

Volatile Compounds of Deep-Oil Fried, Microwave-Heated, and Oven-Baked Garlic Slices

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Fried, oil-cooked, microwave-fried, baked, and microwave-baked garlic samples were prepared in this study. After being isolated by a modified Likens-Nickerson steam distillation/solvent extraction apparatus, the volatile compounds in these garlic samples were analyzed by using GC and GC-MS. A total of 41 volatile compounds were identified from these garlic samples. Among these volatile components, diallyl disulfide and diallyl trisulfide were the dominant compounds found in baked or microwave-baked garlic samples. Diallyl disulfide, methyl allyl disulfide, and vinylidithiins were the dominant compounds found in fried, oil-cooked, and microwave-fried garlic samples. Oil treatments of garlic favored the formation of vinylidithiins, and the content of diallyl trisulfide in oil-treated garlic samples was very low. Significant amounts of nitrogen-containing volatile compounds were found in baked or oil-treated garlic samples. These nitrogen-containing compounds were mainly generated from the interactions of reducing sugars and flavor precursors of garlic.

INTRODUCTION

Garlic (*Allium sativum* Linn.) has been extensively used worldwide as an important vegetable, spice, and seasoning. Many kinds of garlic products, such as garlic oil, garlic powder, garlic salt, garlic paste, and garlic flakes, have been used in the home or in the food industry. These garlic products can be divided into the following forms according to their preparation methods: raw garlic, dried garlic, boiled garlic, baked garlic, and fried garlic. The difference in preparation methods can result in different flavor sensations of these garlic products.

It has been reported that intact garlic cloves contain a flavor precursor, alliin (*S*-allylcysteine *S*-oxide), and an enzyme, alliinase, which converts alliin into allicin, the pungent principle of raw garlic, when the cellular tissue of garlic is disrupted (Stoll and Seebach, 1951). After the enzyme alliinase was deactivated by boiling the garlic bulb or homogenizing the garlic bulb with alcohol containing limited quantities of water, no pungent odor was detected from the garlic samples, and alliin was not converted to allicin (Stoll and Seebach, 1951; Ueda et al., 1990).

Besides alliin, *S*-methylcysteine *S*-oxide, *S*-(*E*)-1-propenylcysteine *S*-oxide, and their precursors, γ -glutamylalk(en)ylcysteines, were found in intact garlic cloves (Thompson et al., 1964; Ziegler and Sticher, 1985; Ueda et al., 1990; Iberl et al., 1990b; Lawson et al., 1991b; Lawson, 1992; Block, 1992; Block et al., 1992a). During storage of garlic cloves, these γ -glutamylalk(en)ylcysteines could be converted to alk(en)ylcysteine *S*-oxides (Lawson et al., 1991b; Lawson, 1992). After the garlic cloves were disrupted, these alk(en)ylcysteine *S*-oxides could be converted enzymatically to related alk(en)yl thiosulfonates, the primary flavor compounds of raw garlic. Dimethyl, allyl methyl, methyl allyl, (*E* and *Z*)-1-propenyl methyl, methyl (*E*)-1-propenyl, diallyl, allyl (*E*)-1-propenyl, and (*E* and *Z*)-1-propenyl allyl thiosulfonate have been identified from garlic or elephant garlic homogenate (Block, 1985, 1992; Saito et al., 1989; Blania and Spangenberg,

1991; Lawson et al., 1991a,c; Lawson and Hughes, 1992; Lawson, 1992; Block et al., 1992a,b). Most of these thiosulfonates, especially allicin, are very unstable and can decompose or rearrange to form sulfide compounds, vinylidithiins, or ajoenes (Block et al., 1986; Yu and Wu, 1989; Iberl et al., 1990a; Lawson et al., 1991c; Lawson, 1992; Block, 1992). Allicin and some of its transformation products were found to have biochemical and physiological effects (Stoll and Seebach, 1951; Sreenivasamurthy et al., 1961; Block, 1985; 1992; Block et al., 1986; Benjamin et al., 1990). The transformation products of alk(en)yl thiosulfonates also give a different flavor sensation to garlic products.

The volatile components of raw garlic, dried garlic, and boiled garlic have been well studied; the contributions of alk(en)yl thiosulfonates and their transformation products to the flavor sensation of garlic products were also well researched (Brodnitz et al., 1971; Vernin et al., 1986; Saito et al., 1989; Yu and Wu, 1989; Yu et al., 1989; Iberl et al., 1990b; Ueda et al., 1990; Blania and Spangenberg, 1991; Lawson et al., 1991a,c; Lawson and Hughes, 1992; Lawson, 1992; Block et al., 1992a,b; Jirovetz et al., 1992; Mazza et al., 1992). However, the volatile components of fried and baked garlic and the contributions of flavor precursors of garlic, e.g., alk(en)ylcysteine *S*-oxides and γ -glutamylalk(en)ylcysteines, to the thermal flavor generation of garlic have not been studied yet. Fried and baked garlic has been widely used in foods, such as Chinese cuisine, garlic bread, and garlic chicken. In the preparation of many Chinese dishes, crushed garlic cloves are stir-fried in a small amount of vegetable oil prior to the addition of other ingredients and foods. This fried garlic flavor is important to these Chinese dishes.

