JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

J. Agric. Food Chem. **2002,** *50,* 2385−2391 **2385**

Use of Gas Chromatography−Olfactometry To Identify Key Odorant Compounds in Dark Chocolate. Comparison of Samples before and after Conching

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After vacuum distillation and liquid−liquid extraction, the volatile fractions of dark chocolates were analyzed by gas chromatography−olfactometry and gas chromatography−mass spectrometry. Aroma extract dilution analysis revealed the presence of 33 potent odorants in the neutral/basic fraction. Three of these had a strong chocolate flavor: 2-methylpropanal, 2-methylbutanal, and 3-methylbutanal. Many others were characterized by cocoa/praline-flavored/nutty/coffee notes: 2,3-dimethylpyrazine, trimethylpyrazine, tetramethylpyrazine, 3(or 2),5-dimethyl-2(or 3)-ethylpyrazine, 3,5(or 6)-diethyl-2-methylpyrazine, and furfurylpyrrole. Comparisons carried out before and after conching indicate that although no new key odorant is synthesized during the heating process, levels of 2-phenyl-5-methyl-2-hexenal, Furaneol, and branched pyrazines are significantly increased while most Strecker aldehydes are lost by evaporation.

KEYWORDS: Chocolate flavor; conching; aroma extract dilution analysis (AEDA); Maillard reactions; Strecker degradation

INTRODUCTION

The secret of the flavor of chocolate, so highly appreciated worldwide, resides mainly in its volatile aromatic fraction. Its complex composition depends on the cocoa bean genotype and is the consequence of several processes (*1*−*4*). Cocoa fermentation is crucial not only to the formation of significant volatile fractions (alcohols, esters, and fatty acids) but also for the development of cocoa-chocolate flavor precursors (amino acids and reducing sugars). Cocoa is dried to minimize the formation of molds and to reduce the acid level and astringency of the beans by decreasing the total quantity of polyphenols. Via Maillard reactions, cocoa roasting converts flavor precursors formed during fermentation to two main classes of odorant compounds: pyrazines and aldehydes (*4*). Finally, conching improves the final flavor and texture of the chocolate.

Conching is one of the most significant operations in chocolate-making. It consists of hot mixing for 8 h or more in tanks called conches. It is usually a two-step process: dry conching, which decreases moisture and improves rheology (*5*), is usually followed by liquid conching, when lecithin is added. Conching results in a change of color due to emulsification and tannin oxidation (*6*). The conching time/temperature conditions can vary somewhat according to the type of chocolate to be processed. Dark chocolate is generally conched at temperatures from 70 to 82 °C (*7*). According to Mohr (*8*), atmospheric oxygen leads to more refined chocolate flavors. The literature provides little and conflicting information on conching chemistry. According to Hoskin and Dimick (*9*), the amino acid content does not change during conching of dark chocolate. The temperature applied and/or the concentrations of free amino acids and sugars would be too low for Maillard reactions. Heinzler and Eichner (*10*), however, report that Amadori compounds previously formed during drying and roasting may decrease during chocolate conching. Pontillon (*5*) suggests that during conching, caramelization of lactose and Maillard reactions with milk proteins, in the case of milk chocolate, can also occur. Olfactive data show in all cases a strong overall flavor decrease after conching (*5*, *9*, *11*).

To date, descriptive studies have identified >600 volatile compounds in cocoa and chocolate products (*2*, *12*−*22*), mainly pyrazines, esters, amines and amides, acids, and hydrocarbons. In 1961, Van Elzakker and Van Zutphen (*23*) showed that none of the 12 odorant compounds obtained from a high-vacuum distillation of cocoa butter gave a cocoa-like odor. According to Mohr (*24*) and Brunner (*25*), the cocoa flavor could come from the heavier fractions. However, Van Praag et al. (*16*) and Lopez and Quesnel (*26*) showed that 3-methylbutanal and dimethyl disulfide (or thiols) together can contribute a cocoa-like odor. In the recent study of Schnermann and Schieberle

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10.1021/jf0114177 CCC: $22.00
Published on Web 03/15/2002

