Evaluation of Key Odorants in Milk Chocolate and Cocoa Mass by Aroma Extract Dilution Analyses

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Application of an aroma extract dilution analysis (AEDA) on the volatiles of a commercial milk chocolate revealed 51 odor-active compounds in the flavor dilution (FD) factor range 8−1024, 44 of which could be identified. The following 13 odorants contributed with the highest FD factors to the overall chocolate flavor: 3-methylbutanal (malty); 2-ethyl-3,5-dimethylpyrazine (potato chip-like); 2- and 3-methylbutanoic acid (sweaty); 5-methyl-(*E*)-2-hepten-4-one (hazelnut-like); 1-octen-3-one (mushroom-like); 2-ethyl-3,6-dimethylpyrazine (nutty, earthy); 2,3-diethyl-5-methylpyrazine (potato chip-like); (*Z*)-2-nonenal (green, tallowy); (*E*,*E*)-2,4-decadienal (fatty, waxy); (*E*,*E*)-2,4-nonadienal (fatty); *R*-*δ*-decalactone (sweet, peach-like); and 2-methyl-3-(methyldithio)furan. Application of the AEDA on the cocoa mass used in the production of the milk chocolate led to the identification of 37 odorants, seven of which were sensorially not detected in the chocolate. By contrast, 11 odorants were present in the milk chocolate but were not sensorially relevant in cocoa mass, e.g., *R*-*δ*-decalactone and 5-methyl-(*E*)-2-hepten-4-one.

Keywords: *Chocolate flavor; cocoa mass flavor; aroma extract dilution analysis; 2-methyl-3-(methyldithio)furan; 5-methyl-(E)-2-hepten-4-one*

INTRODUCTION

The characteristic flavor of chocolate, attracting people all over the world, is generated as a result of several manufacturing steps. Depending on the cocoa variety used, the conditions of cocoa bean fermentation and roasting, and the conching process, different odor qualities were observed (Rohan, 1969; Mohr, 1978; Zak, 1988; Ziegleder and Biehl, 1988). Furthermore, additions of milk solids, nut paste, and/or vanillin to the crushed roasted cocoa beans are further possibilities to vary the chocolate flavor.

Since the pioneering study of Bainbridge and Davies (1912) who identified linalool and some fatty acids and their esters in a distillate prepared from 2000 kg of cocoa, numerous investigations aimed at identifying volatile compounds in cocoa products have been performed (cf. reviews by Flament, 1989, Ziegleder and Biehl, 1988, and Nijssen et al., 1996). Most of the studies were focused on roasted cocoa beans, and more than 525 volatiles have been identified up to now (cf. Nijssen et al., 1996). Among them, 94 pyrazines represent the predominant fraction. Their total concentration in the roasted beans may vary from 1.3 to 8.5 mg/kg depending on the variety and the roasting conditions used (Reineccius et al., 1972).

Only a few groups attempted to evaluate the contribution of the compounds identified to the overall flavor of the cocoa product analyzed. Van Elzakker and van Zutphen (1961) reported the presence of 12 compounds in a distillate obtained by high-vacuum distillation of cocoa butter. A sensory evaluation of a mixture of the twelve compounds identified, however, did not result in a cocoa-like odor.

Applying gas chromatography/effluent sniffing (GC/O) on a flavor extract obtained by steam distillation of roasted cocoa beans, van Praag et al. (1968) found that a mixture of isovaleraldehyde and methyl disulfide, coeluting on the stationary GC phase used, gave a cocoa-like odor. Later on, Lopez and Quesnel (1974) reported that chocolate-like odors were generated from model mixtures of isovaleraldehyde and certain thiols and disulfides, respectively. A correlation with the amounts of these sulfur compounds in cocoa or chocolate was, however, not reported by these authors.

Van Praag et al. (1968) identified 5-methyl-2-phenyl-2-hexenal in roasted cocoa and reported that its odor was associated with “a deep bitter persistent cocoa note”. However, Landschreiber and Mohr (1974) later on questioned the importance of this aldehyde as a contributor to cocoa flavor.

