Volatiles in Selected Commercial Breads[1]

L. M. Seitz,[2–4] O. K. Chung,[2,3] and R. Rengarajan[3]

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ABSTRACT

Selected types of commercial breads obtained from local markets, including white sandwich, Irish oatmeal, soft rye, hearty rye, sour dough, home-like white, and onion-basil, were analyzed for volatiles. Using a purge and trap instrument, volatiles were purged directly from fresh crumb and crust samples of each bread type, collected on a trap (Tenax-TA), and transferred to a gas chromatograph. Separated components were detected and identified using mass and infrared spectroscopic detectors. Many components were present in all of the bread samples, with relative amounts varying among bread types and crust and crumb samples of a given bread type. Alcohols were generally the most abundant, followed in approximate order by aldehydes, esters, ketones, acids, various aromatics, terpenes, and hydrocarbons. Flavor additives, such as limonene, carvone, and other related compounds, were found mostly in rye and onion-basil breads. Composition of volatiles from sour dough bread differed greatly from the other breads, especially in increased levels of aldehydes, acids, and certain esters. Unsaturated aldehydes, such as 2-hexenal and 2-heptenal, were most abundant in sour dough bread.

Because flavor is an important aspect of bread quality, there have been a number of studies on volatiles in breads, as summarized in two extensive reviews (Schieberle and Grosch 1991b, Grosch and Schieberle 1997). Essentially, studies on bread flavor have been conducted with laboratory-baked breads. In a recent study on laboratory-baked breads made from hard red winter and hard white winter wheats, we used a dynamic headspace (purge and trap) method coupled with gas chromatography, mass spectrometry, and infrared spectroscopy (GC-MS-IR) to identify volatiles (Chang et al 1995).

The main objective of the current research was to qualitatively compare volatile profiles, especially major volatiles, among different types of commercial breads and, in addition, determine whether flavoring agents were added to enhance the flavors of some bread types. We used dynamic headspace and GC-MS-IR methods similar to those described in Chang et al (1995) to collect, separate, and identify volatiles.

MATERIALS AND METHODS

Test 1

Five types of commercial breads were obtained at two times from a local market, including white sandwich (WHT), Irish oatmeal (IOM), soft rye (RYE(S)), hearty rye with caraway seeds (RYE(H)), and sour dough (SDO). Strips of crumb or crust of each bread type (≈30 g total) were quickly placed in a special glass sample tube and mounted directly on a purge and trap instrument (Model LSC 2000, Tekmar Co., Cincinnati, OH) equipped with a sample heater and capillary interface module. Each sample was heated to 60°C, and volatiles were purged with helium at 40 mL/min onto a trap (Tenax-TA, Tekmar). After an 8-min sample purge, an 8-min dry purge was performed to remove excess moisture from the trap. The collected volatiles were thermally desorbed (200°C for 4 min) from the trap and transferred to the capillary interface module, where they were cryofocused at –140°C at the top of the GC column. The cryofocused zone was heated at 200°C for 0.75 min before initiation of the analytical run.

A model 5890 Series II GC column coupled with a model 5965B IR detector (IRD) and a model 5970 mass selective detector (MSD) (Hewlett-Packard Co., Palo Alto, CA) were used to analyze bread volatiles. A column (50 m × 0.32 mm i.d. × 0.25-μm film thickness) (BPX5, Scientific Glass Engineering, Austin, TX) was used for separation. Column head pressure was 89.5 kPa (13.0 psi) at 50°C, which gave a helium flow rate of ≈1.7 mL/min. The flow rate was held constant by automatically increasing pressure as oven temperature increased. Oven temperature initially was held at 50°C for 2 min and was increased to 140°C at a rate of 7°C/min and to 230°C at a rate of 17.5°C/min. Effluent from the column first passed through the IRD and then into the MSD.

Compounds were identified by comparing, with the aid of a computer and careful visual examination, experimental infrared and mass spectra of compounds with standard spectra in two IR vapor-phase libraries (HP 59963A EPA and HP 59964A, Flavors and Fragrances) and in the HP 59943B Wiley PBM MS database, respectively. A mass spectral database from The National Institute of Standards and Technology (NIST/EPA/NIH, PC version 4.5, U.S. Department of Commerce) also was used when necessary. GC retention times were considered in compound identification, and authentic standards were utilized when possible. In addition, compound identifications were based on information (GC retention times, and MS and IR spectra of authentic standards) from many previous studies conducted in this laboratory on volatiles in grains, breads, and wetted millet samples (Seitz et al 1993, Chang et al 1995, Seitz 1995).

Because it was apparent that some compounds were only slightly separated, peaks recorded by MS and IR detectors were carefully evaluated by examining MS and IR spectra across the entire width of the peaks. Extracted ion (MS) and wavelength (IR) techniques were used to identify the exact locations of compounds in chromatograms. When necessary, because one compound was eluted close to another compound, the abundance of the compound in question was estimated by first integrating an extracted ion chromatogram generated with an ion unique to the compound and then converting the extracted ion response to total ion response based on the percentage of extracted ion represented in the mass spectrum of the compound.

Test 2

Test 2 was similar to Test 1, except an HP purge and trap unit (model G1901A-60500) was installed on the analysis system in place of the Tekmar model LSC 2000 and the GC column was a Supelcowax-10 column (30 m × 0.32 mm i.d. × 0.25-μm film

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[2] Research chemist and supervisory research chemist, respectively, USDA-ARS, U.S. Grain Marketing Research Laboratory, Grain Marketing and Production Research Center, Manhattan, KS 66502.

[3] Adjunct professors and research assistant, respectively, Department of Grain Science and Industry, Kansas State University, Manhattan 66506.