Table 1. Compounds Tentatively Identified in the Neutral/Basic Fraction of Dark Chocolates A and B after Conching

no.	compound	RI	identification[a]	FD value[g] A	FD value[g] B	odor description (GCO)
	Alcohols					
1	1-pentanol	757	MS, RI			
2	2-heptanol[b]	879	MS, RI			
3	benzyl alcohol[f]	1010	MS, RI			
4	3,7-dimethyl-1,6-octadien-3-ol (*linalool*)[b,e]	1086	MS, RI			
5	2-phenylethanol[c,d,e,f]	1090	MS, RI	16	128	flowery
	Aldehydes					
6	2-methylpropanal (*isobutanal*)[e]	566	RI, GCO	2048	128	chocolate
7	3-methylbutanal[b,c,d,e]	633	RI, GCO	>4096	2048	chocolate
8	2-methylbutanal[e]	643	RI, GCO	512	256	chocolate
9	2-methyl-2-butenal[b]	764	MS			
10	3-(methylthio)propionaldehyde (*methional*)	866	MS, RI, GCO	128	256	potato
11	heptanal[e]	877	MS			
12	benzaldehyde[b,e,f]	935	MS, RI, GCO			
13	phenylacetaldehyde[c,d,e,f]	1015	MS, RI, GCO	>4096	512	flowery, honey
14	nonanal[b,d,e]	1082	MS, RI			
15	2-phenyl-2-butenal[f]	1242	MS, GCO	4	32	cocoa, sweet, roasted, rum
16	2-phenyl-5-methyl-2-hexenal[b,f]	1485	MS, RI			
	Esters					
17	ethylbenzoylformate	1039	MS			
18	ethylbenzoate[b,f]	1156	MS			
19	ethyloctanoate[b,e]	1176	MS, RI			
20	2-phenylethyl acetate[b,c,d]	1233	MS, RI			
	Furans					
21	dihydro-2-methyl-3(2*H*)-furanone[f]	781	MS, RI			
22	furancarboxaldehyde (*furfural*)[b,e,f]	805	MS, RI			
23	furfuryl alcohol (*furfurol*)[b,e,f]	827	MS, RI			
24	1-(2-furanyl)ethanone (*acetylfuran*)[b,e,f]	884	MS, RI			
25	5-methyl-2-furancarboxaldehyde[b,e,f]	931	MS, RI			
26	5-ethenyltetrahydro-α,α,5-trimethyl-*cis*-2-furanmethanol (*linalool oxide*)	1076	MS			
27	3-phenylfuran	1208	MS	32	16	cocoa, green, mint
	Hydrocarbons					
28	methylbenzene (*toluene*)	767	MS, RI			
	Ketones					
29	2,3-butanedione (*diacetyl*)[c,d,e,f]	578	RI, GCO	4	8	buttery
30	2-heptanone[e,f]	868	MS, RI			
	Nitrogen Compounds					
31	benzonitrile[b,f]	951	MS, RI			
	Pyrans					
32	3,4-dihydro-8-hydroxy-3-methyl-1*H*-2-benzopyran-1-one	1517	MS			
	Pyrazines					
33	pyrazine	731	MS, RI			
34	methylpyrazine[b]	803	MS, RI, GCO		2	hazelnut, green
35	2,5-dimethylpyrazine[b,f]	889	MS, RI			
36	ethylpyrazine[b]	895	MS, RI, GCO	32	32	green, ether, rum
37	2,3-dimethylpyrazine[b]	899	MS, RI, GCO	>4096	256	hazelnut, roasted
38	ethenylpyrazine	907	MS, RI			
39	2-ethyl-5(or 6)-methylpyrazine [b,f]	973	MS			
40	trimethylpyrazine[b,c,d,f]	980	MS, RI, GCO	256	256	cocoa, roasted, green
41	2-ethyl-3-methylpyrazine[b]	983	MS, RI			
42	2-ethenyl-6-methylpyrazine	992	MS, GCO	16	8	hazelnut, roasted
43	3(or 2),5-dimethyl-2(or 3)-ethylpyrazine[c,d,f]	1057	MS, RI, GCO	32	256	roasted, smoky, praline, rum
44	tetramethylpyrazine[b,f]	1065	MS, RI, GCO	>4096	2048	milk coffee, mocha, roasted, green
45	2-isopropyl-3-methoxypyrazine[c,d]	1081	RI, GCO	512	128	garden peas, green, hazelnut
46	2,3-diethyl-5-methylpyrazine[c,d]	1135	MS, RI			
47	3,5(or 6)-diethyl-2-methylpyrazine[f]	1137	MS, GCO	>4096	>4096	cocoa, chocolate, rum, sweet, roasted
48	3,5(or 6)-diethyl-2-methylpyrazine[f]	1139	MS			
49	2,5(or 6)-dimethyl-3-(2-methylpropyl)pyrazine	1184	MS, GCO	128	2	hazelnut
50	2,5-dimethyl-3-(3-methylbutyl)pyrazine	1296	MS, GCO	32	32	roasted, sweet, green
	Pyridines					
51	pyridine	724	MS, RI			
52	2-methylpyridine	800	MS, RI			
53	1-(2-pyridinyl)-1-propanone	1114	MS			
	Pyrroles					
54	2-carboxaldehyde-1*H*-pyrrole	986	MS			
55	1-(1*H*-pyrrol-2-yl)ethanone (*acetylpyrrole*)[b,f]	1030	MS, RI, GCO	64	64	cocoa, chocolate, hazelnut, roasted
56	3-ethyl-2,5-dimethyl-1*H*-pyrrole	1119	MS, GCO		2	cocoa, hazelnut, coffee, roasted
57	1-(2-furanylmethyl)-1*H*-pyrrole (*furfurylpyrrole*)	1166	MS, RI, GCO	128	512	roasted, chocolate, green
58	1*H*-indole	1276	MS, RI			