In general, the Strecker aldehydes 2-phenylacetaldehyde and 3-methylbutanal are recognized as important odorants in cocoa flavor (van Praag et al., 1968). However, because exact quantitative data on the amounts present in the different cocoa products are not available, their flavor contribution is yet unclear.

An aroma extract dilution analysis (AEDA) is a potent tool to screen the most odor-active volatiles in food extracts and has already been successfully applied to identify key flavor compounds in various foods (cf. review by Schieberle, 1995). Although milk chocolate belongs to the most preferred cocoa products (Zak, 1988), only one study on the volatiles present in this type of chocolate has appeared in the literature (Ziegleder and Stojacic, 1988).

In the following study, the potent flavor compounds of a commercial milk chocolate were characterized by AEDA. Furthermore, the most potent flavor compounds in the cocoa mass used in the production of the milk chocolate were identified to indicate the influence of further ingredients in supplying chocolate aroma compounds.

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Table 1. Mass Spectral Data of Chiral Lactones Identified in Milk Chocolate

lactone	*m*/*z* (intensity) MS/EI	MS/CI
R-δ-octenolactone (5-hydroxyoct-2-enoic acid lactone)	97 (100), 68 (70), 69 (18), 41 (18), 98 (5)	141 (100), 142 (10)
R-γ-nonalactone	85 (100), 56 (8), 43 (6), 41 (6)	157 (100), 158 (10)
R-δ-decalactone	99 (100), 71 (31), 55 (30), 42 (26), 70 (22), 43 (20), 41 (18), 56 (10), 114 (10), 69 (7)	171 (100), 172 (10)
R-δ-decenolactone (5-hydroxydec-2-enoic acid lactone)	97 (100), 68 (58)	169 (100), 170 (10)

EXPERIMENTAL PROCEDURES

Materials. Milk chocolate (ingredients: sugar, milk powder, cocoa butter, cocoa mass, hazelnut paste, lecithin as emulsifier; vanillin as nature-identical aroma) and the corresponding cocoa mass used for its production were supplied by a chocolate manufacturer.

Chemicals. The reference compounds of the odorants listed in Tables 1−5 were purchased from the following commercial sources: nos. 1−3, 9−11, 13−15, 20, 23, 24, 26−29, 31, 32, 34−37, 39, 41, 43−45, and 48−51 were from Aldrich, Steinheim, Germany, and nos. 4 and 8 were from Lancaster, Mühlheim, Germany. No. 6 (Alfa, Karlsruhe, Germany) and no. 7 (>90% (*E*)-isomers) were gifts from Dr. M. Güntert (Haarmann and Reimer, Holzminden, Germany). The following compounds were synthesized according to the cited literature: 2-ethyl-3,5- and 2-ethyl-3,6-dimethylpyrazine (Cerny and Grosch, 1993), (*Z*)-2-nonenal (Ullrich and Grosch, 1987), 2-methyl-3-(methyldithio)furan (Gasser and Grosch, 1990).

Enantiomerically pure *R*- and *S*-lactones nos. 40, 42, 46, and 47 were gifts from Prof. Dr. Schneider and Mr. Haase (Institute of Organic Chemistry, University of Wuppertal) and have been synthesized as previously reported by this group (Haase and Schneider, 1993). Their mass spectral data are summarized in Table 1.

Isolation of the Volatiles; Separation into Acidic and Neutral/Basic Compounds. Chocolate (200 g) was cut into pieces, frozen in liquid nitrogen, and then ground by means of a commercial blendor (Moulinette, Quelle, Nürnberg, Germany). The chocolate powder was extracted for 8 h at 40 °C with diethyl ether (800 mL) in a Soxhlet apparatus. The extract was concentrated to 200 mL by using a Vigreux column (50 cm × 1 cm internal diameter). To remove the nonvolatile material, the concentrate was then distilled by using the equipment recently described (Guth and Grosch, 1989). By treatment of the distillate with aqueous sodium bicarbonate (Hofmann and Schieberle, 1995), a fraction of the acidic volatiles (fraction AV) and of the neutral/basic volatiles (fraction NBV) was obtained. After drying over Na_2SO_4, both fractions were concentrated to 200 μL (cf. Schieberle, 1991) and the odor-active compounds evaluated by AEDA.

