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Flavor Components of Roasted Almond

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Roasted almond volatiles were separated into basic, carbonyl and non-carbonyl fractions. Each fraction was analyzed by combination gas chromatography-mass spectrometry. Twenty-five compounds, in addition to eighteen known components, were identified. Many of the components identified were considered to contribute to the overall flavor. 2,5-Dimethyl-4-hydroxy-3(2H)-furanone, which was identified from methanol extract of roasted almond, seemed to make the largest contribution to the sweet aroma of roasted almond.

In a previous paper,[1] we reported the isolation of roasted almond volatiles and identification of the components of the basic fraction. Seventeen pyrazines and 2-formyl pyrrole were, identified and considered to contribute to the roasted flavor. However, much still remains to be learned about the compounds contributing to the flavor of roasted almond.

Basic, carbonyl and non-carbonyl fractions of roasted almond volatiles were analyzed and many new compounds were identified which were considered to contribute to the roasted and burnt character of roasted almond flavor. Other components contributing to the sweet character of almond flavor seemed to remain in the residual aqueous layer after extraction of the basic fraction. To investigate the water-soluble components, methanol extract from almond oleoresin was prepared and analyzed after fractionation by silica gel column chromatography. This paper reports the results obtained.

EXPERIMENTAL

Material and the method of isolation of roasted almond volatiles used in this investigation were the same as described in the previous paper[1] and the yield of aroma concentrate was 1.24 g (0.11%) from 1.15 kg of the acetone extract (oleoresin), from 2.5 kg of roasted almond.

Fractionation of roasted almond volatiles. The basic fraction was isolated by the same method described in the previous paper[1] (0.14 g from 1.01 g of aroma concentrate) and has a popcorn-like roasted flavor.

The experimental procedure for the fractionation into carbonyl and non-carbonyl fractions was the usual method, as described by Teïtelbaum.[2] Non-carbonyl fraction was washed with isopentane before extraction with ether to remove glycerides and had a roasted and burnt flavor (Yield 0.13 g). Carbonyl fraction (0.04 g) had an oily and raw soybean-like odor and isopentane extract (0.25 g) had an oily odor.

Preparation of methanol extract. Seven-hundred and seventy grams of the acetone extract (oleoresin) was extracted four times with 200 ml each of methanol. The combined extract was washed with 500 ml of hexane to remove glycerides, dried with sodium sulfate and concentrated on a rotary evaporator at 20～30°C under reduced pressure (100～200 mmHg), leaving 4 g of residual reddish brown liquid. The residue had a strong sweet roasted almond flavor.

Fractionation of methanol extract. Four grams of methanol extract was subjected to silica gel column chromatography using hexane and ether as developing solvents, as shown in Table I (Silica gel; Wako Junyaku Co. C-2, 50 g). The yield and aroma of each fraction are both shown. The total amount of concentrates from each fraction amounted to 2.92 g.

Analysis by GC-MS. A mass spectrometer (Hitachi Ltd. RMU-4) combined with gas chromatography (Hitachi Model K 53) was used for analysis. Three fractions of volatiles were analyzed, using a 45 m×0.5 mm (*i.d.*) Carbowax 20 M open tubular column. The gas chromatograms are shown in Fig. 1.

Fractions 3, 5, 8, 10, 11, 13, 14, 15, 16 and 18 from methanol extract were analyzed using a column 1 m×3 mm (*i.d.*) packed with 23% Silicone SE-30 coated on Shimalite W (60～80 mesh). Four typical gas chromatograms, containing characteristic compounds of the methanol extract, are shown in Fig. 2.