Table 1 (Continued)

no.	compound	RI	identification[a]	FD value[g] A	FD value[g] B	odor description (GCO)
	Sulfur Compounds					
59	dimethyl disulfide	743	MS, RI			
60	dimethyl trisulfide[c,d]	969	MS, RI, GCO	16	32	onion, cabbage, sweaty

[a] Compound identified by GC-MS (MS) and/or by retention index on CP-Sil5-CB (RI) and/or by GC–olfactometry (GCO). [b] Compound previously identified in a dark semisweet chocolate before conching in ref *38*. [c] Compound previously reported as key odorant in bitter chocolate in ref *39*. [d] Compound previously reported as key odorant in milk chocolate in ref *22*. [e] Compound previously identified in chocolate (type not defined) in ref *40*. [f] Compound previously identified in milk chocolate in ref *19*. [g] FD = dilution factor = 2^{n-1}, where *n* is the number of dilutions (factor 2) until no odor was perceived.

(*22*), 3-methylbutanal, 2-ethyl-3,5-dimethylpyrazine, 1-octen-3-one, 2-ethyl-3,6-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine, (*Z*)-2-nonenal, 2-methyl-3-(methyldithio)furan, (*E*,*E*)-2,4-nononadienal, (*E*,*E*)-2,4-decadienal, and *R*-*δ*-decalactone were shown to be the key neutral/basic odorants of milk chocolate. Comparisons with the cocoa mass indicated that dimethyl trisulfide and Furaneol can be generated at the higher temperatures applied during conching. In the present study, a similar aroma extract dilution analysis (AEDA) approach has been used to identify the key odorants in dark chocolate, and samples taken before and after conching are compared.

EXPERIMENTAL PROCEDURES

Materials. Two dark chocolates, A and B (same chocolate formula but coming from two different cocoa mass batches; ingredients at the beginning of conching were sugar, cocoa butter, cocoa mass, vanillin as aroma; lecithin was added as emulsifier during conching), analyzed before and after conching, were supplied by Belcolade chocolate manufacture (Puratos Group, Belgium).

Chemicals. All compounds were from Sigma-Aldrich (Bornem, Belgium) except 2-phenyl-5-methyl-2-hexenal, which was from Aldrich-Flavors and Fragrances (Steinheim, Germany), and dichloromethane, which was from Romil (Cambridge, U.K.).

Flavor Distillation. Dark chocolate (300 g) was reduced to a powder with a mixer and then introduced into a flask with 500 mL of distilled water. The volatile flavor compounds were then isolated using a vacuum distillation apparatus (*27*). All of the traps were cooled with liquid nitrogen. The temperature of the water bath (Cenco) was maintained at 35 °C to avoid new aroma formation. After 3 h of distillation, the 400 mL condensate was kept at −4 °C and melted overnight.