[4] Corresponding author. E-mail: larry@usgmrl.ksu.edu

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thickness) (Supelco, Bellefonte, PA). The HP purge and trap unit was modified by replacing the original nickel sample-path tubing with silicosteel tubing supplied as a kit (no. 14-6084-002, Tekmar) and by installing a mount heater (part 14-61-08-000, Tekmar). After installation of these parts, the HP unit was essentially the same as a Tekmar model 3000D purge and trap unit. The silicosteel tubing was necessary to prevent decomposition of sensitive compounds in heated portions of the instrument. The HP unit had a built-in moisture control system (MCS) for reducing the amount of water transferred to the GC column during desorption of the trap. The extent of moisture and other polar compounds removed by the MCS could be modified by changing the temperature of the MCS.

Samples analyzed in Test 2 consisted of home-like white (HLW) and SDO breads obtained from the same local market as in Test 1. An onion-basil bread obtained from a local specialty shop also was analyzed. Procedures for placing strips of bread in the glass sample tube, mounting on the purge and trap instrument, heating the sample, and use of Tenax-TA for trapping compounds were the same as for Test 1.

RESULTS AND DISCUSSION

Test 1

Many compounds were identified in crumb and crust samples from each bread type (Table I). Many aliphatic and some aromatic hydrocarbons, many of which could not be positively identified, also were found in bread samples. In the interest of brevity and probable low impact on bread flavor, these hydrocarbons were not included in Table I. The results are from one group of breads purchased on the same day. Analyses of another complete group of breads obtained at a different time but from the same store produced essentially the same results. Differences in volatiles among bread types were compared graphically, as illustrated by the MS total ion chromatograms from RYE(S) and SDO breads shown in Fig. 1.

TABLE I
Volatile Compounds of Commercial Breads Analyzed in Test 1

		Relative Abundance of Volatiles[b]									
		White Sandwich		Irish Oatmeal		Soft Rye		Hearty Rye		Sour Dough	
No., Compound	Ret. Time[a] (min)	Crumb	Crust	Crumb	Crust	Crumb	Crust	Crumb	Crust	Crumb	Crust
1, Ethanol	3.35	9,200	5,900	3,800	2,700	24,700	5,200	9,400	7,200	9,400	4,100
2, 2-Methylpropanal	3.53	510	190	1,100	740	35	440	710	860	420	7,300
3, 1-Propanol	3.63	120	36	170	170	210	250	140	210	160	140
4, 2,3-Butanedione	3.75	5,700	3,600	1,400	970	5,100	3,400	4,000	4,600	1,100	1,100
5, Ethyl acetate	3.87	180	41	120	80	53	160	350	220	3,200	2,200
6, 2-Butanone	4.09	110	41	98	74	73	79	120	68	340	400
7, 2-Methyl-1-propanol	4.21	11,100	19,300	17,600	13,000	24,400	18,700	26,600	21,600	3,600	3,300
8, 3-Methylbutanal	4.14	1,400	470	460	290	600	1,200	2,600	1,500	1,300	12,700
9, 2-Methylbutanal	4.37	200	75	290	170	110	380	570	630	140	5,600
10, 1-Penten-3-ol	4.65	18	31	3	1	1	10	28	9	1	18
11, 2,3-Pentanedione	4.71	270	110	120	70	120	90	890	280	0	550
12, Pentanal	4.73	86	90	81	65	130	170	530	420	4,500	2,700
13, Ethyl propionate	4.85	68	13	13	9	120	170	0	67	0	0
14, 3-Hydroxy-2-butanone	5.03	220	13	250	220	170	97	130	820	0	0
15, Acetic acid	5.17	7	18	30	33	270	380	1,400	1,400	730	3,500
16, 3/2-Methyl-1-butanol	5.39	3,400	17,900	10,700	8,900	22,000	15,800	21,600	21,400	19,900	12,400
17, Dimethyl disulfide	5.48	31	87	78	120	22	140	160	200	320	400
18, 1-Pentanol	5.99	210	190	47	36	120	46	150	130	180	230
19, Propanoic acid	6.00	150	230	240	220	260	290	750	800	480	440
20, Hexanal	6.37	470	300	230	200	550	580	840	780	30,200	15,200
21, 3-Hydroxy-2-pentanone	6.59	55	140	130	65	57	25	160	53	0	0
22, Ethyl lactate	6.69	140	280	100	160	180	51	270	170	640	490
23, 3-Furfural	6.80	3	1	2	1	14	9	19	12	57	49
24, Unknown (an oxazolidinone)	6.96	0	0	0	0	0	0	0	0	0	42
25, Methyl pyrazine	7.05	4	4	24	15	26	2	30	30	1	36
26, Unknown	7.06	0	0	0	0	0	0	0	0	0	11
27, Unknown (an oxazolidinone)	7.11	0	0	0	0	0	0	0	0	0	26
28, 2-Furfural	7.21	25	18	87	69	350	270	51	63	960	1,400
29, (*E*)-2-Hexenal	7.50	0	0	0	0	0	0	3	2	81	74
30, 1-Hexanol	7.82	400	390	160	97	470	290	630	570	230	220
31, 3-Methyl-1-butanyl acetate	7.90	0	0	0	0	0	0	0	0	320	120
32, 2-Furanmethanol	7.90	0	0	44	39	35	1	1	1	0	68
33, 2-Butylfuran	8.11	2	1	2	1	2	3	6	6	210	72
34, 2-Heptanone	8.17	6	4	5	3	18	12	21	19	87	78
35, Styrene	8.27	220	130	220	290	190	290	1,500	390	120	10
36, Heptanal	8.41	39	48	33	73	150	140	290	220	610	310
37, Methional	8.70	0	1	0	1	1	1	0	1	0	1
38, 1-(2-Furanyl)-ethanone	8.76	3	2	24	16	31	32	17	9	1	150
39, Methyl hexanoate	8.82	6	7	7	15	7	10	68	26	1	2
40, Ethylpyrazine + dimethylpyrazine	8.93	3	4	22	18	12	8	22	17	0	23
41, α-Pinene[c]	9.10	5	6	12	13	36	51	91	71	9	10
42, (*E*,*E*)-2,4-Hexadienal	9.30	0	0	0	0	0	0	0	0	33	27
43, Dihydro-2(3*H*)-furanone	9.33	0	0	0	0	0	0	0	1	0	3
44, 2-Ethyl-1-hexanol	9.47	0	0	0	0	0	0	0	0	35	41
45, (*E*)-2-Heptenal	9.76	9	13	6	9	30	32	21	41	680	440
46, 1-Heptanol	9.83	39	35	8	16	2	3	9	7	19	4