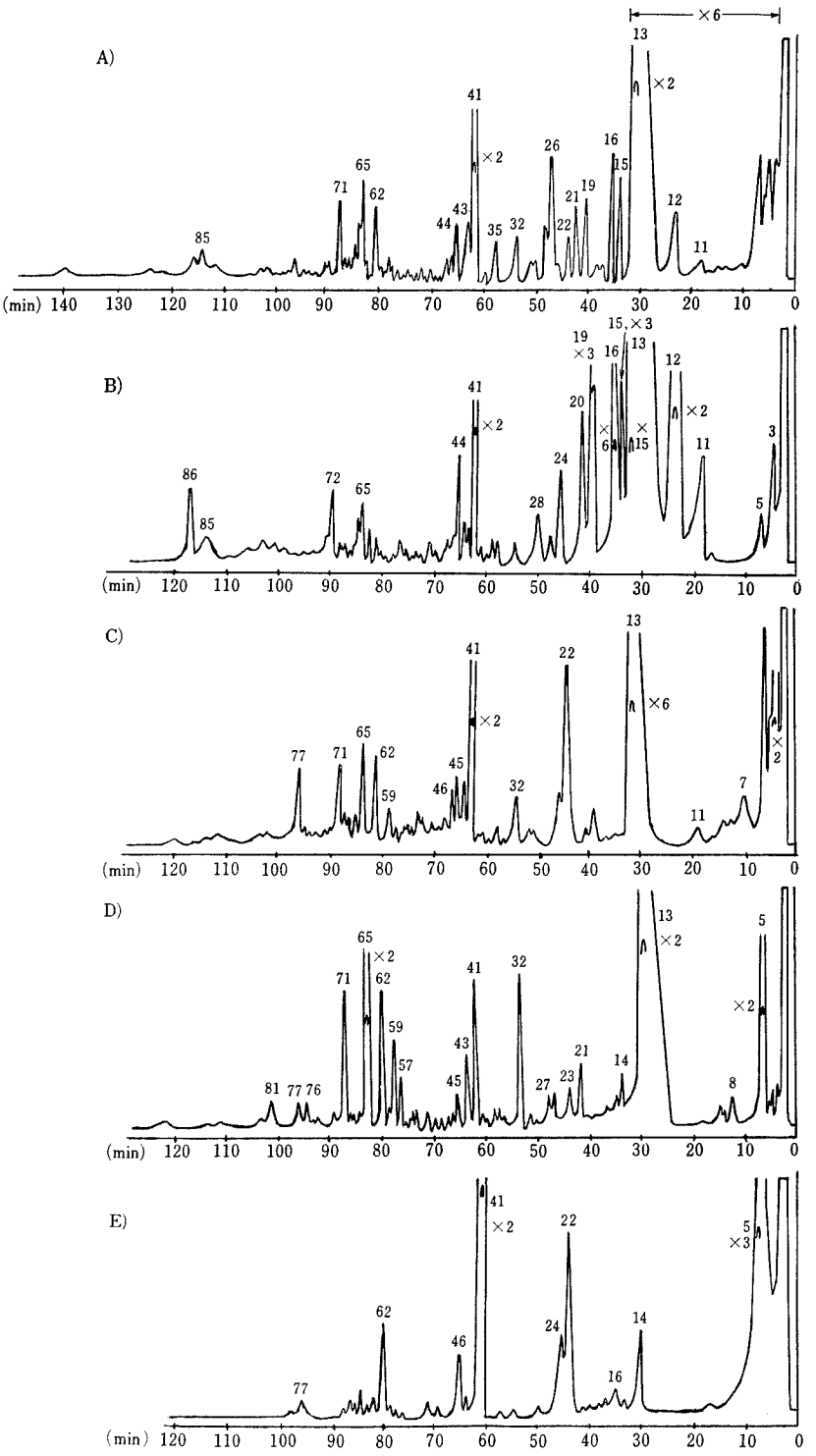

FIG. 1. Gas Chromatograms of Roasted Almond Volatiles.

A) Total volatiles; B) Basic fraction; C) Neutral fraction; D), Carbonyl fraction; E), Non-carbonyl fraction.

Column: Golay column, Carbowax 20 M, 0.5 mm (*i.d.*) × 45 m. Column Temp.: 50°C (10 min hold) $\xrightarrow{1°C/min}$ 75°C $\xrightarrow{2°C/min}$ 180°C. Flow rate: 4 ml/min (He).