Flavor Extraction: Separation into a Basic/Neutral Fraction and an Acidic Fraction. The aqueous condensate was adjusted to pH 13 with NaOH and then extracted with doubly distilled dichloromethane (4 × 125 mL). The first organic fraction was the basic/neutral volatile fraction. The water phase was then adjusted to pH 5 with 37% HCl and extracted with doubly distilled dichloromethane (4 × 125 mL). This second organic fraction was the acidic volatile fraction. Both fractions were concentrated to 0.25 mL at 46 °C in a Snyder−Kuderna column (Alltech). Decane (5 mL of a 5 ppm dichloromethane solution) was added before concentration, as external standard.

Gas Chromatography. The gas chromatograph was an HP5890 equipped with an on-column injector UP7673, an FID, and a Shimadzu CR3A integrator. Compounds were separated using a 50 m × 0.32 mm i.d., wall-coated open tubular (WCOT) nonpolar CP-Sil5-CB capillary column of 1.2 μm film thickness (Varian). The oven temperature was programmed from 36 to 85 °C at 20 °C/min, to 145 °C at 1 °C/min, to 250 °C at 3 °C/min, and then to held constant at 250 °C for 30 min. The FID was maintained at 260 °C. The injected sample volume was 1 μL. Retention index (RI) was calculated by using *n*-alkanes as references.

Standard Addition Method. This method involves the addition before vacuum distillation of increasing concentrations of each aroma to the chocolate matrix (300 g of chocolate and 500 mL of water). When no commercial standard is available, a quantification in equivalents is proposed by using the slope obtained for an analogue.

Table 2. RI Values and Odors of Unidentified Compounds with FD Value >64 after Conching

no.	RI on CP-Sil5-CB	FD value[a] A	FD value[a] B	odor description (GCO)
73	562	512		chocolate
74	770		64	green
75	861	2048	16	potato, hazelnut
76	947	64	256	cocoa, hazelnut, roasted
77	977		64	sweet, rum
78	1001	1024	128	hazelnut, cocoa
79	1305	128	512	cocoa, sweet
80	1323		128	orange flower
81	1377	32	512	flowery, cocoa, hazelnut

[a] FD = dilution factor = 2^{n-1}, where *n* is the number of dilutions (factor 2) until no odor was perceived.

Mass Spectrometry. MS analyses were carried out with an HP5988 quadrupole mass spectrometer. Electron impact mass spectra were recorded at 70 eV (2.45 scans per second). Spectral recording throughout elution was automatically performed with the HP59970 C software. MS chromatographic parameters are the same as the ones mentioned under Gas Chromatography.

Aroma Extract Dilution Analysis. The flavor dilution (FD) factors of the odorants in the acidic and basic/neutral volatile fractions were determined at the sniffing port according to the AEDA procedure (*28*). Extract (2 μL) was injected into the column, half of the volume being split into the FID. Odor qualities were defined by five assessors while stepwise dilution analysis (dilution factor = 2) was performed once. Chromatographic parameters are the same as the ones mentioned under Gas Chromatography.

RESULTS AND DISCUSSION

Identification of Volatile Compounds. *Neutral/Basic Fraction.* A total of 60 compounds were identified in the neutral/basic fraction of our two dark chocolates, mainly nitrogen and oxygen heterocycles, aldehydes and ketones, esters, alcohols, hydrocarbons, nitriles, and sulfides (**Table 1**). Among them, 10 with MS and RI confirmations have never been described as chocolate constituents: 1-pentanol (**1**), 3-(methylthio)-propionaldehyde (**10**), methylbenzene (**28**), pyrazine (**33**), ethenylpyrazine (**38**), pyridine (**51**), 2-methylpyridine (**52**), 1-(2-furanylmethyl)-1*H*-pyrrole (**57**), 1*H*-indole (**58**), and dimethyl disulfide (**59**). Two others, benzyl alcohol (**3**) and dihydro-2-methyl-3(2*H*)-furanone (**21**), have been described so far only in milk chocolate.

As depicted in **Table 4**, concentrations of most flavors were revealed to be different in samples A and B even before conching, indicating that cocoa fermentation and drying are not reproducible from batch to batch.