Column Chromatography. The concentrated distillate of the neutral/basic fraction (2 mL) obtained from 1 kg of chocolate or cocoa mass, respectively, was separated by flash chromatography on a silica gel phase (silica gel for flash chromatography; J.T. Baker, Deventer, Holland) using the equipment described recently (Hofmann and Schieberle, 1995). Using *n*-pentane/diethyl ether mixtures, the following fractions were obtained: fraction I (*n*-pentane; 160 mL), fraction II (95 + 5 by vol.; 200 mL), fraction III (9 + 1 by vol.; 200 mL), fraction IV (85 + 15 by vol.; 200 mL), fraction V (7 + 3 by vol.; 200 mL), fraction VI (1 + 1 by vol.; 200 mL), and fraction VII (diethyl ether; 200 mL).

Capillary Gas Chromatography (HRGC); Mass Spectrometry. HRGC was performed by means of a Fisons gas chromatograph, type 8165 (Fisons Instruments, Mainz, Germany) using the following fused silica thin-film capillaries: capillary SE-54 (DB-5), capillary FFAP (each 30 m × 0.32 mm; J. and W. Scientific, Fisons, Mainz, Germany; film thickness, 0.25 μm) and capillary Lipodex E (25 m × 0.25 mm i.d.; octakis(3-*O*-butyryl-2,6-di-*O*-pentyl)-γ-cyclodextrin [60% in OV-1701]; Machery and Nagel, Düren, Germany). The chiral stationary phase was used to separate the enantiomers of the lactones 40, 42, 46, and 47 in Table 2. Samples were applied by the "cold on-column" technique at 35 °C. After 2 min, the temperature of the oven was raised by 40 °C/min to 60 °C, held 2 min isothermally, then raised by 6 °C/min to 180 °C and, finally, by 10 °C/min to 240 °C. Capillary Lipodex E was used isothermally at 120 °C. The flow rate of the carrier gas helium was 2.3 mL/min = 40 cm/min. The retention indices were calculated by using n-alkanes as the reference (Schieberle, 1991). MS analysis was performed by means of an MAT 95 S (Finnigan, Bremen, Germany) in tandem with the capillaries described above. Mass spectra in the electron impact mode (MS/EI) were generated at 70 eV and in the chemical ionization mode (MS/CI) at 110 eV with isobutane as the reagent gas.

Aroma Extract Dilution Analysis (AEDA). The flavor dilution (FD) factors of the odorants in fractions AV and NBV of milk chocolate or cocoa mass, respectively, were determined by AEDA (cf. review by Schieberle, 1995): An aliquot of the respective distillate (0.5 μL of 200 μL) was separated on capillary FFAP, the effluent was split to an FID and a sniffing port (1 + 1 by vol.), and the odor-active regions and the odor qualities were assigned by three assessors (GC/O). The extract was stepwise diluted with diethyl ether (1 + 1 by vol.), and aliquots of the dilutions (0.5 μL) were evaluated by two assessors. The FD chromatogram (FD factors vs retention indices) was plotted. Static headspace analysis/olfactometry (SHO) was performed as described recently (Hofmann and Schieberle, 1995) using 50 g of chocolate.

