ID basis[b]		FD factors	
			OR	WA	OR	WA
517	dimethyl sulfide*[T]	smelly, sulfury, gas line leak	RIL	RIL	8	1024
544	2,3-butanedione (diacetyl)	diacetyl, dairy	RI	RI	32	32
582	ethanoic acid (acetic acid)	vegetal, pungent, sour	MS, RI	MS, RI	64	128
661	thiacyclopentadiene (thiophene)*[T]	green, resin, plastic	RIL	ND	32	
685	propyl acetate*[T]	sweet, fruity	RIL	RIL	1	4
698	ethyl propanoate*	sweet, fruity, green	RIL	RIL	64	8
720	dimethyl disulfide*	gas line leak, garlic bologna	RI	RI	8	2
750	ethyl 2-methylpropanoate*	fruity, banana, sweet, juicy	RI	RI	64	64
767	2-methylthiacyclopentadiene (2-methylthiophene)*[T]	garlic bologna, vegetal	RIL	ND	32	
790	unknown	spicy, pungent, floral, fruity			4	32
798	hexanal	cut grass, green, apple	MS, RI	MS, RI	2048	2048
812	butanoic acid	pungent, cheesy, rancid, sour	MS, RI	MS, RI	64	64
815	unknown	sweet, fruity	ND			64
832	ethyl 2-methyl/3-methylbutanoate	sweet, fruity, juicy	ND	RI		32
851	(*E*)-2-hexenal	fruity, floral, green	MS, RI	MS, RI	64	64
857	2-methylbutanoic acid[T]	pungent, chemical, sour	RIL	MS, RIL	64	8
884	1-hexanol[T]	sweet, fruity, woody	ND	RIL		256
890	2-heptanone[T]	green, berry, fruity	ND	MS, RIL		4
892	heptanal[T]	rubber, green, resin, plastic	RIL	RIL	32	16
908	3-methylmercaptopropionaldehyde (methional)*	french fries, baked potato	RI	RI	256	128
931	methyl hexanoate[T]	fruity, cinnamon, spicy, floral	RIL	RIL	1	8
939	2,6,6-trimethylbicyclo[3.1.1]hept-2-ene (α-pinene)[T]	herbal, tea, spicy	MS, RIL	MS, RIL	4	8
965	cyclohexane carbaldehyde (benzaldehyde)[T]	floral, fruity, melon, spicy	MS, RIL	MS, RIL	16	16
983	6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane (β-pinene)[T]	cut grass, piney, pungent	MS, RIL	MS, RIL	2048	1024
983	1-octen-3-ol*	mushroom	RI	ND	64	
992	7-methyl-3-methylene-1,6-octadiene (β-myrcene)[T]	vegetal, resin, piney, pungent	MS, RIL	MS, RIL	1024	256
1006	ethyl hexanoate	floral, watermelon, berry	RI	RI	32	32
1011	5-isopropyl-2-methylcyclohexa-1,3-diene (α-phellandrene)[T]	spicy, incense	ND	MS, RIL		2
1043	(*E*)-β-3,7-dimethyl-1,3,6-octatriene ((*E*)-β-ocimene)[T]	tart raspberry, herbal, floral	RIL	RIL	2048	1024
1052	phenylmethanol (benzyl alcohol)[T]	fruity, woody, floral	RIL	MS, RIL	2	16
1076	2,5-dimethyl-4-hydroxy-3-(2H)-furanone (strawberry furanone)	sweet, berry, fruity	ND	MS, RI		512
1103	nonanal	floral, berry, fruity, sweet	RI	RI	2	4
1111	2,6-dimethyl-2,7-octadien-6-ol (linalool)	fresh, cucumber floral	RI	RI	64	128
1121	2-phenylethanol (phenethyl alcohol)	fruity, citrus, floral	RI	RI	8	16
1149	neo-allo-3,7-dimethyl-1,3,6-octatriene (neo-allo-ocimene)*[T]	fruity, floral, sweet	ND	RIL		64
1187	ethyl cyclohexane carboxylate (ethyl benzoate)[T]	herbal, fruity, spicy, floral	RIL	RIL	32	2
1189	2-(4-methylcyclohex-3-enyl)propan-2-ol (α-terpineol)[T]	floral, sweet	RIL	RIL	16	64
1189	unknown	fruity, floral, sweet			64	
1217	5-ethyl-3-hydroxy-4-methyl-2-(5H)-furanone (maple furanone)*[T]	sweet, cooked fruit, floral	RIL	RIL	16	128
1248	3,7-dimethyl-1,6-octadien-3-yl acetate (linalyl acetate)[T]	grass, berry, woody, sweet	ND	RIL		128
1248	(*E*)-3-phenyl-2-propen-1-ol (cinnamic alcohol)[T]	pungent, fruity, cinnamon	ND	RIL		2
1256	phenyl ethanoic acid (phenylacetic acid)[T]	sweet, berry, fruity, woody	ND	RIL		128
1290	(*E*)-3,7-dimethyl-2,6-octadien-1-ol (geraniol)[T]	sweet, cooked fruit, berry	RIL	RIL	16	8
1307	unknown	sweet, warm spices, fruity			32	256
1324	unknown	caramelized fruit, citrus			32	32
1366	4-allyl-2-methoxyphenol (eugenol)	sweet, spice, acrid	RI	MS, RI	4	2
1370	1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)–2-buten-1-one (β-damascenone)[T]	sweet, cooked pineapple	RIL	RIL	1	4
1406	3-methoxy-4-hydroxy-cyclohexane carbaldehyde (3-methoxy-4-hydroxybenzaldehyde, vanillin)[T]	sweet, spicy, floral	ND	MS, RIL		4
1437	4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one (α-ionone)[T]	sweet, cooked fruit, perfume	MS, RIL	MS, RIL	2	4
1452	(3*E*)-4-(2,6,6-trimethylcyclohex-1-enyl)-3-buten-2-one (dihydro-β-ionone)[T]	floral, pungent, citrus	ND	MS		1
1496	4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (β-ionone)[T]	woody, sweet, citrus, floral	MS, RIL	MS, RIL	1	4
1560	4-(*p*-hydroxyphenyl)-2-butanone[T] (raspberry ketone)	perfume, hot tea, woody	ND	MS, RIL		2
1656	4-(4-hydroxy-3-methoxyphenyl)-2-butanone (zingerone)[T]	sweet, fruity, cooked pears	MS, RIL	MS, RIL	64	2