Surprisingly, only a few volatiles with parts per million levels emerged as key odorants on the basis of gas chromatography−olfactometry (GCO) (**Table 1**). They included four Strecker aldehydes, 2-methylpropanal (**6**), 3-methylbutanal (**7**), 2-meth-

Table 3. Compounds Identified in the Acidic Fraction of Dark Chocolates A and B after Conching

no.	compound	RI	identification[a]	odor description (GCO)
	Alcohols			
61	2,4-hexadien-1-ol	831	MS	
	Aldehydes			
7	3-methylbutanal[b,c,d,e]	633	RI, GCO	chocolate (low intensity)
8	2-methylbutanal[e]	643	RI, GCO	chocolate (low intensity)
	Furans			
23	furfuryl alcohol (*furfurol*)[b,e,f]	827	MS, RI	
62	2,5-dimethyl-4-hydroxy-3(2*H*)furanone (*Furaneol*)[c,d]	1023	RI, GCO	caramel-like, sweet
	Hydrocarbons			
28	methylbenzene (*toluene*)	772	MS, RI	
	Ketones			
29	2,3-butanedione (*diacetyl*)[c,d,e,f]	578	RI, GCO	buttery (low intensity)
63	4-methylcyclohexanone	998	MS	
64	3,4,4-trimethyl-2-cyclopenten-1-one	1064	MS	
	Phenols			
65	phenol[f]	961	MS, RI	
66	4-methylphenol	1031	MS	
67	2-methoxyphenol (*guaiacol*)	1063	MS, RI	smoked, sweet (low intensity)
68	4-hydroxy-3-methoxybenzaldehyde (*vanillin*)[c,d,e,f]	1366	MS, RI, GCO	vanilla-like
	Pyrazines			
51	2,5-dimethyl-3-(3-methylbutyl)pyrazine	1289	MS	
	Pyridines			
69	2-pyridinamine	803	MS	
	Pyrones			
70	3-hydroxy-2-methyl-4-pyrone (*maltol*)[d]	1086	MS, RI	
	Pyrroles			
71	2,3-dimethyl-1*H*-pyrrole	804	MS	
	Thiazoles			
72	4,5-dihydro-2-methylthiazole	1151	MS	

[a] Compound identified by GC/MS (MS) and/or by retention index on CP-Sil5-CB (RI) and/or by GC–olfactometry (GCO). [b] Compound previously identified in a dark semisweet chocolate before conching in ref *38*. [c] Compound previously reported as key odorant in bitter chocolate in ref *39*. [d] Compound previously reported as key odorant in milk chocolate in ref *22*. [e] Compound previously identified in chocolate (type not defined) in ref *40*. [f] Compound previously identified in milk chocolate in ref *19*.

ylbutanal (**8**), and phenylacetaldehyde (**13**), respectively derived from valine, leucine, isoleucine, and phenylalanine. The first three, with strong chocolate notes, most probably have a great impact on the flavor of dark chocolate (FD = 128−4096).

3-(Methylthio)propionaldehyde (**10**) is another Strecker aldehyde strongly perceived at the sniffing port (FD = 128 and 256 in samples A and B, respectively), despite its very low concentration (45 ppb in B). This compound, with a potato, worty flavor, derived from methionine, is usually perceived at levels close to 0.05 ppb in alcohol-free model solutions and near 0.1 ppb in alcoholic model solutions (*29*). It is a well-known precursor of sulfides such as dimethyl disulfide and dimethyl trisulfide after radical- or light-initiated degradation to methanethiol and acrolein (*30*−*32*), so it was not surprising that we also detected dimethyl trisulfide (**60**), with its characteristic onion flavor (threshold value = 0.1 ppb, *33*) by GCO (FD = 16 and 32 in samples A and B, respectively).

Nitrogen heterocycles, also derived from Maillard reactions, emerge here as probably the most interesting compounds of dark chocolate. 3(or 2),5-Dimethyl-2(or 3)-ethylpyrazine (**43**), 3,5-(or 6)-diethyl-2-methylpyrazine (**47**), acetylpyrrole (**55**), and furfurylpyrrole (**57**) provide praline and chocolate flavors (FD = 32−4096). The presence of an ethyl group in the two pyrazine compounds suggests a key role for alanine and/or its Strecker aldehyde, acetaldehyde, in chocolate flavor synthesis (*34*, *35*). The presence of four other heterocycles, with FD values between 128 and 4096, is worth stressing: 2,3-dimethylpyrazine (**37**), trimethylpyrazine (**40**), tetramethylpyrazine (**44**), and 2-isopropyl-3-methoxypyrazine (**45**). Tetramethylpyrazine (**44**), the most abundant pyrazine in our two dark chocolates with a concentration >6 ppm, exhibits a milk coffee−mocha−roasted flavor at the sniffing port. According to Koehler et al. (*36*), the odor threshold of tetramethylpyrazine in water is 10 ppm. This compound could thus reasonably influence the odor by synergic effects. Trimethylpyrazine (**40**), with an odor threshold of 9 ppm in water (*35*), leads to an FD value of 256 with its concentration of ∼2 ppm. 2,3-Dimethylpyrazine (**37**), with an odor threshold of 400 ppb (*37*) and a concentration of ∼600−800 ppb, gives a hazelnut tone to dark chocolate.