TABLE I. SOLVENT SYSTEMS USED FOR SILICA GEL COLUMN CHROMATOGRAPHY OF METHANOL EXTRACT, AND YIELD AND AROMA OF EACH FRACTION

Fr. No.	Developing solvent Hexane (ml)	Ether (ml)	Yield[a] (%)	Aroma
1	50	0	27.7	Roasted peanut-like, oily
2	50	0	23.9	〃
3	50	0	10.2	〃
4	50	0	9.3	Pop corn-like
5	50	0	5.9	〃
6	50	0	4.6	〃
7	50	0	3.0	Sweet and roasted
8	50	0	1.9	Sweet and sponge cake-like
9	50	0	1.6	〃
10	100	0	0.9	〃
11	100	0	1.0	Strong sweet
12	54	6	1.6	〃
13	54	6	1.2	Sweet and pound cake-like
14	126	14	2.3	〃
15	77	33	1.7	Sweet and burnt
16	70	30	0.5	Burnt
17	70	30	0.4	〃
18	50	50	1.3	Slightly burnt
19	100	100	1.0	〃

[a] After concentration.

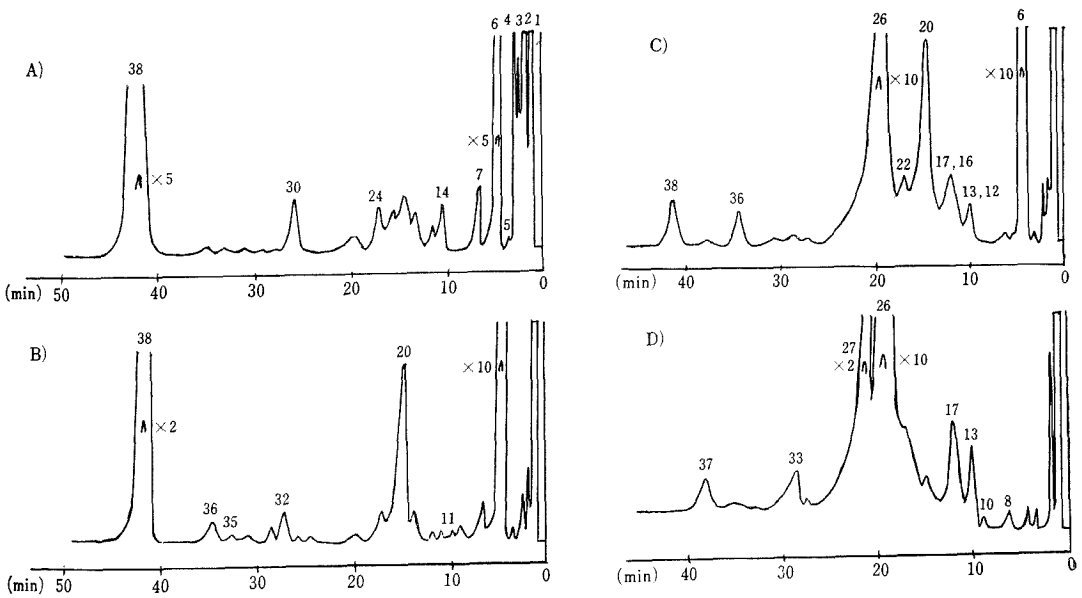

FIG. 2. Gas Chromatograms of Methanol Extract Separated by Silica Gel Column Chromatography.

A) Fraction 8; B) Fraction 11; C) Fraction 15; D) Fraction 18.
Column: 23% Silicone SE 30 on Shimalite W (60~80 mesh), 3 mm (*i.d.*)×1 m, stainless steel. Column Temp.: 100°C (5 min hold) $\xrightarrow{3°C/min}$ 180°C. Flow rate: 30 ml/min (He).