[a] *, not previously reported in red raspberry; T, tentative identification. [b] MS, mass spectral data; RIL, retention index (literature); RI, retention index (standards); ND, not detected.

the most dilute extract that still allows detection (*39*). Although FD factors do not conclusively determine that one sample contains more of a given aroma compound than another, they are proportional to the compound's odor activity value (OAV), the ratio of the aroma concentration to its odor threshold in air (*39*). Because of this proportionality, relative quantitative comparisons of individual odorants between samples may be made through "comparative AEDA", using FD factors obtained from samples identically extracted and analyzed (*39*).

Tables 1 and **2** were combined to generate a comparative AEDA of the most significant odor active volatiles in the two red raspberry samples (FD $\geq$ 16, FD factors $\pm$ one dilution are considered equivalent); 4-(*p*-hydroxyphenyl)-2-butanone (raspberry ketone) is also included, as it is described as the major character impact compound in raspberry flavor (*40*). Twenty-one compounds had potent, equivalent odor impact in both Meeker samples. The most intense compounds included the strawberry furanone, hexanal, β-ionone, (*E*)-β-3,7-dimethyl-1,3,6-octatriene (*E*-β-ocimene), 1-octanol, and 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane (β-pinene) (FD = 2048); β-damascenone (FD = 512); acetic acid, (*Z*)-3-hexenal, and methional (FD = 256); (*Z*)-3-hexenol and linalool (FD = 128); butanoic