(continued on next page)

[a] Retention time.
[b] Peak areas from mass spectrometry, total ion chromatograms are reported.
[c] Relative retention times of terpenes and related compounds were consistent with those reported by Adams (1989).

Alcohols were generally the most abundant compounds detected. The most abundant alcohols included ethanol (no. 1 in Table I), 2-methyl-1-propanol (no. 7), and 3/2-methyl-1-butanol (no. 16). 1-Propanol (no. 3), 1-pentanol (no. 18), and 1-hexanol (no. 30) were less abundant (Table I and Fig. 2). Ethanol was the most abundant alcohol, but its abundance was underestimated due to inefficient collection on the trap (Tenax-TA has a low affinity for water and low molecular weight alcohols, according to a breakthrough volume chart available from Scientific Instrument Services, Ringoes, NJ). Compared to the other breads, SDO was low in 2-methyl-1-propanol, WHT was low in 3/2-methyl-1-butanol, and IOM was low in 1-pentanol (Fig. 2). The unsaturated alcohol 1-octen-3-ol (no. 52) was lowest in IOM and highest in SDO (Table I). The branched alcohol 2-ethyl-1-hexanol (no. 44) was found only in SDO (Table I). Otherwise, differences in alcohol abundance among bread types were fairly slight.

Aldehydes were generally most abundant in SDO. The saturated aldehydes that were present in nearly all of the samples included 2-methylpropanal (no. 2), 2- and 3-methylbutanal (nos. 8 and 9), pentanal (no. 12), hexanal (no. 20), heptanal (no. 36), octanal (no. 58), and nonanal (no. 78) (Table I and Fig. 3). Hexanal, which corresponds to the large peak at ≈6.7 min in the lower chromatogram in Fig. 1, was more than 20 times stronger in SDO than in the other breads. Pentanal, heptanal, octanal, and nonanal abundance was definitely highest in SDO, and 3-methylbutanal was higher in SDO and RYE(H) than in WHT and IOM. Levels of most unsaturated aldehydes, especially (*E*)-2-hexenal (no. 29), (*E*)-2-heptenal (no. 45), (*E*)-2-octenal (no. 74), (*E*,*E*)-2,4-hexadienal (no. 42), (*E*,*E*)-2,4-heptadienal (no. 62), (*E*,*E*)-2,4-nonadienal (no. 91), were highest in SDO (Fig. 3). The crust of SDO bread had greatly enhanced levels of some aldehydes (i.e., 2-methylpropanal [no. 2], 2- and 3-methylbutanal [nos. 8 and 9], 5-methylfurfural [no. 47],

