

Quantitative Comparison of Volatile Flavor Compounds in Deep-Roasted and Light-Roasted Sesame Seed Oil

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The effect of roasting degree on the formation of volatile compounds in sesame seeds was investigated. Light- and deep-roasted sesame seed oils were steam distilled under reduced pressure, and volatiles from the distillate were separated by an adsorptive column method. The recoveries of total volatiles were 9726 and 2014 ppb from deep- and light-roasted oils, respectively. The relative amount of monoalkylpyrazines decreased in contrast to the increases of di- and trialkylpyrazines with increase in the degree of roasting. 1*H*-Pyrrole-2-carboxyaldehyde, the most abundant pyrrole, was the only volatile that decreased in deep-roasted oil. 4,5-Dimethylisothiazole, 4,5-dimethylthiazole, 2-propyl-4-methylthiazole, and 2-butyl-5-methylthiazole increased their relative amounts in deep-roasted oil. Hexanal, (*E*)-2-heptenal, and (*E,E*)-2,4-decadienal occurred in almost the same levels. Guaiacol and 2-furanmethanethiol increased from 32 to 321 ppb and from 6 to 40 ppb, respectively, in deep-roasted oil.

Keywords: Volatiles; flavor compounds; sesame seed oil; roasting

INTRODUCTION

In the manufacture of sesame seed oil, sesame seeds are roasted by various techniques to develop a characteristic roast odor. The roasting process, therefore, is the most important step in sesame seed oil manufacturing because of its great influence on the odor quality and intensity.

Several studies have been carried out concerning flavor components of sesame seed oil (Kinoshita and Yamanishi, 1973; Manley et al., 1974; Soliman et al., 1975, 1985, 1986). In addition, our previous paper (Shimoda et al., 1996) described further identification and quantification of volatile flavor components in a commercial sesame seed oil.

The present paper deals with the effect of roasting degree on the formation of volatile flavor compounds in sesame seeds.

MATERIALS AND METHODS

Materials. Two types of sesame seed oil produced from light-roasted and deep-roasted sesame seeds were obtained from Ajinomoto Co., Ltd. (Tokyo, Japan). Deep-roasted oil was produced from sesame seeds roasted at 180 °C for 10 min, and light-roasted oil was produced from sesame seeds roasted at 150 °C for 10 min. These were evaluated as the products with characteristic flavor attributes and without any defects by three professional testers.

Isolation of Volatile Flavor Compounds. Three hundred milliliters of deionized water was added to the sesame seed oil (100 mL). Volatiles were separated from the dispersion by a combination of steam distillation under reduced pressure (~90 mmHg) and column concentration (Shimoda et al., 1996). Ten microliters of 1% 3-phenyl-1-propanol/diethyl ether solution was added as an internal standard to 60 mL of ethyl ether eluate of volatiles. Then, the eluate was dried over anhydrous sodium sulfate and concentrated to about 200 μ L.

Capillary Gas Chromatography (GC) and Capillary Gas Chromatography/Mass Spectrometry (GC/MS).

GC analysis was carried out on a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector (FID) and connected to a Shimadzu Chromopak C-R5A. Separation was achieved on a 60 m \times 0.25 mm i.d. fused silica capillary column that was coated with cross-linked polyethylene glycol 20M (PEG 20M) to a film thickness of 0.25 μ m (DB-Wax; J&W Scientific, Folsom, CA). The oven temperature was programmed from 50 to 230 °C at 2 °C/min (60 min hold). The injector and detector temperatures were 230 °C. The helium carrier gas flow rate was 22 cm/s, with an injection splitter at a split ratio of 30:1. Retention indices were estimated in accordance with a modified Kovats method (Van den Dool and Kratz, 1963). GC/MS analysis was carried out on a JEOL Automass 50 mass spectrometer interfaced to a Hewlett-Packard 5890 Series II gas chromatograph. The column and chromatographic conditions were the same as described for GC analysis. Other details were described in our previous paper (Shimoda et al., 1996).