TABLE II. IDENTIFIED COMPONENTS AND THEIR CONTENTS IN ROASTED ALMOND VOLATILES

(Reference to Fig. 1)

Peak No.	Content (Peak area %)	Identified comp.	M^+	MS data *m/e* (%)	Evidence besides MS
5	4.1	4-Methyl-3-penten-2-one[2]	98	55(100), 83(84), 43(54), 98(41)	
7	3.0	*n*-Butanol[7]	74	56(100), 43(75), 41(65)	
8	3.6	Furfurylmethylether[6]	112	81(100), 53(45), 112(33), 82(22)	
9	1.9	2-Methyltetrahydrofuran-3-one[7]	100	43(100), 72(25), 100(18)	
11	5.5	Methylpyrazine[b]	94	94(100), 43(65), 67(56), 58(24)	
12	11.0	2,5 and 2,6-Dimethylpyrazine[b]	108	42(100), 108(74), 39(32), 81(15)	Rt
13	/	Diacetonealcohol	116	43(100), 58(30), 59(28), 101(7)	IR, NMR
15	5.0	2-Methyl-6-ethylpyrazine[b]	122	121(100), 122(70), 39(21), 94(18)	
16	6.1	Trimethylpyrazine[b]	122	42(100), 122(64), 39(25), 81(17)	Rt
19	3.1	2,5-Dimethyl-3-ethylpyrazine[b]	136	135(100), 136(90), 42(76), 56(36)	
20	0.1	2,6-Dimethyl-3-ethylpyrazine[b]	136	135(100), 136(68), 39(65), 42(60)	
21	1.4	Furfural	96	96(100), 95(96), 39(77), 43(19)	Rt
22	0.8	Decanal[7]	156	57(100), 43(48), 41(42), 55(29)	
24	0.2	2,5-Diethyl-3-methylpyrazine[b]	150	149(100), 150(83), 39(47), 42(34)	
25	4.3	2,6-Diethyl-3-methylpyrazine	150	149(100), 150(92), 135(90), 122(84)	
26		2-Acetylfuran[b]	110	95(100), 110(40), 43(32), 39(28)	Rt
27	0.8	Benzaldehyde	106	77(100), 106(84), 105(81), 51(43)	Rt
28	0.6	2,5-Dimethyl-3-vinylpyrazine[a]	134	42(100), 133(74), 134(53), 39(53)	
29	0.6	Furfurylacetate	140	43(100), 81(45), 98(19), 140(19)	Rt
32	1.1	5-Methylfurfural[9]	110	110(100), 109(86), 53(63), 43(43)	
33	0.3	Methylfuroate	126	95(100), 96(48), 126(31), 81(28)	Rt
34	0.1	Ethylfuroate[a]	140	83(100), 58(99), 140(61)	
36	0.7	1-Methyl-2-acetylpyrrole[a]	123	123(100), 43(99), 94(60), 53(53)	
37	0.4	1-Methyl-2-formylpyrrole[8]	109	109(100), 108(73), 53(52), 80(30)	
38	0.6	Acetylpyrazine[3]	122	43(100), 80(49), 53(40), 122(34)	
39	trace	5-Methyl-6,7-di-	134	119(100), 134(51),	Rt

Table II. (Continued)