Table I ***(continued from preceding page)***

		Relative Abundance of Volatiles[b]									
		White Sandwich		Irish Oatmeal		Soft Rye		Hearty Rye		Sour Dough	
No., Compound	Ret. Time[a] (min)	Crumb	Crust	Crumb	Crust	Crumb	Crust	Crumb	Crust	Crumb	Crust
47, 5-Methylfurfural	9.96	1	0	7	5	38	33	5	3	2	59
48, Sabinene[c]	10.01	2	1	3	3	39	25	60	40	1	1
49, Benzaldehyde	10.04	73	63	55	61	120	92	170	110	220	170
50, 1-Octen-3-one	10.13	2	2	2	3	4	8	6	10	41	72
51, Dimethyl trisulfide	10.14	4	20	10	18	0	14	14	18	3	40
52, 1-Octen-3-ol	10.15	47	24	7	8	23	13	26	16	54	62
53, 2,3-Octanedione	10.25	7	7	0	0	0	0	0	0	94	68
54, β-Myrcene[c]	10.27	2	2	2	2	87	40	130	93	7	5
55, 3-Methyl-5-oxazolidinone	10.34	0	0	0	0	0	0	0	0	1	22
56, 2-Pentylfuran	10.40	46	21	24	15	150	87	43	33	790	400
57, Ethyl hexanoate	10.48	17	11	3	2	29	14	34	24	44	14
58, Octanal	10.71	7	12	10	18	14	17	57	50	260	170
59, 1-Phellandrene[c]	10.78	9	6	6	6	370	270	400	330	3	5
60, Hexyl acetate	10.80	12	2	14	8	2	2	4	6	52	34
61, Methyl heptanoate	11.02	12	29	8	64	11	52	200	130	0	0
62, (*E*,*E*)-2,4-Heptadienal	11.03	2	1	1	0	4	2	2	3	24	22
63, 1-Limonene[c]	11.25	260	280	130	120	16,900	11,200	16,800	14,100	130	120
64, 1,4-Dichlorobenzene	11.17	7	3	15	10	3	5	15	7	8	20
65, 5-Ethyl-1-cyclopentene-carboxaldehyde	11.48	2	1	0	0	35	22	35	32	220	170
66, 3-Octen-2-one	11.50	2	1	1	0	7	5	12	6	20	22
67, *cis*-Ocimene[c]	11.58	0	0	0	0	4	13	30	20	0	0
68, Unknown ((*Z*)-2-octenal?)	11.70	0	0	0	0	0	0	0	0	10	27
69, Nitrohexane	11.74	1	1	1	1	1	1	1	1	1	1
70, Indene	11.79	18	36	13	93	24	73	460	230	1	0
71, Phenylacetaldehyde	11.86	12	8	5	4	16	15	11	22	8	250
72, Unknown	11.86	67	53	9	7	9	12	39	27	5	4
73, γ-Terpinene[c]	11.93	0	0	0	0	59	36	28	19	0	0
74, (*E*)-2-octenal	11.99	11	9	2	2	22	12	15	12	190	160
75, 4-Nonenal	12.70	0	0	0	0	0	0	0	0	1	53
76, Fenchone[c]	12.74	0	0	0	0	110	92	11	10	0	0
77, Linalool[c]	12.80	0	0	0	0	32	17	34	21	0	0
78, Nonanal	12.90	36	41	30	73	61	45	150	130	410	270
79, 1-Chloro-4-methoxybenzene	13.13	0	0	0	9	0	0	27	20	0	0
80, Methyl octanoate	13.22	0	0	0	4	0	4	0	12	0	0
81, 2-Phenylethanol	13.55	16	26	9	14	22	8	10	10	30	15
82, 2-Ethyl-hexyl acetate	13.68	19	16	6	3	19	20	21	15	3	28
83, Unknown aromatic ketone	14.12	1	5	0	26	2	6	63	70	0	0
84, (*E*)-2-nonenal	14.14	9	9	7	3	17	6	10	16	18	49
85, Ethyl octanoate	14.68	68	35	22	18	67	31	86	56	26	10
86, Unknown	14.82	0	0	0	0	92	54	120	80	0	0
87, Estragole[c]	14.95	0	0	0	0	1,000	510	9	17	9	8
88, Decanal	15.02	8	11	14	21	0	0	0	0	19	60
89, (*Z*)-Dihydrocarvone[c]	15.13	0	0	0	0	1,400	740	1,200	1,100	0	0
90, (*E*)-Dihydrocarvone[c]	15.26	0	0	0	0	320	190	420	330	0	0
91, (*E*,*E*)-2,4-Nonadienal	15.45	0	0	0	0	0	0	0	0	34	30
92, Iso-dihydrocarveol[c]	15.63	0	0	0	0	31	13	80	63	0	0
93, Carvone[c]	15.92	4	64	3	10	1,100	5,500	17,600	12,200	170	87
94, Perillaldehyde[c]	16.58	0	0	0	0	24	7	34	17	0	0
95, (*E*)-Anethole[c]	16.60	0	0	0	0	88	34	7	3	1	1
96, (*E*,*E*)-2,4-Decadienal	16.98	6	5	6	3	12	5	8	6	3	8
97, Unknown (a terpene aldehyde)	17.05	0	0	0	0	1	1	2	1	3	11

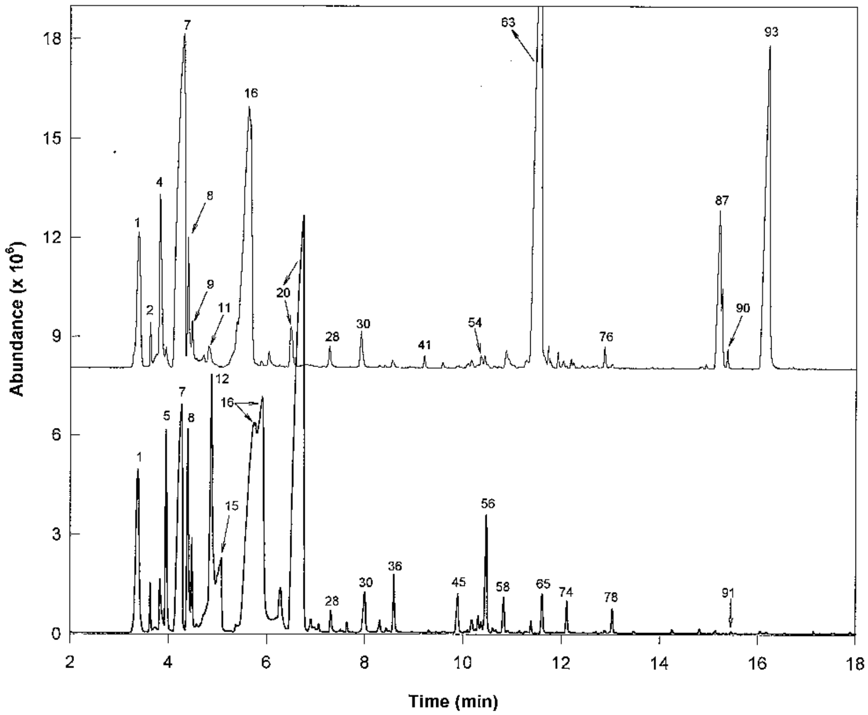

Fig. 1. Comparison of total ion chromatograms of volatiles from crumb of soft rye (upper curve) and sour dough (lower curve) breads. Numbers on selected peaks indicate compounds listed in Table I.

benzeneacetaldehyde [no. 71], and 4-nonenal [no. 75]) compared to the crumb of SDO and the crumb and crust of the other breads.

Figure 4 shows the relative amounts of some esters, acids, ketones, and other oxygenated compounds found in the bread samples. SDO had the highest levels of ethyl acetate (no. 5), ethyl lactate (no. 22), and 2-pentylfuran (no. 56). Acetic and propanoic acid contents (nos. 15 and 19) were relatively high in SDO and RYE(H) and low in WHT compared to the other breads (Fig. 4 and Table I). The prominent ketones were 2-butanone (no. 6), 2,3-butanedione (no. 4) and 2,3-pentanedione (no. 11). 2,3-Pentanedione was absent in SDO crumb, whereas 2-butanone was relatively high in SDO crumb and crust (Table I). 2-Furfural (no. 28) was lowest in WHT. Hydroxy-ketones (3-hydroxy-2-butanone [no. 14], 3-hydroxy-2-pentanone [no. 21]) and ethyl propionate (no. 13) were present in all the breads, except the crumb and crust of SDO. Also, ethyl propionate was not found in RYE(H) crumb. SDO crumb and crust contained higher levels of 1-octen-3-one (no. 50), 2,3-octanedione (no. 53), 3-octen-2-one (no. 66), and 2-heptanone (no. 34) than the crumb and crust of the other breads (Table I). The ester 3-methyl-1-butanyl acetate (no. 31) was found only in SDO crumb and crust (Table I).