RESULTS AND DISCUSSION

The yields of total volatiles were 9726 ppb from deep-roasted oil and 2014 ppb from light-roasted oil. These quantitative values are only approximate concentration since they were calculated from peak area to internal standard and related to the weight of oil products. Table 1 includes 20 pyrazines, 9 pyrroles, 4 pyridines, 9 thiazoles, 7 furans, 10 aliphatic aldehydes, 3 alcohols, 2 ketones, 3 fatty acids, 8 aromatic compounds, and 6 miscellaneous compounds. The ratio of the amount of volatile component in deep- and light-roasted oil showed that almost all of the volatiles increased by 2–7 times in deep-roasted oil.

Pyrazines have been well characterized as the volatiles contributing to the roasted and aromatic odor in high-temperature-processed food products (Belitz and Grosch, 1987a,b; Vernin, 1982). They were the chemical family with the highest proportion, comprising about 45% of the total volatiles in both oils. The compositional ratios of total pyrazines were in almost the same levels, but the ratios of mono-, di-, and trialkyl-substituted

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Table 1. Effect of Roasting Degree on the Formation of Volatile Compounds in Sesame Seeds

Kovats index ^a	compound	content (ppb), deep-roasted ^b	composition (%), light-roasted ^c	deep/light ratio ^d
Pyrazines				
1271	2-methylpyrazine	779	195	4.0
1329	2,5-dimethylpyrazine	735	158	4.7
1334	2,6-dimethylpyrazine	383	82	4.7
1338	2-ethylpyrazine	153	35	4.4
1352	2,3-dimethylpyrazine	101	23	4.4
1390	2-ethyl-6-methylpyrazine	237	47	5.0
1397	2-ethyl-5-methylpyrazine	212	40	5.3
1410	2,3,4-trimethylpyrazine	346	65	5.3
1438	2-ethenylpyrazine	46	12	3.8
1449	3-ethyl-2,5-dimethylpyrazine	542	104	5.2
1462	2-ethyl-3,5-dimethylpyrazine	154	45	3.4
1479	2-(1-methylpropyl)pyrazine	23	5	4.6
1490	2-ethenyl-6-methylpyrazine	55	9	6.2
1494	2,3-diethyl-5-methylpyrazine	22	4	5.5
1496	3,5-diethyl-2-methylpyrazine	92	21	4.4
1535	2-methyl-6-(1-propenyl)pyrazine	47	8	5.7
1543	2-isopropenylpyrazine	48	8	6.3
1627	2-acetylpyrazine	178	35	5.1
1671	(<i>E</i>)-2-methyl-6-(1-propenyl)pyrazine	51	11	4.6
1680	2,3-dimethyl-5-isopentylpyrazine	28	tr ^e	
	total amount of pyrazines	4232 (43.5)	907 (45.0)	4.7
Pyrroles				
1183	2-ethyl-1 <i>H</i> -pyrrole	19	3	5.6
1505	1 <i>H</i> -pyrrole	70	16	4.4
1569	3-methyl-1 <i>H</i> -pyrrole	26	tr	
1598	1-methyl-1 <i>H</i> -pyrrole-2-acetonitrile	40	7	5.6
1610	1-ethyl-1 <i>H</i> -pyrrole-2-carboxyaldehyde	29	5	6.0
1657	1-(1-methyl-1 <i>H</i> -pyrrol-2-yl)ethanone	22	tr	
1970	1-(1 <i>H</i> -pyrrol-2-yl)ethanone	71	17	4.2
2030	1 <i>H</i> -pyrrole-2-carboxyaldehyde	127	143	0.9
2058	methyl pyrrole-2-carboxylate	33	tr	
	total amount of pyrroles	437 (4.5)	191 (9.5)	2.3
Pyridines				
1603	1-(2-pyridinyl)ethanone	16	tr	
1643	4-pyridinyl acetate	67	13	5.2
1782	methyl 4-pyridinecarboxylate	55	10	5.5
2110	2-pyridinemethanol	58	9	6.4
	total amount of pyridines	196 (2.0)	32 (1.6)	6.1
Thiazoles				
1281	4-ethylthiazole	35	7	5.1
1285	2,4-dimethylthiazole	58	12	4.8
1326	2,5-dimethylthiazole	115	20	5.8
1400	4,5-dimethylisothiazole	39	8	5.1
1409	4,5-dimethylthiazole	110	22	5.0
1467	4-methyl-5-ethylthiazole	23	5	5.1
1486	2-ethyl-5-methylthiazole	28	8	3.5
1695	2-propyl-4-methylthiazole	123	21	5.9
1738	2-butyl-5-methylthiazole	45	5	9.0
	total amount of thiazoles	575 (5.9)	107 (5.3)	5.4
Furans				
1228	2-pentylfuran	50	8	6.1
1456	2-furfural	51	10	5.1
1521	2-furanmethyl acetate	75	13	5.8
1574	5-methyl-2-furfural	220	47	4.7
1664	furfuryl alcohol	316	49	6.4
1686	1-(5-methyl-2-furanyl)-1-propanone	70	10	7.0
1837	α -methyl- α -vinyl-2-furanacetaldehyde	25	8	3.3
	total amount of furans	807 (8.3)	145 (7.2)	5.6
Aliphatic Aldehydes				
987	pentanal	36	15	2.4
1086	hexanal	263	59	4.5
1095	2-methyl-2-butenal	31	15	2.1
1186	heptanal	30	7	4.4
1291	octanal	26	6	4.2
1430	(<i>E</i>)-2-heptenal	82	13	6.3