RESULTS

Milk Chocolate. In the FD chromatogram obtained by applying the AEDA on an extract containing the neutral/basic volatiles of the milk chocolate, 37 odor-active compounds were sensorially detected (Figure 1). Among them, 12 odorants showed very high FD factors of 1024 and 512, respectively (nos. 1, 7, 8, 16, 18, 20, 21, 24, 30, 31, 34, and 46; Figure 1). After enrichment by flash chromatography on a silica gel phase, followed by HRGC/Olfactometry and HRGC/MS of the fractions obtained, all of these key odorants could be identified on the basis of the criteria given in footnote *b* of Table 2. 3-Methylbutanal (no. 1; Table 2), eliciting a malty odor and 2-ethyl-3,5-dimethylpyrazine with a potato chip-like smell (no. 18) showed the highest FD factors, followed by the additional ten odorants 5-methyl-(*E*)-2-hepten-3-one (no. 7; hazelnut-like), 1-octen-3-one (no. 8; mushroom-like), 2-ethyl-3,6-dimethylpyrazine (no. 16; nutty, earthy), 2,3-diethyl-5-methylpyrazine (no. 20; potato chip-like), (*Z*)-2-nonenal (no. 21; green, tallowy), (*E*,*Z*)-2,6-nonadienal (no. 24; cucumber-like), 2-methyl-3-(methyldithio)furan (no. 30; cooked meat-like), (*E*,*E*)-2,4-nonadienal (no. 31; fatty, waxy), (*E*,*E*)-2,4-decadienal (no. 34; fatty, waxy); and *R*-δ-decalactone (no. 46; sweet, peach-like). Four of these aroma compounds have been earlier reported as volatiles in cocoa products (nos. 1, 16, 18, and 20), whereas the other eight have not. Of the additional 25 odor-active compounds showing somewhat lower FD factors, 21 odorants could be identified. The results of the identification experiments are summarized in Table 2.

In the fraction of the acidic volatiles another 14 odorants were identified (Table 3). Among them, vanillin (no. 51; vanilla-like) followed by 2- and 3-methyl-

Table 2. Most Odor-Active, Neutral/Basic Volatiles (FD Factor ≥ 8) in Milk Chocolate

no.[a]	odorant[b]	odor quality[c]	RI[d] on FFAP	RI[d] on SE-54	FD factor	earlier reported as volatile compound[e]
1	3-methylbutanal	malty	920	652	1024	(1)
2	2,3-butandione (diacetyl)	buttery	984	592	128	(2)
3	hexanal	green	1083	801	16	(3)
4	1-hexen-3-one	linseed oil-like	1101	775	8	–
5	unknown	geranium-like	1195	–	128	–
6	(*Z*)-4-heptenal[f]	sweet, biscuit-like	1246	899	64	–
7	5-methyl-(*E*)-2-hepten-4-one	hazelnut-like	1287	972	512	–
8	1-octen-3-one[f]	mushroom-like	1304	980	512	–
9	dimethyl trisulfide	sulfurous	1384	969	256	(4)
10	nonanal	soapy	1400	1093	64	(3)
11	trimethylpyrazine	earthy	1406	1000	32	(5)
12	unknown	fruity, waxy	1422	–	64	–
13	2-methoxy-3-isopropylpyrazine[f]	earthy, beany	1428	1097	64	–
14	(*E*)-2-octenal	fatty, waxy	1433	1060	128	–
16	2-ethyl-3,6-dimethylpyrazine	nutty, earthy	1445	1079	512	(6)
17	unknown	tallowy	1454	–	128	–
18	2-ethyl-3,5-dimethylpyrazine	potato chip-like	1461	1083	1024	(5)
20	2,3-diethyl-5-methylpyrazine	potato chip-like	1490	1158	512	(7)
21	(*Z*)-2-nonenal	green, tallowy	1513	1148	512	–
23	(*E*)-2-nonenal	green, fatty	1528	1161	256	–
24	(*E*,*Z*)-2,6-nonadienal	cucumber-like	1579	1154	512	–
25	(*Z*)-2-decenal[g]	tallowy	1601	1250	128	–
27	(*E*)-2-decenal	fatty, green	1647	1262	16	–
28	phenylacetaldehyde	sweet, honey-like	1652	1047	256	(5)
30	2-methyl-3-(methyldithio)furan	cooked meat-like	1667	1170	512	–
31	(*E*,*E*)-2,4-nonadienal	fatty, waxy	1703	1215	512	–
33	ethyl phenylacetate	sweet, waxy	1724	–	128	–
34	(*E*,*E*)-2,4-decadienal	fatty, waxy	1812	1318	512	–
35	phenylethyl acetate	fruity, sweet	1821	1244	8	(8)
37	2-phenylethanol	sweet, yeast-like	1915	1118	128	(5)
40	*R*-δ-octenolactone (99%)	sweet, coconut-like	2009	1261	256	–
42	*R*-γ-nonalactone (80%)	sweet, coconut-like	2038	1663	128	(9)
43	ethyl cinnamate	sweet, cinnamon-like	2125	1469	256	(9)
44	γ-decalactone	sweet, peach-like	2155	1470	256	–
46	*R*-δ-decalactone (84%)	sweet, peach-like	2208	1469	512	(10)
47	*R*-δ-decenolactone (99%)	sweet, peach-like	2241	1477	32	–
49	3-methylindol (skatole)[f]	mothball-like	2494	1388	32	–