Peak No.	Content (Peak area %)	Identified comp.	M^+	MS data *m/e* (%)	Evidence besides MS
		hydro-5H-cyclo-pentapyrazine[b]		133(25), 39(21)	
40	0.1	6,7-Dihydro-5H-cyclopentapyrazine[b]	120	120(100), 119(78), 66(25), 93(20)	
41	3.2	Furfurylalcohol	98	98(100), 41(87), 39(66), 81(59)	Rt
42	0.1	2(or 3),5-Dimethyl-6,7-dihydro-5H-cyclopentapyrazine[b]	148	133(100), 148(43), 53(19), 147(18)	
43	2.3	5-Methyl-2-acetylpyrazine[a]	136	43(100), 94(57), 136(48), 93(47)	
44	1.5	2-Methyl-6,7-dihydro-5H-cyclo-pentapyrazine[b]	134	134(100), 133(91), 66(60), 39(55)	
45		1-Acetyl-2-methylpyrrole[a]	123	80(100), 53(43), 43(37), 123(32)	
46	0.7	5-Methylfurfuryl-alcohol[a]	112	95(100), 44(87), 94(78), 112(73)	
47	0.8	6-Ethyl-2-acetyl-pyrazine[a]	150	43(100), 107(46), 150(42), 108(33)	
49	0.1	1-Ethyl-2-formyl-pyrrole[6]	123	123(100), 122(98), 53(66), 94(52)	
50	0.3	2,3-Dimethyl-6,7-dihydro-5H-cyclo-pentapyrazine[b]	148	148(100), 44(58), 147(55), 43(55)	
51	0.1	2,4-Decadienal[2]	152	81(100), 41(40), 55(22), 67(21)	
52	0.1	1-Furfurylpyrrole[7]	147	81(100), 147(30), 53(30)	
53	0.1	α-Ionone	192	121(100), 93(88), 136(71), 43(48)	Rt
55	0.2	2-Acetyl-5-methoxypyrazine[a]	152	109(100), 43(70), 95(40), 57(39)	
56	0.1	2-Acetyl-6-allylpyridine[a]	161	146(100), 161(22), 160(18), 53(17)	
57	0.1	*o*-Hydroxyacetophenone[a]	136	43(100), 55(88), 121(82), 136(49)	
59	0.2	2-Phenylbutenal[7]	146	117(100), 115(77), 146(75), 91(48)	
60	0.1	β-Ionone	192	177(100), 43(58), 41(25), 192(8)	Rt
61	0.2	5-Methylquinoxaline[b]	144	144(100), 117(63) 76(38), 44(32)	
62	0.1	2-Acetylpyrrole	109	94(100), 109(83), 66(68), 39(38)	Rt
63	0.1	2,5-Diacetylpyrazine[a]	164	122(100), 43(88), 121(27), 164(26)	
64	0.3	2-(2′-Furyl) pyrazine[b]	146	146(100), 43(44), 93(38), 57(20)	Rt
65	1.6	2-Formylpyrrole[b]	95	95(100), 94(68), 66(67), 39(49)	Rt
67	0.4	3-Methyl-2-(2′-	160	45(100), 44(77),	Rt

Table II. (Continued)

Peak No.	Content (Peak area%)	Identified comp.	M+	MS data *m/e* (%)	Ebidence besides MS
		furyl) pyrazine[b]		93(35), 160(35)	
71	0.1	5-Methyl-2-formylpyrrole[7]	109	109(100), 108(84), 53(57), 80(55)	
72	0.3	5-Vinyl-2-formylpyrrole[a]	121	121(100), 43(56), 45(45), 44(41)	
76	0.2	1-Furfuryl-2-formylpyrrole[6]	175	81(100), 53(30), 175(24), 45(23)	
77	0.9	2,4-Dimethoxy-3-hydroxypyridine[a]	155	95(100), 155(84), 73(70), 54(67)	
81	0.4	2-Methoxy-3-hydro-oxy-4-formylpyridine[a]	153	55(100), 153(95), 122(89), 95(87)	
85	1.8	5-Hydroxymethyl-furfural	126	97(100), 126(77), 69(62)	Rt

[a] These compounds were tentatively identified.
[b] These compounds were previously reported.[1]
[1]~[9] denote the appropriate reference numbers.

RESULTS AND DISCUSSION

The compounds found in roased almond volatiles are listed in Table II. Eighteen compounds among them were reported in our previous work.[1] Twenty-five new compounds, including ten furanic compounds and five pyrroles, identified by comparison of their mass spectra with reference spectra[2~9] seemed to contribute to the roasted and burnt flavor. Fourteen were tentatively identified from their mass spectra.

To investigate the water-soluble compounds of the characteristic sweet aroma, which could not be isolated by carbon dioxide distillation, methanol extract was prepared. The methanol extract, which had a powerful sweet aroma of roasted almond, was subjected to silica gel column chromatography to remove high-molecular compounds. The new components found in the ten fractions are listed in TableIII.