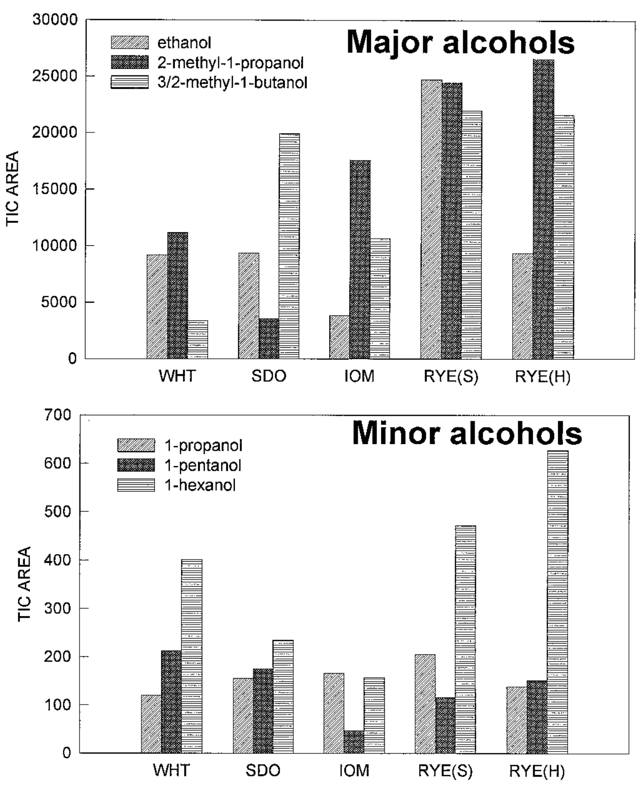

Fig. 2. Major and minor alcohols found in crumb of commercial breads: WHT = white sandwich, SDO = sour dough, IOM = Irish oatmeal, RYE(S) = soft rye, RYE(H) = hearty rye.

Terpene compounds were definitely most prevalent in the rye breads (Fig. 5). It was apparent from the high abundance of limonene and carvone (the large peaks at ≈11.4 and 16.2 min, respectively, nos. 63 and 93 in the upper chromatogram in Fig. 1) that these compounds were flavor additives in rye breads. These compounds are the main constituents of caraway fruit oil, of which carvone is the character impact compound (Boelens 1991). Limonene was present in low levels in the other bread types. Flavor additives used in the two rye breads were apparently different, as evidenced by different levels in the crumb and crust of RYE(S) and RYE(H) (i.e., indene [no. 70], fenchone [no. 76], estragole [no. 87], carvone [no. 93], and (*E*)-anethole [no. 95]) (Table I and Fig. 5). Also, the levels of some aldehydes and acids was higher in RYE(H) than in RYE(S) (Table I). Detection of 1-chloro-4-methoxybenzene (no. 79) in RYE(H) crumb and crust was somewhat surprising. We recently found that this compound is associated with moldy-musty grain (*unpublished data*), but there was no apparent moldiness in the breads we analyzed.

Volatile content of crumb and crust samples from the commercial breads appeared to be more similar than crumb and crust samples from breads baked in a laboratory for a previous study (Chang et al 1995). Laboratory breads were probably baked longer and had firmer, darker crusts than commercial breads. With the commercial breads, it was difficult to cleanly separate crust from crumb. There were some differences in the levels of two sulfur compounds found in the commercial breads, as shown in Fig. 6. The abundance of dimethyl disulfide was always higher than that of dimethyl trisulfide in both crumb and crust, and levels of both compounds in all bread types were always lower in crumb than in crust. Other differences between crumb and crust were noted (i.e., the high content of benzeneacetaldehyde [no. 71], 2-methylpropanal [no. 2], 2- and 3-methylbutanal [nos. 8 and 9], and 1-(2-furanyl)-ethanone [no. 38] in SDO crust; Table I). In general, fewer pyrazines were found in the commercial breads than in the laboratory-baked breads analyzed in a previous study (Chang et al 1995).