Table 3. AEDA Summary of Oregon and Washington Red Raspberry cv. Meeker

sample	compound[a]	sample	compound[a]
		acids	
both	ethanoic acid (acetic acid)	both	2-methylbutanoic acid
both	butanoic acid	WA	phenyl ethanoic acid (phenylacetic acid)[T]
		alcohols	
both	phenylmethanol (benzyl alcohol)[T]	both	2,6-dimethyl-2,7-octadien-6-ol (linalool)
WA	(*E*)-3-phenyl-2-propen-1-ol (cinnamic alcohol)[T]	both	2-nonanol*[T]
both	(*E*)-3,7-dimethyl-2,6-octadien-1-ol (geraniol)[T]	both	1-octanol
WA	1-hexanol[T]	OR	1-octen-3-ol*
both	(*Z*)-3-hexenol	both	2-phenylethanol (phenethyl alcohol)
both	4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-ol (α-ionol)*[T]	both	2-(4-methylcyclohex-3-enyl)propan-2-ol (α-terpineol)[T]
both	4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-butan-2-ol (dihydro-β-ionol)*[T]		
		aldehydes	
both	cyclohexane carbaldehyde (benzaldehyde)[T]	both	(*E*)-2-hexenal
both	heptanal[T]	both	3-methylmercaptopropionaldehyde (methional)*
both	hexanal	WA	3-methoxy-4-hydroxy-cyclohexane carbaldehyde (3-methoxy-4-hydroxybenzaldehyde, vanillin)[T]
both	(*Z*)-3-hexenal[T]	both	nonanal
		esters	
OR	butyl acetate*	OR	ethyl octanoate*[T]
WA	ethyl acetate	both	ethyl propanoate*
both	ethyl cyclohexane carboxylate (ethyl benzoate)[T]	both	(*Z*)-3-hexenyl acetate[T]
both	ethyl butanoate	both	hexyl formate*[T]
OR	ethyl 2-butenoate*[T]	WA	3,7-dimethyl-1,6-octadien-3-yl acetate (linalyl acetate)[T]
both	ethyl hexanoate	both	3-methylbutyl acetate*[T]
both	ethyl 2-methylbutanoate	both	methyl hexanoate
both	ethyl 2-methylpropanoate*	both	propyl acetate*[T]
		furans	
both	2,5-dimethyl-4-hydroxy-3-(2H)-furanone (strawberry furanone)	WA	2-ethyl-4-hydroxy-5-methyl-3-(2H)-furanone*[T]
both	4,5-dimethyl-3-hydroxy-2-(5H)-furanone (sotolon)[T]	both	5-ethyl-3-hydroxy-4-methyl-2-(5H)-furanone (maple furanone)*[T]
		hydrocarbons	
WA	(*E*)-α-2,6-dimethyl-6-(4-methylpent-3-enyl)bicyclo[3.1.1]-hept-2-ene ((*E*)-α-bergamotene)*[T]	both	2,6,6-trimethylbicyclo[3.1.1]hept-2-ene (α-pinene)[T]
both	1-methyl-4-isopropenylcyclohex-1-ene (limonene)	both	6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane (β-pinene)[T]
both	7-methyl-3-methylene-1,6-octadiene (β-myrcene)[T]	both	5-isopropyl-2-methylcyclohexa-1,3-diene (α-phellandrene)[T]
both	(*E*)-β-3,7-dimethyl-1,3,6-octatriene ((*E*)-β-ocimene)[T]	both	1-isopropyl-4-methylenebicyclo[3.1.0]hexane (sabinene)[T]
WA	neo-allo-3,7-dimethyl-1,3,6-octatriene (neo-allo-ocimene)*[T]	OR	1-isopropyl-4-methyl-1,4-cyclohexadiene (γ-terpinene)[T]
		ketones	
both	2,3 butanedione (diacetyl)	both	4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one (α-ionone)[T]
both	1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one (β-damascenone)	both	4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (β-ionone)
WA	(3*E*)-4-(2,6,6-trimethylcyclohex-1-enyl)-3-buten-2-one (dihydro-β-ionone)[T]	WA	2-nonanone[T]
WA	2-heptanone	both	1-octen-3-one
both	4-(4-hydroxy-3-methoxyphenyl)-2-butanone (zingerone)[T]	OR	4-oxo-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (4-oxo-β-ionone)*[T]
both	4-(*p*-hydroxyphenyl)-2-butanone (raspberry ketone)	both	2-undecanone
		lactones	
OR	5-decanolide (δ-decalactone)[T]	WA	5-octanolide (δ-octalactone)[T]
WA	4-ethylbutanolide (γ-hexalactone)[T]		
		phenols	
both	4-allyl-2-methoxyphenol (eugenol)		
		sulfur	
both	dimethyl disulfide*	OR	2-methylthiacyclopentadiene (2-methylthiophene)*[T]
both	dimethyl sulfide*[T]	both	thiacyclopentadiene (thiophene)*[T]

[a] *, not previously reported in red raspberry; T, tentative identification.

acid, ethyl 2-methylpropanoate, (*E*)-2-hexenal, and hexyl formate (FD = 64); diacetyl, heptanal, and thiacyclopentadiene (thiophene) (FD = 32); cyclohexane carbaldehyde (benzaldehyde) and geraniol (FD = 16); and raspberry ketone (FD = 8).