2,5-Dimethyl-4-hydroxy-3(2H)-furanone, identified by matching the mass spectrum with published data,[10] has a strong sweet aroma and is considered to contribute to the characteristic sweet aroma of roasted almond. This compound was first prepared by Hodge *et al.* from rhamnose,[11] was synthesized by several groups[12,13] and has been isolated from pineapple[14,15] and beef broth.[10]

4-Hydroxy-2-hydroxymethyl-5-methyl-3(2H)-furanone, identified by matching the MS, NMR and IR spectra with the spectra given by Shaw *et al.*,[16] has a week burnt odor and has been isolated from degradation products of carbohydrates,[16,17] pyrolysis products of Amadori compounds[18,19] and browning products of dehydrated orange juice.[20] The structure of this compound was proposed by Mills *et al.* to be 2,3-dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one.[18]

Peak No. 38, having a weakly burnt and boiled red beanlike odor, could not be determined from the MS and IR data.

As can be seen in Tables II and III, fifty-five compounds have been identified and twenty have been tentatively confirmed by mass spectrometry. These compounds accounted for more than 90% of the flavor constituents in roasted almond.

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TABLE III. NEW COMPONENTS FOUND IN THE TEN FRACTIONS FROM METHANOL EXTRACT

Peak No.	Content[b] (Peak area %)	Compound	M+	MS data *m/e*	Evidence
2	/	*n*-Hexane	86	43(100), 57(86), 41(59), 56(40)	MS, Rt
3	/	3-Methylcyclopentane[7]	84	56(over), 41(over), 69(over), 42(100)	MS
4	/	*n*-Heptane[7]	100	43(100), 41(47), 57(42), 71(38)	MS
5	/	Toluene[7]	92	91(100), 92(52), 43(17), 39(17)	MS
8	trace	Methylallylketone[a]	84	55(100), 43(47), 84(43), 42(38)	
10	〃	2,3-Pentandione[7]	100	43(100), 57(34), 44(32), 100(12)	MS
11	〃	1-Methyl-3-ethylbenzene[7]	120	105(100), 120(42), 91(28), 77(17)	MS
12	〃	Phenol	94	94(100), 66(23), 65(22), 39(22)	MS, Rt
13	0.2	N-Acetylpropylamine[a]	87	43(100), 87(24), 44(9), 55(6)	
16	trace	Cyclotene	112	112(100), 55(66), 69(64), 56(34)	MS, Rt
17	0.3	Unknown	—	43(100), 71(98), 39(40), 57(27)	
20	2.7	2,5-Dimethyl-4-hydroxy-3(2H)-furanone[10]	128	43(100), 57(52), 128(40), 85(22)	MS
22	0.1	Hexanol[7]	102	43(100), 102(19), 56(17), 57(15)	MS
24	1.3	β-Angelicalactone[16]	98	83(100), 55(41), 43(40), 98(10)	MS
26	1.7	4-Hydroxy-2-hydroxymethyl-5-methyl-3(2H)-furanone[16]	144	43(100), 44(65), 101(27), 144(25)	MS, IR, NMR
32	0.2	*p*-Hydroxybenzaldehyde[a]	122	121(100), 43(84), 39(30), 41(22)	
33	0.2	2-Carboethoxypyrrole[a]	139	43(100), 39(31), 94(28), 139(23)	
35	0.6	2-Acetyl-3-hydroxy-5-methyl-6,7-dihydro-5H-cyclopentapyrazine[a]	192	133(100), 41(76), 132(72), 108(67)	
36	0.5	Pyrrylthiophenylketone[a]	177	111(100), 43(68), 83(54), 55(54)	
37	trace	Unknown	179	179(100), 134(45), 135(45), 106(44)	
38	20.4	Unknown	179	150(100), 179(62), 41(51), 53(41)	

[a] These compounds were tentatively identified.
[b] Approximate amounts were estimated as the total of A×B÷100, where A: Peak area (%) of each fraction. B: Yield (%) of each fraction.
[7]~[16] denote the appropriate reference numbers.

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