We identified some compounds not previously reported in breads. An unsaturated aldehyde (no. 65) found at 11.49 min was most prevalent in SDO and also was found at moderate levels in the rye breads (Table I). The compound was tentatively identified as 5-ethyl-1-cyclopentenecarboxaldehyde, based on the following evidence. The same or a similar compound was found in flavor volatiles from cooked pork and chicken (Werkhoff et al 1993). Peaks in the IR spectrum at 2,803, 2,717, 1,705, and 1,620 cm^{-1} clearly indicated that this compound was an aldehyde. Carbonyl absorbance at 1,705 cm^{-1} plus a smaller peak at 1,620 cm^{-1} agreed with an aldehyde group conjugated to a carbon-carbon double bond in a ring structure. Weak absorbance at 3,053 cm^{-1} indicated hydrogen bonded to unsaturated carbon. The mass spectrum consisted of significant masses, *m/z* (% abundance), at 39 (26), 41 (26), 51 (7), 53 (9), 55 (10), 65 (19), 67 (100), 77 (11), 79 (10), 81 (14), 91 (9), 93 (7), 95 (47), 109 (17), 123 (3), and 124 (28, apparent M^+). The major masses can be explained by loss of a methyl group to give mass 109, loss of the ethyl or aldehyde group to give mass 95, and loss of ethyl and carbonyl groups to give mass 67. We believe the lack of major mass 81 suggests the compound is not a dimethylcyclopentenyl compound, and low intensity of mass 123 may be due to the ethyl group inhibiting loss of hydrogen from the adjacent aldehyde group. A minor unknown compound (no. 72) was detected at 11.86 min and had *m/z* 69, 83, 97, 125, 153, and 168; it appears to be similar to other minor compounds we have noted in raw grains. The rye breads contained an unidentified compound (no. 86), observed at 14.82 min (*m/z* 69, 91, 93, 95, 109, 124, 137 [base peak], 151, and 152), that was apparently associated with added flavorings. The crust of SDO contained a compound (no. 55) at 10.34 min that we identified from MS and IR spectra as 3-methyl-5-oxazolidinone (Table I), which had major masses at 45 (100), 56 (44), 73 (78), and 101 (48, apparent M^+). Because the compound was very close to 2-pentylfuran (no. 56), it was impossible to clearly discern all IR absorbances from the oxazolidinone, but it was clear that the carbonyl absorbance at 1,828 cm^{-1} was consistent with the assigned structure. Mass and IR spectra indicated two other oxazolidinones (nos. 24 and 27) at 6.96 and 7.11 min in SDO bread crust (Table I). A minor unknown terpene aldehyde (no. 97) with the aldehyde group that conjugated to a carbon-carbon double bond (shown by IR) was found at 17.05 min in the chromatograms for RYE(S), RYE(H), and SDO (Table I).

Test 2

Volatile compounds observed in the crumb of HLW and SDO breads and the crumb and crust of an onion-basil bread are shown in Table II. In general, many of the compounds found in Test 2 also were found in test 1, especially the major alcohols, aldehydes, and ketones. Ethanol, 1-propanol, 2-methyl-1-propanol, and 3-methyl-1-butanol levels were definitely highest in HLW. Again, saturated and unsaturated aldehydes were clearly more prevalent in crumb of SDO than in the other breads. Hexanal abundance was very high in SDO, as it was in Test 1. The 5-ethyl-1-cyclopentenecarboxaldehyde compound, along with essentially all of the other aldehydes that were most abundant in SDO in Test 1, were found in SDO in Test 2. Levels of ethyl acetate, ethyl lactate, 2,3-octa-

TABLE II
Volatile Components of Breads Analyzed in Test 2

		Relative Abundance of Volatiles[b]			
	Ret. time[a]	HLW	SDO	Onion-Basil	
Compound	(min)	Crumb	Crumb	Crumb	Crust
Propanal	1.40	0	250	110	590
2-Methylpropanal	1.49	4,100	3,600	1,200	9,300
Butanal	1.67	0	520	0	60
2-Methylfuran	1.69	0	0	0	580
Ethyl acetate	1.71	810	3,000	490	960
2-Butanone	1.84	0	0	0	400
3-Methylbutanal	1.86	2,700	6,700	1,300	7,500
Ethanol	2.10	22,200	12,700	10,600	11,600
2,3-Butanedione	2.24	4,200	0	2,600	4,700
Pentanal	2.27	0	8,700	0	0
A terpene	2.60	0	0	120	130
Toluene	2.78	89	54	19	44
1-Propanol	2.90	4,900	1,100	2,400	2,500
2,3-Pentanedione	3.06	41	830	490	930
Dimethyl disulfide	3.11	43	51	69	220
Hexanal	3.26	1,900	37,800	540	890
2-Methyl-1-propanol	3.69	39,900	7,800	14,600	17,500
3-Methyl-1-butanyl acetate	3.79	0	320	0	0
2-Butylfuran	3.86	20	310	2	30
Enal+dimethylbenzene	3.93	0	130	0	0
l-Phellandrene	4.23	0	0	1,500	1,400
1-Butanol	4.27	170	260	0	0
1-Penten-3-ol	4.46	230	280	0	0
Heptanal	4.66	90	1,000	0	0
Limonene	4.70	300	1,400	860	1,300
1,8-cineole	5.02	0	0	1,300	970
3-Methyl-1-butanol	5.30	50,600	20,400	21,200	25,600
(*E*)-2-Hexenal	5.34	40	142	5	14
2-Pentylfuran	5.37	440	2,000	0	0
Ethyl hexanoate	5.56	0	55	0	0
Dimethylthiophene	5.72	0	0	50	77
Styrene	5.81	24	45	110	110
1-Pentanol	5.82	440	1,400	88	180
1-Methyl-4-(1-methyl-ethyl)-benzene	6.04	0	0	210	260
Methylpyrazine	6.06	38	8	58	92
3-Hydroxy-2-butanone	6.46	8,700	1,000	5,200	8,600
An enal	6.62	0	73	0	0
1-Octen-3-one	6.65	0	27	0	0
Unknown	6.66	0	0	38	0
(*E*)-2-Heptenal	7.00	150	1,000	10	29
2,3-Octanedione	7.08	6	200	0	6
Ethyl lactate	7.43	24	660	2	1
1-Hexanol	7.55	790	1,100	230	300
Dimethyl trisulfide	7.85	6	6	6	36
2-Chloroethanol	7.98	0	0	83	110
Nonanal	8.14	100	310	0	0
3-Octen-2-one	8.45	0	100	0	0
5-Ethyl-1-cyclopentene-carboxaldehyde	8.53	27	580	1	3
(*E*)-2-Octenal	8.79	38	610	0	0
3-Furfural	8.88	0	40	0	0
Ethyl octanoate	8.93	200	25	96	90
1,4-Dichlorobenzene	9.00	5	31	2	2
1-Octen-3-ol	9.24	66	110	0	0
Methional	9.27	1	0	0	1
1-Heptanol	9.30	46	0	0	0
Acetic acid	9.34	47	1,200	510	800
2-Furfural	9.46	330	640	64	140
2-Ethyl-1-hexanol	9.90	130	0	0	0
(*E,E*)-2,4-heptadienal	9.90	0	130	0	0
Alcohol (unidentified)	9.99	47	0	0	0
1-(2-Furanyl)-ethanone	10.12	61	27	0	0
Camphor	10.13	0	0	61	67
Benzaldehyde	10.36	340	380	61	76
(*E*)-2-Nonenal	10.59	86	50	10	29
Linalool	10.90	0	0	470	540
Unknown	11.26	0	0	0	24
Methyl 2-cyanopro-panoate	11.41	74	0	0	0
(*Z*)-Dihydrocarvone	11.71	0	0	62	48
(*E*)-Dihydrocarvone	12.01	0	0	110	81
Phenylacetaldehyde	12.35	21	14	9	18
2-Furanmethanol	12.73	17	43	30	76
Estragole	12.79	0	0	2,100	2,500
Carvone	13.69	0	0	110	81
Methyl cyanoacetate	13.98	88	0	0	0