The most abundant alcohol, 2-phenylethanol (**5**), present at levels up to 7 ppm, gives a typical flowery note to dark chocolate extracts (FD = 16 and 128 in samples A and B, respectively).

Table 2 shows the other odors with high FD values (at least 64 in one sample). Among these, five chocolate−cocoa flavors have yet to be identified (mass spectra for **79** and **81** (**Figure 1**)).

Acidic Fraction. In the acidic fraction, exhibiting a phenolic, sweet-type odor very different from that of the neutral/basic fraction with its essentially chocolate flavor, 18 compounds were detected by FID/MS (**Table 3**). Only six of them were perceived at the sniffing port, even without dilution. The two most interesting flavors are given by Furaneol (**62**) and vanillin (**68**), the latter being added by the producer before conching. Furaneol was perceived as sweet, caramel-like in both samples.

Evolution of Odorant Compounds during Conching. As depicted in **Table 4**, most of the key odorants found in dark

Table 4. Concentrations of Identified Compounds (RI and MS Confirmations except for Those Marked by an Asterisk) in Chocolates A and B before and after Conching

		concn in A (ppb)		concn in B (ppb)	
no.	compound[a]	before conching	after conching	before conching	after conching
	Alcohols				
1	1-pentanol	121	145	67	58
2	2-heptanol	–[e]	–	–	–
3	benzyl alcohol	119	190	81	108
4	3,7-dimethyl-1,6-octadien-3-ol (*linalool*)	8516	5698	9630	5720
5	2-phenylethanol	839	1728	800	7277
	Aldehydes				
6	2-methylpropanal (*isobutanal*)	18787	13030	10450	9500
7	3-methylbutanal	19371	12454	11700	8400
8	2-methylbutanal	11951	10800	7800	7660
10	3-(methylthio)propionaldehyde (*methional*)	–	–	49	45
12	benzaldehyde	2098	2500	710	970
13	phenylacetaldehyde	7228	4468	3380	1660
14	nonanal	247	124	215	150
16	2-phenyl-5-methyl-2-hexenal	251	496	307	546
	Esters				
19	ethyl octanoate	32	100	8	15
20	2-phenylethyl acetate	198	102	53	41
	Furans				
21	dihydro-2-methyl-3(2*H*)-furanone	172	215	125	162
22	furancarboxaldehyde (*furfural*)	1292	1398	457	566
23	furfuryl alcohol (*furfurol*)	1247	1972	920	1238
24	1-(2-furanyl)ethanone (*acetylfuran*)	218	230	40	46
25	5-methyl-2-furancarboxaldehyde	215	325	104	184
62	2,5-dimethyl-4-hydroxy-3(2*H*)-furanone *(Furaneol)*	584	1034	1680	5670
	Hydrocarbons				
28	methylbenzene (*toluene*)	–	–	–	–
	Ketones				
29	2,3-butanedione (*diacetyl*)	857	170	1093	400
30	2-heptanone	111	241	120	176
	Phenols				
65	phenol	217	333	100	174
67	2-methoxyphenol (*guaiacol*)	66	99	75	85
	Pyrazines				
33	pyrazine	350	144	–	–
34	methylpyrazine	1932	2544	1028	1329
35	2,5-dimethylpyrazine	802	1434	44	94
36	ethylpyrazine	743	539	333	336
37	2,3-dimethylpyrazine	2023	802	1355	590
38	ethenylpyrazine	16	42	13	27
40	trimethylpyrazine	1659	2359	1242	1702
41	2-ethyl-3-methylpyrazine	311	342	294	345
43	3(or 2),5-dimethyl-2(or 3)-ethylpyrazine	893	1177	518	728
44	tetramethylpyrazine	6578	7983	4777	6135
47	3,5(or 6)-diethyl-2-methylpyrazine*[c]	121	172	97	152
49	2,5(or 6)-dimethyl-3-(2-methylpropyl)pyrazine*[d]	130	191	89	146
50	2,5-dimethyl-3-(3-methylbutyl)pyrazine*[d]	205	392	227	435
	Pyridines				
51	pyridine	658	1046	60	97
52	2-methylpyridine	–	–	–	–
	Pyrones				
70	3-hydroxy-2-methyl-4-pyrone (*maltol*)	4139	28379	820	4230
	Pyrroles				
55	1-(1*H*-pyrrol-2-yl)ethanone (*acetylpyrrole*)	1153	2850	1410	2137
57	1-(2-furanylmethyl)-1*H*-pyrrole (*furfurylpyrrole*)	39	64	16	46
58	1*H*-indole	55	184	86	151
	Sulfur Compounds				
59	dimethyl disulfide	106	111	27	38
60	dimethyl trisulfide	148	139	77	76

