ANALYTICAL SCIENCE & TECHNOLOGY
Vol. 9, No. 4, 1996
Printed in the Republic of Korea

Analysis of Volatiles in Sesame Oil Collected by Simultaneous Distillation/Extraction(SDE) and Dynamic Headspace Sampling (DHS)

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(Received June 27, 1996)

연속수증기증류법(SDE)과 동적헤드스페이스법(DHS)에 의한 참기름 중의 향기성분의 분석

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(1996. 6. 27. 접수)

Abstract : The flavor compounds of the oil from roasted sesame seeds were collected by simultaneous steam distillation/extraction(SDE) and dynamic headspace sampling(DHS) and were analyzed using a gas chromatograph equipped with a flame ionization detector and connected into a mass spectrometer. Among the flavor compounds collected by the SDE method, 46 compounds were identified. They consisted of 6 alcohols, 6 aldehydes, 5 ketones or acids, 4 furans or phenols, 12 pyrazines, 4 pyridines or thiazoles, and others.

Thirty six compounds were identified by DHS and many of them were the same as those identified by the SDE method. However, some compounds such as 1-hexanol, pentanal, and dimethylsulfide were identified only by the DHS method.

요약 : 참기름 중의 향기성분을 연속수증기증류법(SDE)과 동적헤드스페이스법(DHS)으로 포집하여 GC와 GC-MSD로 동정하였다. SDE로 분석하였을 때 alcohol 6종, aldehyde 6종, ketone 및 acid류 5종, furan 및 phenol류 4종, pyrazine 화합물 12종, pyridine 및 thiazole류 4종, 기타 9종으로 총 46종이 확인되었다. DHS로 분석한 경우 alcohol 3종, aldehyde 6종, ketone, furan 및 phenol류 6종, pyrazine류 12종, pyridine 및 thiazole 4종, 기타 5종으로 모두 36종이 확인되었다. 대부분의 화합물이 SDE법에서 분리된 것이었으나 1-hexanol, pentanal, dimethylsulfide 등은 DHS법에 의해서만 분리되었다.

Key words : steam distillation, dynamic headspace, sesame oil, flavor

1. Introduction

Sesame oil has been widely used in Korea as a type of seasoning oils, having a distinctive aroma and taste as affected by roasting conditions. The conventional methods for the preparation of sesame oil involves cleaning, drying, roasting and processing but not refining. The roasting process is the key step for making sesame oil as it influences color, aroma and quality.[1~3]

Studies on the aroma of oil from roasted sesame seed have been carried out by many workers.[4~9] Yamanish et al.[8] isolated the aroma concentrate of sesame oil by steam distillation and identified aldehydes such as *n*-pentanal, *n*-hexanal, etc. Takei et al.[9] fractionated the aroma concentrate from sesame oil, identifying guaiacol, acetylpyrazine and 2-acetylpyrrole. Nakamura et al.[7] extracted the volatiles of sesame oil by steam distillation, reporting one hundred and forty six compounds identified by a gas chromatograph, a gas chromatograph/fourier transform-infrared, and a gas chromatograph/mass spectrometry. Recently Lee et al.[10] separated the volatiles in sesame oil and identified thirty one compounds by gas chromatography and gas chromatography/mass spectrometry. Most of the researches to date were carried out by using steam distillation to separate the aroma of sesame oil. In this study, the aroma in the sesame oil was extracted by simultaneous distillation and extraction(SDE) and dynamic headspace sampling(DHS), and the compounds were separated and identified by GC and GC-MSD.[11]

2. Experimental

2.1. Preparation of sesame oil

Washed and dried sesame seeds were roasted at 210℃±(2℃) for 10 minutes with a hot air roasting machine. Sesame oil was obtained from the seeds by a screw-type oil expeller.

2.2. Simultaneous distillation and extraction(SDE)

A Likens-Nickerson type SDE head(Part No. 320-1000, J & W Scientific, California) was used for preparation of the SDE extract. A 1L round bottom flask was used to contain 50mL of sesame oil sample and 500mL of distilled water. A 100mL pear-shape flask containing 50mL pentane(Junsei Co., 99%)/ether(Junsei Co. 99%)(2:1, v/v) mixture solvent was attached to the solvent arm of the SDE head. Contents in the sample and solvent flasks were heated to boil and distillation/extraction was continued for 2 hr. The aqueous layer in the extract was removed as ice after freezing the extract at −20℃ for 12 hr. Then, the volume of the extract was reduced to 10mL by evaporation under a gentle nitrogen stream. The residual moisture in the extract was adsorbed into 1 g anhydrous sodium sulfate. The volume of the extract was further reduced to approx. 0.2mL under a nitrogen stream for further analysis.