Ranging from 2 to 11 orders of magnitude, Oregon Meeker had 14 odorants with higher FD factors than Washington Meeker. These compounds included α-ionone, 1-octanol, and 5-isopropyl-2-methylcyclohexa-1,3-diene (α-phellandrene) (FD = 2048, Washington FD = 8, 128, and 1, respectively); 7-methyl-3-methylene-1,6-octadiene (β-myrcene) (FD = 1024, Washington FD = 256); ethyl hexanoate and 3-methylbutyl acetate (FD = 128, Washington FD = 32 and 16, respectively); ethyl propanoate, 4-(4-hydroxy-3-methoxyphenyl)-2-butanone (zingerone), 2-methylbutanoic acid, and 1-octen-3-ol (FD = 64, Washington FD = 8, 2, 8, and not detected (ND), respectively); ethyl cyclohexane carboxylate (ethyl benzoate) and 2-methylthiacyclopentadiene (2-methylthiophene) (FD = 32, Washington FD = 2 and ND, respectively); and (*Z*)-3-hexenyl acetate and 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-ol (α-ionol) (FD = 16, Washington FD = 4).

Ranging from 3 to 7 orders of magnitude, Washington Meeker had 16 odorants with higher FD factors than Oregon Meeker. These compounds were 5-ethyl-3-hydroxy-4-methyl-2-(5H)-furanone (maple furanone) (FD = 2048, Oregon FD = 128); dimethyl sulfide and 2-ethyl-4-hydroxy-5-methyl-3-(2H)-furanone (FD = 1024, Oregon FD = 8 and ND, respectively);

1-hexanol (FD = 256, Oregon FD = ND); ethyl 2-methylbutanoate, 3,7-dimethyl-1,6-octadien-3-yl acetate (linalyl acetate), methyl hexanoate, and phenylethanoic acid (phenylacetic acid) (FD = 128, Oregon FD = 2, ND, ND, and ND, respectively); neo-allo-3,7-dimethyl-1,3,6-octatriene (neo-allo-ocimene), 2-nonanone, and 2-(4-methylcyclohex-3-enyl)propan-2-ol (α-terpineol) (FD = 64, Oregon FD = ND, ND, and 16, respectively); and benzyl alcohol, 5-octanolide (δ-octalactone), phenylethyl alcohol, 1-isopropyl-4-methylenebicyclo[3.1.0]-hexane (sabinene), and 2-undecanone (FD = 16, Oregon FD = 2, ND, 8, 2, and 4, respectively).

Overall, the red raspberry samples have comparable compound types and numbers, and 50 of 75 identified volatiles are potent odorants as defined previously. Of the 10 aroma compounds suggested to be important to red raspberry (*22*), this study identified eight; acetoin and hexanoic acid were not detected. Six of the eight identified compounds were found in both Oregon and Washington Meeker red raspberry, at an equal sample odor potency: β-ionone, acetic acid, linalool, (*Z*)-3-hexenol, geraniol, and raspberry ketone. Interestingly, raspberry ketone, described as the primary character impact compound in raspberry (*16*, *40*), was the only compound of the 10 considered important to raspberry aroma with a "nonpotent" FD factor (FD = 8). On the basis of FD factors, Oregon Meeker contained 3 orders of magnitude more α-ionone than the Washington Meeker, while the Washington Meeker had an order of magnitude more benzyl alcohol than that of Oregon Meeker. Some of the prominent odor impact differences of the compounds in Oregon or Washington Meeker red raspberry, for example, α-ionone or maple furanone, may be the result of growth and cultivation differences between the fruit (*14*, *16*), while others, for example, 1-octen-3-ol or benzyl alcohol, as well as the "low" impact raspberry ketone, may be due to odorant physical or chemical degradation losses during isolation or to aroma perception gaps, variables inherent in any olfactory screening procedure, including AEDA (*16*, *41*).

Because the aroma profile of a food is, among others, a function of volatile concentrations and odor thresholds, it is prudent to correct for the implicit simplifications of AEDA. While comparative AEDA is useful to quantify and compare relatively a compound's odor impact in different samples, the method does not give an unambiguous comparison of the true odor impact of different compounds within a sample. True odor impact is better measured using an OAV, the ratio of an odorant concentration to its odor threshold in air (*39*). To confirm and further refine the differences in potent odorants between the Oregon and the Washington Meeker red raspberry reported here, chemical quantification of these potent odorants and generation of their OAVs should be performed.