Table 1 (Continued)

Kovats index ^a	compound	content (ppb), deep-roasted ^b	composition (%), light-roasted ^c	deep/light ratio ^d
1528	(<i>E</i>)-2-octenal	48	16	3.0
1706	(<i>E,E</i>)-2,4-nonadienal	32	12	2.7
1766	(<i>E,Z</i>)-2,4-decadienal	35	tr	
1811	(<i>E,E</i>)-2,4-decadienal	154	36	4.3
	total amount of aliphatic aldehydes	737 (7.6)	179 (8.9)	4.1
Aliphatic Alcohols, Ketones, and Acids				
1185	2-heptanone	31	6	5.6
1354	hexanol	79	12	6.6
1393	2-nonanone	62	11	5.6
1562	octanol	26	9	2.8
1834	hexanoic acid	32	8	3.9
1953	heptanoic acid	32	5	6.7
1977	dodecanol	69	12	5.8
2062	octanoic acid	86	tr	
	total amount of aliphatic alcohols, ketones and acids	417 (4.3)	63 (3.1)	6.6
Aromatic Compounds				
1512	benzaldehyde	240	53	4.5
1651	1-phenylethanone	142	24	5.9
1846	guaiacol	321	32	10
1868	benzenemethanol	69	16	4.3
1893	benzeneethanol	47	10	4.9
1922	α -ethylidenbenzeneacetaldehyde	47	tr	
2169	2-methoxy-5-(1-propenyl)phenol	33	7	4.9
2200	1-(3-methoxyphenyl)ethanone	177	37	4.8
	total amount of phenyl compounds	1076 (11.1)	179 (8.9)	6.0
Miscellaneous Compounds				
891	ethyl acetate	45	12	3.8
1194	<i>d</i> -limonene	27	7	4.0
1617	3,5,5-trimethyl-2-cyclopenten-1-one	37	tr	
1647	2,3-dihydro-1 <i>H</i> -indole	37	7	5.4
1693	3-formylthiophene	38	6	6.1
1802	2-furanmethanethiol	40	6	6.3
	total amount of miscellaneous compounds	224 (2.3)	38 (1.9)	5.9
Unknown Compounds				
	total amount of 28 compounds	1024 (10.5)	173 (8.6)	5.9
	total	9726 (100)	2014 (100)	4.8

^a Modified Kovats indices calculated for DB-Wax capillary column on the GC system. ^b Deep-roasted oil. ^c Light-roasted oil. ^d Ratio of the amount of volatile compound in deep and light sesame seed roasted sesame seed oil. ^e tr, trace concentrations of <3 ppb.

pyrazines changed from 13.8%, 18.6%, and 11.8%, respectively, in light-roasted oil to 11.8%, 18.9%, and 12.3%, respectively, in deep-roasted oil. Thus, the relative amount of monoalkylpyrazines decreased in contrast to the increases of di- and trialkylpyrazines with increase in the degree of roasting. For example, the relative amounts of 2-ethyl-6-methylpyrazine, 2-ethyl-5-methylpyrazine, and 3-ethyl-2,5-dimethylpyrazine, which were considered to be important contributors to the aroma of sesame seed oil (Shimoda et al., 1996), increased in deep-roasted oil.