[a] Retention time.
[b] Peak areas from mass spectrometry, total ion chromatograms. HLW = home-like white; SDO = sour dough.

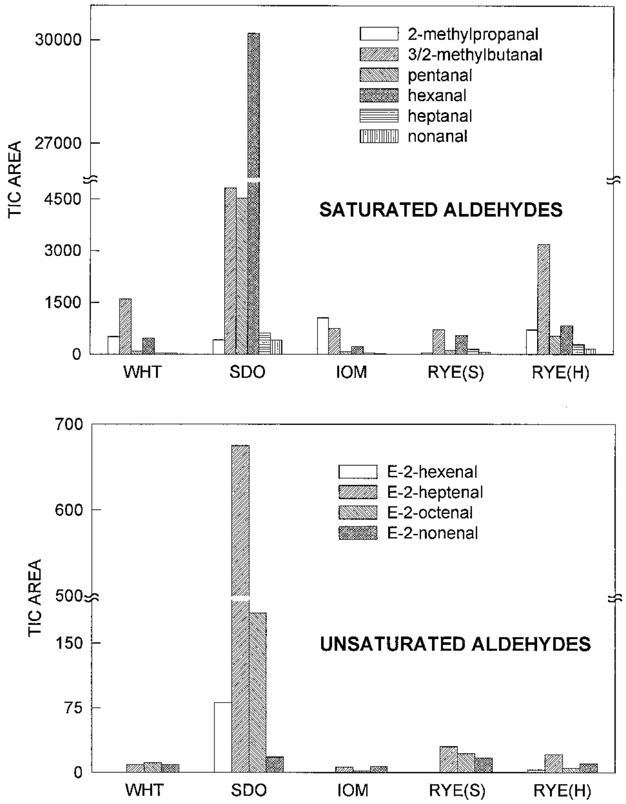

Fig. 3. Major saturated and unsaturated aldehydes found in crumb of commercial breads: WHT = white sandwich, SDO = sour dough, IOM = Irish oatmeal, RYE(S) = soft rye, RYE(H) = hearty rye.

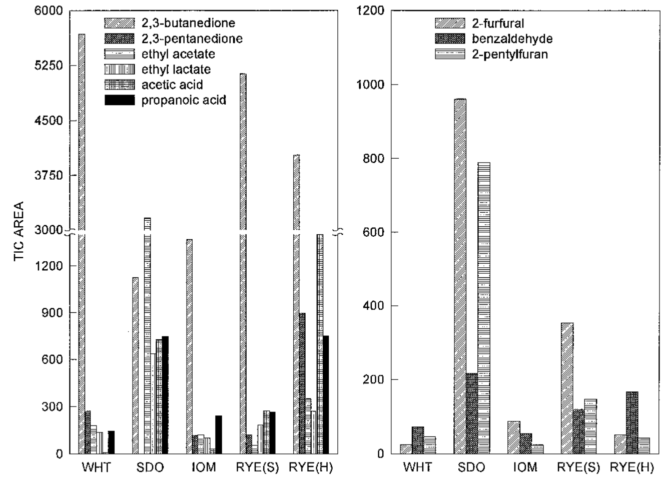

Fig. 4. Some esters, acids, ketones, and other oxygenated compounds found in crumb of commercial breads: WHT = white sandwich, SDO = sour dough, IOM = Irish oatmeal, RYE(S) = soft rye, RYE(H) = hearty rye.

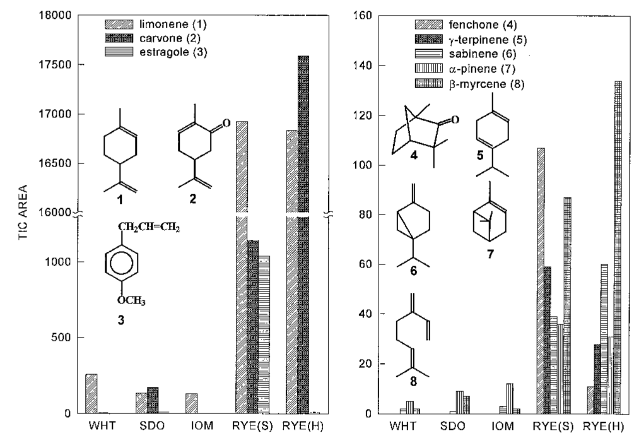

Fig. 5. Terpenes and apparent flavor additives found in crumb of commercial breads: WHT = white sandwich, SDO = sour dough, IOM = Irish oatmeal, RYE(S) = soft rye, RYE(H) = hearty rye.

dione, and 2-furfural were also high in SDO compared to the other breads in Test 2.