[a] Numbers refer to Figure 1. [b] Odorants were identified by comparing them with the reference compound on the basis of the following criteria: retention index (RI) on two different stationary HRGC phases detailed in the table, mass spectra obtained by MS(EI) and MS(CI), odor quality and odor threshold (ratio of FID signal to FD-factor) at the sniffing port. [c] Odor quality perceived at the sniffing port. [d] Retention index. [e] Reported earlier as volatile compound in either cocoa, cocoa products, or chocolate, respectively. (1) Bailey et al., 1962; (2) Mohr, 1958; (3) Rohan, 1969; (4) van Praag et al., 1968; (5) Marion et al., 1967; (6) Rizzi, 1967; (7) Vitzthum et al., 1975); (8) Dietrich et al., 1964; (9) Flament et al., 1967; (10) Ziegleder and Stojacic, 1988. [f] The MS signals were to weak for an unequivocal interpretation. The compound was identified on the basis of the resting criteria given in footnote *b*. [g] Tentatively identified by comparing the retention index and the odor quality with a 2-decenal isomer present in the commercial sample of (*E*)-2-decenal.

Table 3. Most Odor-Active, Acidic Volatiles (FD Factor ≥ 4) in Milk Chocolate

no.	odorant[a]	odor quality[b]	RI on FFAP	RI on SE-54	FD factor	earlier reported as volatile compound[c]
15	acetic acid	sour	1439	600	4	(1)
19	unknown	waxy	1478	–	32	–
22	unknown	green	1522	–	32	–
26	butanoic acid	buttery, rancid	1610	821	64	(1)
29	2- and 3-methylbutanoic acid	sweaty	1652	873/877	512	(2)
32	pentanoic acid	sweaty, pungent	1721	911	16	(2)
36	hexanoic acid	sweaty, pungent	1829	1019	32	(2)
38	unknown	sour	1936	–	8	–
39	3-hydroxy-2-methylpyran-4-one (maltol)	caramel-like	1961	1111	16	(2)
41	4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (furaneol)	caramel-like	2022	1070	64	(3)
45	3-hydroxy-4,5-dimethyl-2(5*H*)-furanone (sotolon)	seasoning-like, spicy	2182	1110	128	–
48	3-hydroxy-5-ethyl-4-methyl-2-(5*H*)-furanone (abhexon)	seasoning-like, spicy	2250	1198	16	–
50	phenylacetic acid	sweet, flowery	2254	1262	64	(4)
51	3-methoxy-4-hydroxybenzaldehyde (vanillin)	vanilla-like	2577	1406	>1024	(5)

[a] Cf. footnote *b* in Table 1. [b] Cf. footnote *c* in Table 1. [c] Reported as volatile compound in either cocoa, cocoa products or chocolate, respectively: (1) Bainbridge and Davies, 1912; (2) Dietrich et al., 1964; (3) Ziegleder, 1991; (4) Quesnel et al., 1963; (5) Ziegleder and Stojacic, 1988.

butanoic acid (no. 29; buttery, rancid) and sotolon (no. 45; seasoning-like) showed the highest odor intensities.