2.3. Dynamic headspace sampling(DHS)

A Tekmar dynamic headspace concentrator(Model LSC 2000, Cincinati, Ohio) was used with 1mL of sesame oil. The headspace was swept with helium (He) onto a porous polymer Tenax trap column(polymer of 2,6-diphenyl-p-phenylene oxide, 12″×1/8″) at 40℃ on a water bath. The volatiles trapped on the Tenax column were thermally desorbed and swept directly into the split/splitless injection port of a capillary gas chromatograph.

Operational parameters for concentrating the volatiles from sesame oil were as follows : dry purging, 4min at 150℃ ; purging, 5min at 30mL per min with He at room temperature ; desorption, 8min at 220℃ ; baking-out, Tenax trap heated to 220℃ for 30min.

2.4. Gas Chromatography

Gas chromatographic separations were carried out on a capillary column(BP-20, 0.32mm i.d.×30m in length, wall coated with polyethylene glycol, film thickness 0.25μm, Scientific Glass Engineering, Australia). The column was temperature programmed from 40℃ to 230℃ at 3℃/min. with a linear helium velocity of 25cm/sec.

2.5. Gas Chromatography/Mass Spectrometry

A Hewlett Packard(Palo Alto, CA) GC 5890 series II and Concept II (Kratos Analytical, Manchester, UK) mass spectrometer was used for separation of the compounds and aquisition of the electron ionization mass spectra. One μL of extract was injected in the split mode of 50:1 into a fused silica capillary column(BP-20, 0.22mm i.d.×30m in length, wall coated with polyethylene glycol, film thickness 0.25μm, Scientific Glass Engineering, Australia). For analysis, the column temperature was programmed to remain at 40℃ for 3min. increased from 40 to 230℃ at 3℃/min., and then maintained at 230℃ for 10 min. For the SDE extract, the column temperature was set at the same condition as DHS analysis. The GC/MS conditions were as follows : helium carrier gas flow rate, 1.0mL/min.; injector temperature, 180℃; capillary direct MS interface temperature, 230℃; ion source temperature 230℃; ionization voltage, 70eV; mass range, mass/charge 30~300 amu. Tentative identifications were based mainly on the mass spectra of unknowns compared with those in the Wiley/NBS mass spectral library.

3. Results & Discussion

3.1. Volatile compounds extracted by DHS and SDE

Typical gas chromatograms of the volatile flavor compounds in sesame oil by the SDE and the DHS are shown in *Figs.* 1 and 2, respectively. Compounds identified are listed in *Table* 1 and 2. Forty six compounds were separated and identified in the SDE and 36 in the DHS. The volatile compounds in the vapor phase can often be sampled by DHA. However, since the efficiency of this technique depends on vapor pressure of the compounds, difficulty occurs in detecting important higher boiling aroma components. Volatile aldehydes and ketones eluted in the early part of the chromatograms were more abundant by DHS than by SDE. In DHS, the volatile compounds were trapped inside the Tenax GC; thus, the overall aroma could not be evaluated for comparison with flavors of sesame oil. A few high-