LITERATURE CITED

(1) Bowling, B. L. Brambles. In *The Berry Grower's Companion*; Timber Press: Portland, Oregon, 2000; p 94.

(2) Kalt, W.; Forney, C. F.; Martin, A.; Prior, R. L. Antioxidant capacity, vitamin C, phenolics, and anthocyanins after fresh storage of small fruits. *J. Agric. Food Chem.* **1999**, *47*, 4638−4644.

(3) Ming, L.; Li, X. Q.; Weber, C.; Lee, C. Y.; Brown, J.; Liu, R. H. Antioxidant and antiproliferative activities of raspberries. *J. Agric. Food Chem.* **2002**, *50*, 2926−2930.

(4) Rommel, A.; Wrolstad, R. E.; Durst, R. W. Red raspberry phenolic. Influences of processing, variety, and environmental factors. In *Phenolic Compounds in Food and Their Effects on Health Volume I. Analysis, Occurrence, and Chemistry*; Ho, C., Lee, C., Huang, M., Eds.; Oxford University Press: New York, New York, 1992; pp 259−286.

(5) Wada, L.; Ou, B. Antioxidant activity and phenolic content of Oregon caneberries. *J. Agric. Food Chem.* **2002**, *50*, 3495−3500.

(6) Wang, S. Y.; Lin, H. Antioxidant activity in fruits and leaves of blackberry, raspberry, and strawberry varies with cultivar and developmental stage. *J. Agric. Food Chem.* **2000**, *48*, 140−146.

(7) Weber, C.; Liu, R. H. Antioxidant capacity and anticancer properties of red raspberry. *Acta Hortic.* **2002**, *585*, 451−457.

(8) Seeram, N. P.; Momin, R. A.; Nair, M. G.; Bourquin, L. D. Cyclooxygenase inhibitory and antioxidant cyanidin glycosides in cherries and berries. *Phytomedicine* **2001**, *8*, 362−369.

(9) Huss, U.; Ringbom, T.; Perera, P.; Bohlin, L.; Vasänge, M. Screening of ubiquitous plant constituents for COX-2 inhibition with a scintillation proximity based assay. *J. Nat. Prod.* **2002**, *65*, 1517−1521.

(10) Oomah, B. D.; Ladet, S.; Godfrey, D. V.; Liang, J.; Girard, B. Characteristics of raspberry (*Rubus idaeus* L.) seed oil. *Food Chem.* **2000**, *69*, 187−193.

(11) Will, F.; Dietrich, H.; Schnell, U. Ellagic acid concentrations in raspberry liqueurs, purees, juices, and concentrates. *Fruit Process.* **1999**, *9*, 127−130.

(12) Barch, D. H.; Rundhaugen, L. M.; Stoner, G. D.; Pillay, N. S.; Rosche, W. A. Structure−function relationships of the dietary anticarcinogen ellagic acid. *Carcinogenesis* **1996**, *17*, 265−269.

(13) Borejsza-Wysocki, W.; Goers, S. K.; McArdle, R. N.; Hrazdina, G. (*p*-Hydroxyphenyl) butan-2-one levels in raspberries determined by chromatographic and organoleptic methods. *J. Agric. Food Chem.* **1992**, *40*, 1176−1177.

(14) Casabianca, H.; Graff, J. B. Enantiomeric and isotopic analysis of flavor compounds of some raspberry cultivars. *J. Chromatogr. A* **1994**, *684*, 360−365.

(15) De Ancos, B.; Ibanez, E.; Reglero, G.; Pilar, C. M. Frozen storage effects on anthocyanins and volatile compounds of raspberry fruit. *J. Agric. Food Chem.* **2000**, *48*, 873−879.

(16) Forney, C. F. Horticultural and other factors affecting aroma volatile composition of small fruit. *HortTechnology* **2001**, *11*, 529−538.

(17) Guichard, E.; Issanchou, S. Extraction of volatile compounds from raspberry by different methods. Application of principle component analysis to gas chromatographic data. *Sci. Aliments* **1983**, *3*, 427−438.

(18) Herrmann, K. The flavor compounds of fruit. V. berries (without strawberries). *Erwerbsobstbau* **1992**, *34*, 168−172.

(19) Honkanen, E.; Hirvi, T. The Flavour of Berries. In *Food Flavours Part C. The Flavour of Fruits*; Morton, I. D., Macleod, A. J., Eds.; Elsevier Science Publishers B. V.: New York, New York, 1990; pp 147−158.