Pyrroles, which impart burnt and earthy characteristic odors, comprised 9.5% in light-roasted oil, but in deep-roasted oil their relative amounts decreased to 4.5%. Of nine pyrroles, the most abundant one, 1*H*-pyrrole-2-carboxyaldehyde, was the only volatile that decreased in deep-roasted oil, although the methyl ester of its oxidized compound, methyl pyrrole-2-carboxylate, occurred in a measurable level only in deep-roasted oil. Since 1*H*-pyrrole-2-carboxyaldehyde (Aldrich product) smelled sweet and somewhat medicinal, its distinctive decrease in deep-roasted oil could greatly influence the

aroma characteristics of sesame seed oil. Other pyrroles increased more than 4.2 times in deep-roasted oil.

Pyridines were not a principal chemical class in amount, but all increased more than the average increasing ratio (4.8) of all volatiles between light- and deep-roasted oils.

All thiazoles listed in Table 1 were alkyl-substituted thiazoles, which have green, nutty, and vegetable-like odors (Ho and Jin, 1985). Nine thiazoles comprised 5.3% of the total amount of volatiles in light-roasted oil; on the other hand, their amount increased to 5.9% in deep-roasted oil. Thiazoles increased more than 4.8 times, except for 2-ethyl-5-methylthiazole. 4,5-Dimethylisothiazole, 4,5-dimethylthiazole, and 2-propyl-4-methylthiazole, which smelled peanut-like (Shimoda et al., 1996), increased their relative amounts in deep-roasted oil. It should be, further, noted that 2-butyl-5-methylthiazole, with a large alkyl substituent, increased as much as 9.0 times in deep-roasted oil.

Furans, which generally impart caramel-like and roasted odors (Ohloff and Flament, 1978), comprised 7.2% in light-roasted oil and 8.3% in deep-roasted oil.

Large increases of 1-(5-methyl-2-furanyl)-1-propanone, an important contributor to sesame seed oil (Shimoda et al., 1996), and 2-pentylfuran in deep-roasted oil could contribute to its intense roasted odor.

Aliphatic aldehydes with fewer than six carbon atoms have green and grassy odors, but those with more carbon atoms have oily, fatty, fried, or tallowy odors (Belitz and Grosch, 1987a,b). The relative amount of aldehydes decreased from 8.9% to 7.6% in deep-roasted oil. Especially, the amounts of pentanal and 2-methyl-2-butenal decreased to about half. The most abundant aldehydes, hexanal, (*E*)-2-heptenal, and (*E,E*)-2,4-decadienal, however, occurred in almost the same ratios.

The total amount of aliphatic alcohols, ketones, and acids increased from 3.1% to 4.3%. Although fatty acids with fewer than five carbon atoms could not be isolated by the present technique, quantitative values in Table 1 indicated that the fatty acids with the larger number of carbon atoms increased more with increasing degree of roasting. Both 2-heptanone and 2-nonaone, oxidative cleavage products of unsaturated fatty acids, increased by 5.6 times in deep-roasted oil.

Aromatic compounds increased from 8.9% to 11% in deep-roasted oil. Guaiacol, which has a smoky odor with an extremely low threshold value, 0.02 ppt in water (ASTM, 1978), increased from 32 to 321 ppb in deep-roasted oil. This distinctive increase is responsible for the smoky odor in deep-roasted oil. With the other aromatic compounds, such an extraordinary increase was not observed.

Of the miscellaneous compounds, 2-furanmethanethiol, an important flavor compound with an intense coffee-like odor (Ohloff and Flament, 1978), increased from 6 to 40 ppb in deep-roasted oil. This thiol compound could contribute to the complicated odor of deep-roasted oil.

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