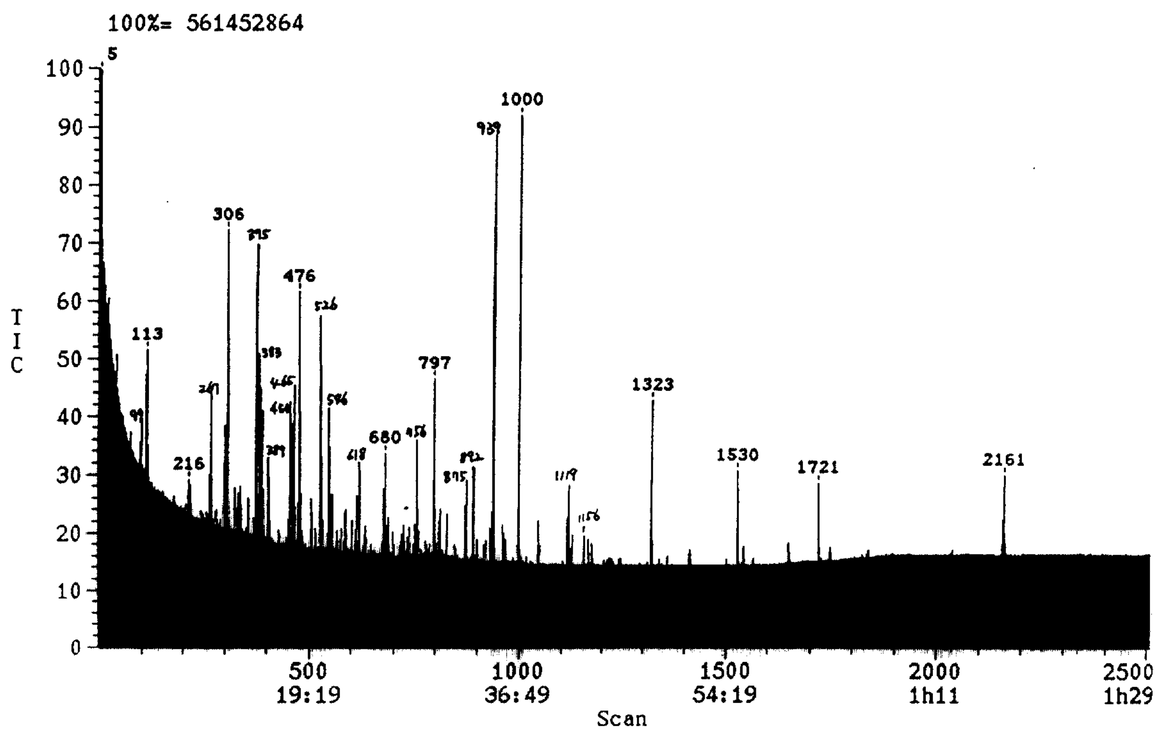

Fig. 1. Total ion chromatogram of the flavor compounds in the oil obtained from sesame seed, collected by the SDE method.

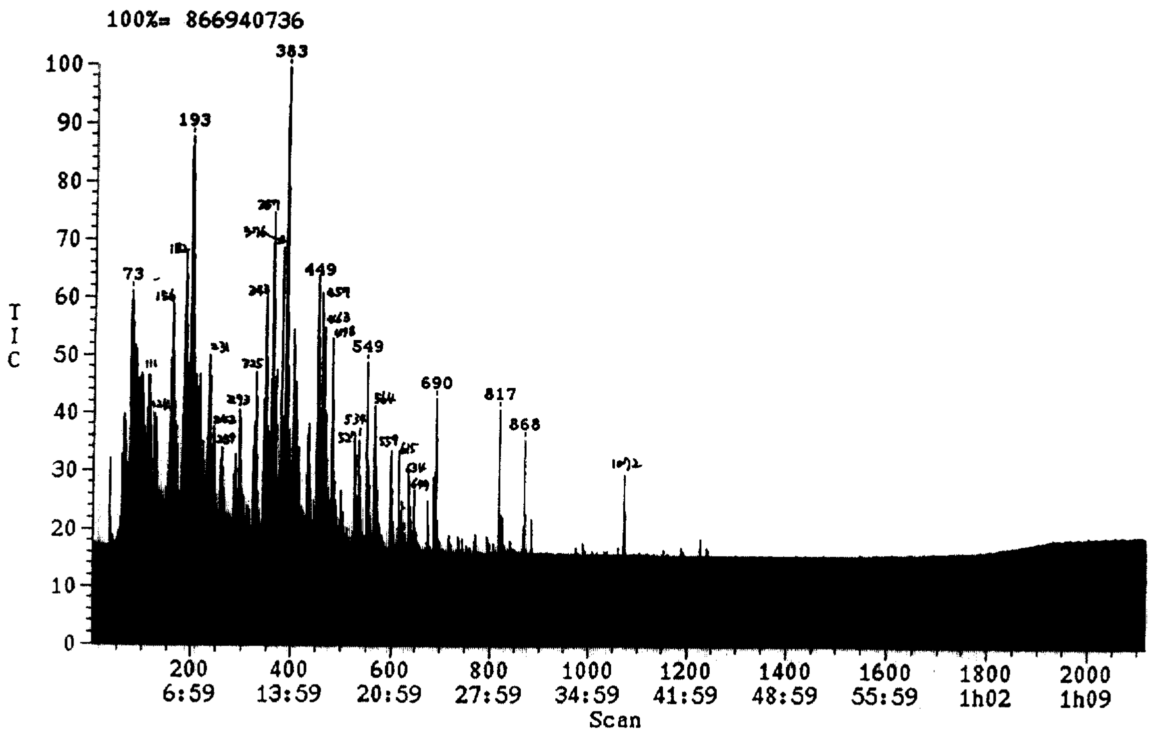

Fig. 2. Total ion chromatogram of the flavor compounds in the oil obtained from sesame seed, collected by the DHS method.

ly volatile compounds were found at higher concentrations in DHS than in SDE as shown in *Fig.* 1 and *Fig.* 2. However, less volatile compounds such as dimethyl pyrazine and trimethyl pyrazine reported by Nakamure et al.[7] were detected in both extractions.