By application of AEDA very volatile odorants might be overlooked due to losses during concentration of the extracts. Static headspace analysis/olfactometry (SHO) might overcome this problem (Guth and Grosch, 1993). Application of this technique on 40 mL of the headspace above warm (40 °C) milk chocolate revealed 15 odor-active compounds (Table 4), of which 14 odorants could be identified. With the exception of 2-methylpropanal,

Table 4. Odorants in Milk Chocolate Detected by Static Headspace/Olfactometry (SHO)

odorant	RI on SE-54	odor quality	volume[a] (mL)	relative flavor dilution[b]
2-methylpropanal	<600	malty	2.5	16
2,3-butandione	592	buttery	2.5	16
3-methylbutanal	652	malty	1.25	32
unknown	–	green	10	4
1-hexen-3-one	775	linseed oil-like	20	2
hexanal	801	green	20	4
dimethyl trisulfide	969	sulfurous	10	4
1-octen-3-one	980	mushroom-like	5	8
2-ethyl-3,5-dimethylpyrazine	1083	potato chip-like	10	4
2-methoxy-3-isopropylpyrazine	1097	earthy, beany	10	4
(*Z*)-2-nonenal	1148	tallowy, green	20	2
(*E*)-2-nonenal	1161	green, fatty	40	1
2-methyl-3-(methyldithio)furan	1170	cooked meat-like	2.5	16
(*E*,*E*)-2,4-nonadienal	1215	fatty, waxy	20	2
(*E*,*E*)-2,4-decadienal	1318	fatty, waxy	20	2

[a] Lowest headspace volume in which the odorant was detected by GC/olfactometry. [b] Calculated by deviding the largest volume analyzed (40 mL) by the lowest volume in which the odorant was detectable by GC/olfactometry.

Table 5. Most Odor-Active Volatiles (FD Factor ≥8) in Cocoa Mass

no.[a]	odorant[b]	odor quality[c]	RI[d] on FFAP	RI[d] on SE-54	FD factor
1	3-methylbutanal	malty	920	652	1024
1a	ethyl 2-methylpropionate	fruity	958	758	32
2	2,3-butandione	buttery	984	592	16
2a	ethyl 2-methylbutanoate[e]	fruity	1045	854	1024
3	hexanal	green	1083	801	512
4	1-hexen-3-one	linseed oil-like	1101	775	16
4a	unknown	pungent, grassy	1168	–	128
6	(*Z*)-4-heptenal[e]	sweet, biscuit-like	1246	899	64
9	dimethyl trisulfide	sulfurous	1384	969	32
10	nonanal	soapy	1400	1093	32
11	trimethylpyrazine	earthy, potato-like	1406	1000	32
12	unknown	fruity, waxy	1422	–	512
13	2-methoxy-3-isopropylpyrazine[e]	earthy, beany	1428	1097	512
14	(*E*)-2-octenal	fatty, waxy	1433	1060	512
16	2-ethyl-3,6-dimethylpyrazine	nutty, earthy	1445	1079	32
18	2-ethyl-3,5-dimethylpyrazine	potato chip-like	1461	1083	256
18a	unknown	tallowy	1471	–	512
20	2,3-diethyl-5-ethylpyrazine	potato chip-like	1490	1158	256
21	(*Z*)-2-nonenal	tallowy, green	1513	1148	32
23	(*E*)-2-nonenal	green, fatty	1528	1161	256
26	butanoic acid	buttery, rancid	1610	–	16[f]
27	(*E*)-2-decenal	fatty, green	1640	1262	32
28	phenylacetaldehyde	honey-like, sweet	1652	1047	64
29	2- and 3-methylbutanoic acid	sweaty	1652	–	2048[f]
30	2-methyl-3-(methyldithio)furan	cooked meat-like	1667	1170	512
31	(*E*,*E*)-2,4-nonadienal	fatty, waxy	1703	1215	32
33	unknown	sweet, waxy	1724	–	128
33a	unknown	sweet	1747	–	32
37	2-phenylethanol	flowery, sweet	1915	1118	32
37a	unknown	sweet, peach-like	1920	–	32
40	δ-octenolactone	sweet, coconut-like	2009	1261	64
40a	unknown	sweet, peach-like	2020	–	32
42	γ-nonalactone	sweet, peach-like	2038	1663	8
43	ethyl cinnamate	sweet, cinnamon-like	2125	1469	32
44	γ-decalactone	sweet, peach-like	2155	1470	64
45	3-hydroxy-4,5-dimethyl-2(5*H*)-furanone (sotolon)	seasoning-like, spicy	2182	–	32[f]
48	3-hydroxy-5-ethyl-4-methyl-2(5*H*)-furanone (abhexone)[e]	seasoning-like, spicy	2250	–	32[f]