[a] Compound quantified in [b] 2-phenylethyl acetate equivalent, [c] 2,3-diethyl-5-methylpyrazine equivalent, [d] 3 (or 2),5-dimethyl-2 (or 3)-ethylpyrozine equivalent. [e] –, peak too low for a quantification or not quantified due to coelution.

chocolate were already present before the 70−80 °C heat treatment. All Strecker aldehydes were even partially lost during the conching process, due to evaporation and/or chemical reactions. On the other hand, 2-phenyl-5-methyl-2-hexenal (**16**)

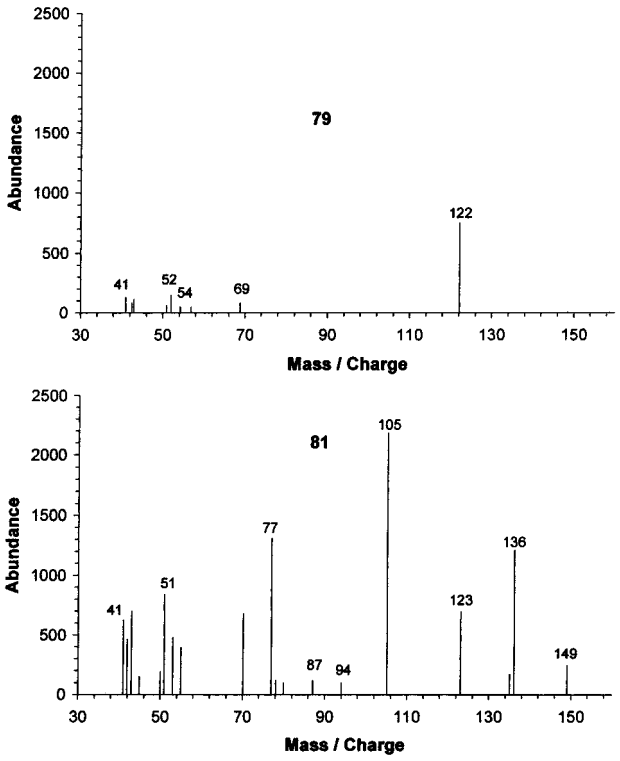

Figure 1. Available mass spectra of unidentified compounds with cocoa flavor: **79** and **81**.

(from 307 to 546 ppb in sample B) was produced in significant amounts, probably by aldol condensation of phenylacetaldehyde and 3-methylbutanal followed by dehydration. Although previously described by Van Praag (*16*) as a strong chocolate−cocoa flavor, this compound was not detected at the sniffing port in our experiments (**Table 1**). As previously suggested by Schnermann and Schieberle (*22*), Furaneol (**62**) and maltol (**70**) were also generated during conching of our two dark chocolates. With respect to heterocycles, only the concentrations of the least volatile compounds were significantly increased, particularly polysubstituted ethyl-, isobutyl-, and isopentylpyrazines (**43**, **47**, **49**, and **50**), tri- or tetramethylpyrazine (**40** and **44**), furans (**21**−**25**), and acetylpyrrole (**55**).

ACKNOWLEDGMENT

We are grateful to Ir. C. de Voghel (Belcolade) and Dr. Filip Arnaut (Puratos Group) for supplying chocolate. We also thank E. Bodart for expert technical assistance.

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Received for review October 29, 2001. Revised manuscript received January 29, 2002. Accepted January 29, 2002. C.C. is grateful to the "Grant FNRS-Spadel" for financial support.

JF0114177