In SDO bread crumb, several compounds were found in Test 2 that were not found in Test 1 (i.e., propanal, butanal, 1-butanol, 3-hydroxy-2-butanone, 2,3-pentanedione, and 2-furanmethanol). However, 2,3-pentanedione, and 2-furanmethanol were observed in SDO crust in Test 1. The moderately polar GC column used in Test 2 may have been more effective in first cyrofocusing and then separating these compounds than the relatively nonpolar column used in Test 1. On the other hand, some compounds found mostly at low levels in Test 1 were not detected in Test 2, including 2-butanone, 2,3-butanedione, 2-ethyl-1-hexanol, propanoic acid, 2-phenylethanol, 2-heptanone, octanal, decanal, (*E,E*)-2,4-hexadienal, (*E,E*)-2,4-nonadienal, (*E,E*)-2,4-decadienal, and α-pinene. The differences in compounds detected could be due to changes in the purge and trap instruments, GC columns, and MSD sensitivity settings, as well as to differences in the bread samples purchased at different times.

The onion-basil bread contained some compounds that were not found in the HLW and SDO breads. Some of these compounds were probably from added flavoring agents (i.e., *l*-phellandrene, 1,8-cineole, dimethylthiophene, linalool, dihydrocarvones, estragole, and carvone). Basil oils contain 1,8-cineole and linalool (Boelens 1991). The source of 2-chloroethanol was unclear, but its presence in onion-basil bread was confirmed by IR and MS. Dimethylthiophene may be associated with onion flavor. Differences in volatiles between crumb and crust of onion-basil bread were generally slight, which agrees with the results of Test 1. Compounds with notably higher levels in crust than crumb included most of the aldehydes, 2-methylfuran, 2-butanone, and dimethyl disulfide (Table II).

CONCLUSIONS

The commercial breads we analyzed had many compounds in common, but the relative levels of the compounds depended greatly on bread type. Alcohols were generally the most abundant, followed in approximate order by aldehydes, esters, ketones, acids, various aromatics, terpenes, and hydrocarbons. Flavor additives in rye and onion-basil breads were relatively high in abundance compared with most volatiles formed naturally in the baking process. Compared with the other breads, increased levels of aldehydes (especially 2-hexenal and 2-heptenal), acids, and certain esters were observed in SDO.

We detected compounds reported to be important in bread flavor (i.e., compounds with high flavor-dilution factors, such as 2-phenylethanol, (*E*)-2-nonenal, (*E,E*)-2,4-decadienal, methional, 3-methylbutanal, 3-methyl-1-butanol, and phenylacetaldehyde) (Grosch and Schieberle 1997). However, some compounds previously reported to have fresh bread-like aromas, such as 2-acetyl-1-pyrroline and 6-acetyltetrahydropyridine (Schieberle and Grosch 1991b, Grosch and Schieberle 1997), were not detected. This might have occurred because 1) the compounds were present below the sensitivity level of our instrument, 2) we analyzed smaller samples (≈30 g) than were used in previous studies (up to 1 kg), and 3) the breads we analyzed differed significantly from breads previously studied. In studies reported by others, low concentration was considered the reason 2-acetyl-1-pyrroline was not observed in headspace volatiles analyzed by GC (Schieberle and Grosch 1992). In addition, the concentration of 2-acetyl-1-pyrroline in bread crust has been reported to decrease rapidly after baking (i.e., by 47 and 89% after 3 and 96 hr, respectively) (Schieberle and Grosch 1992).

We also did not find evidence for epoxyalkenals, such as *trans*-4,5-epoxy-(*E*)-2-decenal reported by Schieberle and Grosch (1991a), any of the hydroxy-furanones mentioned in a recent review (Grosch and Schieberle 1997), or the unsaturated ketone (*E*)-β-damascenone reported by Schieberle and Grosch (1994) to be present in a sour dough rye bread. It was apparent from the results shown in Table I that the rye breads we analyzed were not sour dough breads.

The dynamic headspace method we used was a convenient technique that provided good representation of relative concentrations of most volatiles in bread samples. We believe that data from this type of study could be used to develop instrumentation for monitoring various steps in breadmaking processes (i.e., progress in dough fermentation and baking of bread in ovens).

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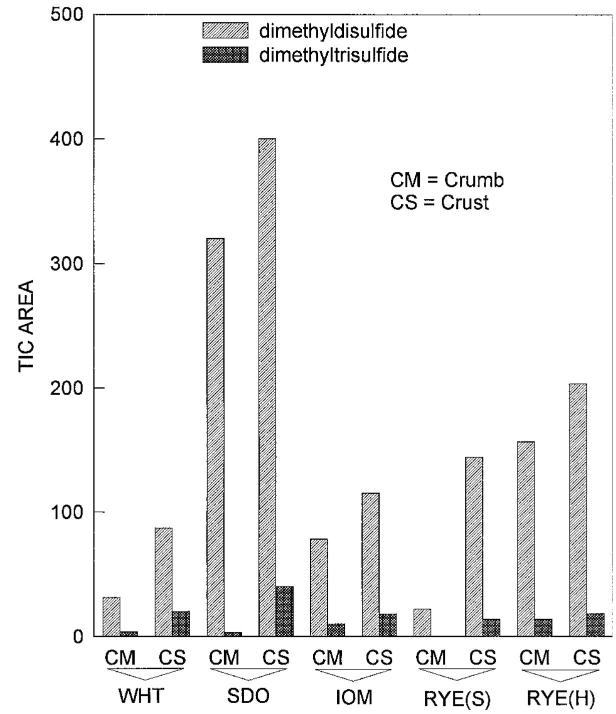

Fig. 6. Sulfides found in crumb and crust from commercial breads: WHT = white sandwich, SDO = sour dough, IOM = Irish oatmeal, RYE(S) = soft rye, RYE(H) = hearty rye with caraway seeds.

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