[a–e] Refer to Table 1. [f] The FD factors were determined in the fraction of the acidic volatiles.

eliciting a malty odor note, the remaining 13 aroma compounds had already been identified in the AEDA of the solvent extract (cf. Table 3). Stepwise reduction of the headspace volume revealed 3-methylbutanal, followed by 2-methylpropanal, 2,3-butandione (diacetyl), and 2-methyl-3-(methyldithio)furan as the most odor-active compounds in the headspace above the milk chocolate being detectable down to 1.25 or 2.5 mL of the headspace, respectively, thereby corroborating the high aroma impact of these four odorants.

Cocoa Mass. In the recipe of the milk chocolate used in these experiments, besides vanillin as a synthetic flavor compound, roasted cocoa beans, milk solids, and nut paste have been used. To indicate, which odorants stem from cocoa mass, the volatile fraction of the cocoa mass used in the production of the milk chocolate was analyzed. Application of the AEDA revealed 37 odor-active compounds, of which 31 odorants could be identified (Table 5). Seven of the nine most important aroma compounds were characterized as follows: 2- and 3-methylbutanoic acid (no. 29; sweaty), 3-methylbutanal (no. 1; malty), hexanal (no. 3; green), 2-methoxy-3-isopropylpyrazine (no. 13; earthy), (*E*)-2-octenal (no. 14; fatty) and 2-methyl-3-(methyldithio)furan (no. 30; cooked

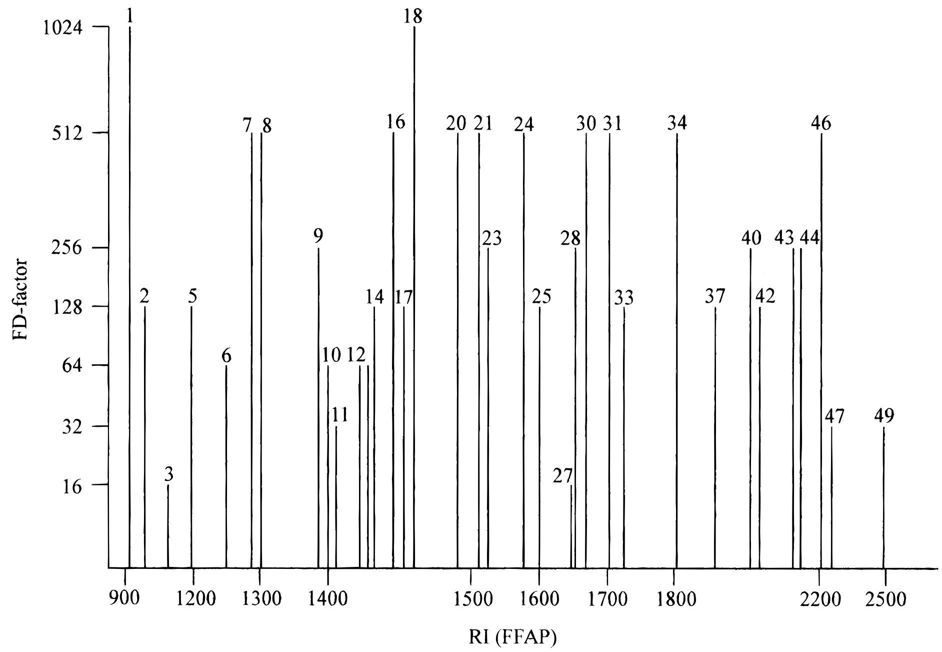

Figure 1. Flavor dilution (FD) chromatogram of the neutral/basic volatiles of milk chocolate. No. 1, malty; no. 18, potato chip-like.