(20) Honkanen, E.; Pyysalo, T.; Hirvi, T. The aroma of Finnish wild raspberries, Rubus idaeus, L. *Z. Lebensm. Unters. Forsch.* **1980**, *171*, 180−182.

(21) Larsen, M.; Poll, L. Odor thresholds of some important aroma compounds in raspberries. *Z. Lebensm. Unters. Forsch.* **1990**, *191*, 129−131.

(22) Larsen, M.; Poll, L.; Callesen, O.; Lewis, M. Relations between the content of aroma compounds and the sensory evaluation of 10 raspberry varieties (*Rubus idaeus* L). *Acta Agric. Scand.* **1991**, *41*, 447−454.

(23) Mestres, R.; Soulie, J. Identification of raspberry flavor by gas chromatography. *Trav. Soc. Pharm. Montpellier.* **1965**, *25*, 239−255 (in French).

(24) Renner, R.; Hartmann, U. Aroma substances in raspberry essence and their evaluation. *Lebensmittelchem. Gerichtl. Chem.* **1985**, *39*, 30−32 (in German).

(25) Shamaila, M.; Skura, B.; Daubeny, H.; Anderson, A. Sensory, chemical and gas chromatographic evaluation of five raspberry cultivars. *Food Res. Int.* **1993**, *26*, 443−449.

(26) Winter, M.; Enggist, P. Aromas. 17. Raspberry aroma. IV. *Helv. Chim. Acta* **1971**, *54*, 1891−1898 (in French).

(27) Wustenfeld, H.; Luckow, C. Evaluation of raspberry juices. *Z. Unters. Lebensm.* **1931**, *61*, 341−345 (in German).

(28) Roberts, D. D.; Acree, T. E. Effects of heating and cream addition on fresh raspberry aroma using a retronasal aroma simulator and gas chromatography olfactometry. *J. Agric. Food Chem.* **1996**, *44*, 3919−3925.

(29) Boelens, M. H. Raspberry (*Rubus idaeus* L.). In *Volatile Compounds in Food Database*; Boelens, M. H., Ed.; Boelens Aroma Chemical Information Service: Huizen, The Netherlands, 1996−1999.

(30) Garibay, R. *Washington 2002 Berry Report*; Washington Agricultural Statistics Service: January 27, 2003.

(31) Martin, R. R. Raspberry viruses in Oregon, Washington, and British Columbia. *Acta Hortic.* **1999**, *505*, 259−262.

(32) Burrows, C.; Moore, P. P. Genotype x environment effects on raspberry fruit quality. *Acta Hortic.* **2002**, *585*, 467−473.

(33) Martin, R. R.; Mathews, H. Engineering resistance to raspberry bushy dwarf virus. *Acta Hortic.* **2001**, *551*, 33−37.

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

(35) Buttery, R. G.; Teranishi, R.; Ling, L. C. Fresh tomato aroma volatiles: a quantitative study. *J. Agric. Food Chem.* **1987**, *35*, 540−544.

(36) Engel, W.; Bahr, W.; Schieberle, P. Solvent assisted flavour evaporation—a new and versatile technique for the careful and direct isolation of aroma compounds from complex food matrixes. *Z. Lebensm. Unters. Forsch.* **1999**, *209*, 237−241.

(37) Van den Dool, H.; Kratz, P. D. A generalization of the retention index system including linear temperature programmed gas−liquid partition chromatography. *J. Chromatogr.* **1963**, *11*, 463−471.

(38) Schieberle, P.; Grosch, W. Evaluation of the flavour of wheat and rye bread crusts by aroma extract dilution analysis. *Z. Lebensm. Unters. Forsch.* **1987**, *185*, 111−113.

(39) Grosch, W. Review: Determination of potent odorants in foods by aroma extract dilution analysis (AEDA) and calculation of odour activity values (OAVs). *Flavour Fragrance J.* **1994**, *9*, 147−158.

(40) Fenaroli, G. Raspberry. In *Fenaroli's Handbook of Flavor Ingredients*, 3rd ed.; Burdock, G. A., Ed.; CRC Press: Boca Raton, Florida, 1995; Vol. II, pp 827−828.

(41) Abbott, N.; Etievant, P.; Issanchou, S.; Langlois, D. Critical evaluation of two commonly used techniques for the treatment of data from extract dilution sniffing analysis. *J. Agric. Food Chem.* **1993**, *41*, 1698−1703.

Received for review January 23, 2004. Revised manuscript received May 3, 2004. Accepted May 8, 2004.

JF0498721