Possible loss of very volatile flavor components during solvent evaporation, as well as interference of the solvent front during GC elution, might have made difficult the detection of highly volatile compounds in the SDE extracts.[11]

3.2. Important volatile flavor compounds in sesame oil

Six alcohols, 6 aldehydes, 12 pyrazines, 5 ketone and acids, 4 furan and phenols, 4 pyridine and thiazoles were separated and identified in the SDE extracts. On the other hand, 3 alcohols, 6 aldehydes, 12 pyrazines, and 15 other aromas were separated and identified in the DHS extracts. Many of these compounds were reported as important volatile aromas of sesame oil.

3.2.1. Alcohols and aldehydes

The alcohol 1-pentanol, 2-hexyl-1-ol, and 1-octanol, and the aldehydes hexanal, and nonanal were separated and identified in sesame aroma. These compounds are the breakdown products of polyunsaturated fatty acids and possess a relatively weak aroma.

3.2.2. Furan and phenols

Furan derivatives greatly affect the aroma, giving rise to a pleasantly sweet effect. It has been suggested that most of them were developed by caramelization of sugar moiety.[12] The phenols had a smoky and/or brown odor, and could be important to the body note of the roasted sesame seed aroma.[7]

3.2.3. Pyrazines

The large concentration of such methylpyrazines as 2-methylpyrazine, 2,5-dimethylpyrazine and 2,6-dimethylpyrazine is remarkable. These products can undergo Strecker degradation to form an amin-

Table 1. Flavor compounds in the oil from sesame seeds, collected by the SDE method.

Components	Peak No.*	Flavor Compounds
Alcohols		
	302	1-Pentanol
	511	2-Hexyl-1-ol
	546	1-Octen-3-ol
	676	1-Octanol
	1127	1-Dodecanol
	1721	1,3-Benzodioxol-5-ol
Aldehydes		
	113	Hexanal
	465	Nonyl aldehyde
	613	Benzaldehyde
	892	2,4-Nonadienal
	1156	Pyrrolecarbaldehyde
	1323	2-Methyl-2-pyrrolecarbaldehyde
Ketones and acids		
	216	2-Heptanone
	461	2-Nonanone
	813	3-(Acetyloxy)-2-cyclo-buten-1-one
	504	(E)-2-Octenoic acid
	902	3-Pyridinecarboxylic acid
Furans and phenol		
	554	Furfural
	680	5-Methylfurfural
	756	Furfuryl alcohol
	1000	Guaiacol
Pyrazines		
	267	Pyrazine
	306	3-Methylpyrazine
	375	2,5-Dimethylpyrazine
	383	2,6-Dimethylpyrazine
	389	2-Ethylpyrazine
	405	2,3-Dimethylpyrazine
	454	2-Ethyl-6-methylpyrazine
	476	2,3,5-Trimethylpyrazine
	526	3-Ethyl-2,5-dimethylpyrazine
	689	Methyl-1,4-dioxidepyrazine
	797	2-Acetyl-5-methylpyrazine
	1119	2-Furfurylpyrazine
Pyridines and thiazoles		
	325	5-Methylisothiazole
	331	2,4-Dimethylthiazole
	356	4-Methylpyridine
	809	2-Methylpyridine
Others		
	99	2-Methyl butane

	587	5-Hydroxy-pentanamide
	618	1H-Pyrrole
	737	5-Acetoxy-3-pentenitrile
	751	1-Benzyl-1-methyl-3-phenylurea
	875	3-Methyl-1-heptene
	939	2-Heptyne
	1530	1H-Indole
	2161	Dioctylphthalate

* see *Fig.* 1.

Table 2. Flavor compounds in the oil from sesame seeds, collected by the DHS method.