Table 6. Comparison of Key Odorants Showing Significant Differences in Their FD Factors in Milk Chocolate (MC) and Cocoa Mass (CM)

odorant	FD factor[a]	
	MC	CM
vanillin	>1024	<8
(*E*,*E*)-2,4-nonadienal	512	<8
(*E*,*E*)-2,4-decadienal	512	<8
R-δ-decalactone	512	<8
5-methyl-(*E*)-2-hepten-4-one	512	<8
1-octen-3-one	512	<8
dimethyl trisulfide	256	32
4-hydroxy-2,5-dimethyl-3(2*H*)-furanone	128	<8
(*Z*)-2-decenal[b] (tallowy)	128	<8
unknown (geranium-like)	128	<8
2-methoxy-3-isopropylpyrazine	64	512
2-ethyl-3,6-dimethylpyrazine	32	512
hexanal	16	512
ethyl 2-methylbutanoate	<8	1024

[a] Data from Tables 1−5. [b] Tentatively identified by comparing the retention index and the odor quality with a 2-decenal isomer present in the commercial sample of (*E*)-2-decenal.

meat-like). Two compounds with high FD factors (nos. 12 and 18a) and showing fruity, waxy, or tallowy odors, respectively, remained unknown.

DISCUSSION

A great number of aroma compounds contributed to the overall odor of the milk chocolate as well as to the cocoa mass flavor. Among them, 3-methylbutanal (no. 1; Tables 2 and 5), (*E*)-2-octenal (no. 14), 2-ethyl-3,5-dimethylpyrazine (no. 18), 2,3-diethyl-5-ethylpyrazine (no. 20), (*E*)-2-nonenal (no. 23), 2-methyl-3-(methyldithio)-furan (no. 30), and 2- and 3-methylbutanoic acid, due to their overall high odor activities or FD factors, respectively, were the most important in both materials. The results indicated that these aroma compounds of milk chocolate undoubtedly stem from the roasted cocoa mass.

By contrast, the 14 odorants summarized in Table 6 showed very significant differences in their odor activities between milk chocolate and the cocoa mass.

In particular, the ten odorants vanillin, *R*-δ-decalactone, 5-methyl-(*E*)-2-hepten-4-one, 1-octen-3-one, (*E*,*E*)-2,4-nonadienal, dimethyl trisulfide, 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone, (*E*,*E*)-2,4-decadienal, (*Z*)-2-decenal, and an unknown compound with a geranium-like odor, were important contributors to milk chocolate but did not much contribute to the cocoa mass flavor.

Because vanillin has been used in the recipe of the milk chocolate, there is no doubt about its origin. δ-Decalactone has also been identified as key contributor to the flavor of butter oil (Widder et al., 1991), butter (Schieberle et al., 1993), and also butter milk (Heiler and Schieberle, 1996), and the *R*-configuration of δ-decalactone in milk products has recently been established by Palm et al. (1991). It seems, therefore, very likely that this odorant is supplied by the milk solids used in the manufacturing of the chocolate.

5-Methyl-(*E*)-2-hepten-4-one has recently been identified as key odorant in hazelnuts (Emberger, 1985; Jauch et al., 1989). Undoubtedly, this aroma compound is supplied by the nut paste used as an ingredient in the milk chocolate.

Although 1-octen-3-one and (*E*,*E*)-2,4-decadienal have been reported as primary odorants of milk products (Widder et al., 1991; Schieberle et al., 1993), it might be speculated that both and, in addition, dimethyl trisulfide and 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone are generated at the higher temperatures applied during conching of the chocolate. However, this has to be proven by quantitative measurements.

On the other hand, ethyl 2-methylbutanoate, 2-methoxy-3-isopropylpyrazine, hexanal, and 2-ethyl-3,6-dimethylpyrazine showed higher FD factors in the cocoa mass compared with the milk chocolate. Although it might be suggested that these aroma compounds might be partially evaporated during the conching process, the reason for this difference has to be clarified by further investigations.

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