Components	Peak No.*	Flavor Compounds
Alcohols		
	259	1-Hexanol
	376	1-Pentanol
	615	1-Octen-3-ol
Aldehydes		
	124	Pentanal
	182	Hexanal
	293	Heptanal
	549	Nonyl aldehyde
	676	Benzal aldehyde
	1072	3-Methyl-2-pyrrolecarbaldehyde
Keton		
	534	2-Nonanone
Furans and phenol		
	111	2,5-Dimethylfuran
	622	Furfural
	744	5-Methylfurfural
	769	Furfuryl alcohol
	988	Guaiacol
Pyrazines		
	367	Pyrazine
	383	2-Methylpyrazine
	449	2,5-Dimethylpyrazine
	457	2,6-Dimethylpyrazine
	463	2-Ethylpyrazine
	478	2,3-Dimethylpyrazine
	527	2-Ethyl-6-methylpyrazine
	564	2,3,5-Trimethylpyrazine
	599	3-Ethyl-2,5-dimethylpyrazine
	689	Methyl-1,4-dioxidepyrazine
	817	2-Acetyl-5-methylpyrazine
	868	2-Methyl-6,7-dihydro-5H-cyclopentapyrazine
Pyridines and thiazoles		
	365	Thiazole

	400	5-Methylisothiazole
	405	2,4-Dimethylthiazole
	431	4-Methylpyridine
Others		
	156	2-Methyl butane
	242	1-Methylpyrrole
	343	2-Methyl-1H-imidazole
	634	5-Hydroxy-pentanamide
	690	1H-Pyrrole

* see *Fig.* 2.

oreducttone which in subsequent steps of self-condensation and oxidation can form 2,5-and 2,6-dimethylprazines.[13,14] The 2,5-dimethyl-pyrazine should be produced regardless of the type of amino acid employed as the nitrogen source. The formation of acetylpyrazine may be the result of the condensation of C-methyl reductone(a known browning reaction product) with glyoxal and amino acid.

The pyrazine compound had a peanut-like, green or roasted note and the acetylpyrazines had a surprisingly intense and characteristic roast resembling that note reminiscent of popcorn. It can be estimated that these pyrazine compounds may contribute to the sweet and roasted flavor notes of oil from roasted sesame seed.[15]

3.2.4. Pyridines, thiazoles and others

2-methyl, 4-methyl pyridines and 5-methylisothiazole were detected in sesame oil. Other significant compounds were 1H-indole and 1H-pyrrole, which have been reported to possess pleasant, sweet and floral odor even at very low concentrations.[7]

References

1. J. H. Ha and D. H. Kim, *Korean J. Food Sci. Technol.*, **28**(2), 246-251(1996).
2. H. S. Shin, *Korean J. Food Sci. Technol.*, **5**(2), 113-118(1973).
3. Y. Fukuda and M. Namiki, *Nippon Shokuhin Kogyo Gakkaishi*, **35**(8), 552-562(1988).
4. G. C. Yen, *J. Sci. Food Agric.*, **50**, 563-570(1990).
5. M. A. Soliman, A. A. A. El-Sawy, H. M. Fadel and F. Osman, *J. Agric. Food Sci.*, **33**, 523-528(1994).
6. C. H. Manley, P. P. Vallon and R. E. Erickson, *J. Food Sci.*, **39**, 73-76(1994).
7. S. Nakamura, O. Nishimura, H. Masuda and S. Mihara, *Agric. Biol. Chem.*, **53**(7), 1891-1899 (1989).
8. T. Yamanishi, Y. Takei and A. Kobayashi, *J. Agric. Chem. Soc. Japan*, **41**(10), 526-533(1967).
9. Y. Takei, Y. Nakamura, A. Kobayashi and T. Yamanishi, *J. Agric. Chem. Soc. Japan*, **43**(9), 667-674(1969).
10. Y. G. Lee, S. U. Lim and J. O. Kim, *J. Korean Agric. Chem. Soc.*, **36**(6), 407-415(1993).
11. U. Tanchotikul and T. C. Y. Hsieh, *J. of Food Soc.*, **56**(2), 327-331(1991).
12. D. H. Kim, "Food Chemistry", 2nd Ed., p. 178, S. W. Hong, Tamkudang, Seoul, Korea, (1990).
13. P. E. Koehler and G. V. Odell, *J. Agric. Food Chem.*, **18**(5), 895-898(1990).
14. P. E. Koehler, M. E. Mason and J. A. Newell, *J. Agric. Food Chem*, **17**(2), 393-396(1969).
15. T. Shibamoto, *J. Food Sci.*, **51**(4), 1098-1099 (1986).