In recent years, microwave ovens have been widely used in food preparation, and researchers have become more and more concerned with the flavor generation and flavor changes of spices or seasoning during microwave cooking. The objectives of this study were to determine the effects of different frying and baking treatments on the flavor formation of garlic and to determine the potential contributions of the flavor precursors related to the thermal flavor generation of garlic.

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EXPERIMENTAL PROCEDURES

Materials. Garlic cloves were purchased in a local market in Taiwan. The vegetable oil used was soybean oil produced in Taiwan.

Sample Preparation. Using a slicer, peeled garlic cloves were cut into slices of approximately 1-mm thickness. Five garlic samples were prepared from these slices and used for flavor isolation and identification in this study.

(A) *Fried Garlic.* Garlic slices (500 g) were put into 1 kg of hot (180 °C) soybean oil and heated in a pot on a gas stove. Immediately after the garlic slices were added, the temperature of the oil dropped to around 105 °C. After the temperature of the oil again reached 180 °C, the mixture of garlic slices and oil was immediately cooled to room temperature using an ice water bath. The total mixture of oil and fried garlic slices was used for flavor isolation.

(B) *Oil-Cooked Garlic.* Garlic slices (500 g) were mixed together with 1 kg of soybean oil in a pot and then heated on a gas stove. Right after the temperature of the oil mixture reached 180 °C, the mixture of garlic slices and oil was immediately cooled to room temperature using an ice water bath. The total mixture of oil and garlic slices was used for flavor isolation.

(C) *Microwave-Fried Garlic.* Garlic slices (500 g) were mixed together with 1 kg of soybean oil in a 3-L beaker and then heated in a microwave oven at full power. Right after the temperature of garlic slices and oil reached 180 °C, the mixture was cooled to room temperature. The total mixture of oil and garlic slices was used for flavor isolation.

(D) *Baked Garlic.* Garlic slices (500 g) were spread on steel plates and then were put into an electric oven preheated to 180 °C. When the weight loss of the garlic slices was close to that in sample A, the baked garlic slices were cooled to room temperature and then used for flavor isolation.

(E) *Microwave-Baked Garlic.* Garlic slices (500 g) were spread on microwaveable plates and heated in a microwave oven at full power. When the weight loss of the garlic slices was close to that in sample A, the baked garlic slices were cooled to room temperature and then used for flavor isolation.

Flavor Isolation. Samples A–E were mixed individually with 1 L of distilled water and then steam-distilled and extracted into 60 mL of a pentane/ether (1:1) solvent system in a modified Likens–Nickerson apparatus for 3 h. After steam distillation/solvent extraction, appropriate amounts of 1-propyl butyrate stock solution (0.0484 g in 50 mL of solvent) were added to the isolate as the internal standard. After being dried over anhydrous sodium sulfate and filtered, the distillate was concentrated to minimum volume using a spinning band distillation apparatus (Kontes). It was further concentrated by blowing with nitrogen gas to a final volume of 0.2 mL.

Gas Chromatographic Analysis. For the quantitative analysis of volatiles of garlic samples, gas chromatography was conducted on a Shimadzu GC-9A equipped with a flame ionization detector (FID). A 50 m × 0.32 mm fused silica WCOT capillary column coated with CP-Wax 52 CB (Chrompack, Inc.) was used. The operating conditions were as follows: injector temperature, 250 °C; detector temperature, 250 °C; hydrogen carrier flow rate, 1.4 mL/min; temperature program, 40 °C (10 min), 1.5 °C/min, 200 °C (60 min). A split ratio of 80:1 was used. Linear retention indices of the volatile components were calculated with *n*-paraffins (C₅–C₂₅) as references (Majlat et al., 1974).

Identification of the Volatile Compounds. Identification of the volatile compounds in the isolate was mostly based on gas chromatography–mass spectrometry (GC–MS). The structural assignment of volatile compounds was accomplished by comparing the mass spectral data with those of authentic compounds available from the Browser–Wiley computer library, the EPA/NIH data base (Heller and Milne, 1980), or previously published literature (Yu and Wu, 1989; Yu et al., 1989) and/or retention index of the authentic compounds.

Gas Chromatography–Mass Spectrometry (GC–MS) Analysis. The concentrated isolate was analyzed by GC–MS using a Hewlett-Packard 5840A gas chromatograph coupled to a Hewlett-Packard 5985B mass spectrometer equipped with a direct split interface and the same column as that used for the gas chromatography. The operating conditions were the same as

Table I. Weight Changes and Heat-Treated Time of Garlic Samples

	sample ^a				
	A	B	C	D	E
original wt, g	1500.0	1500.0	1500.0	500.0	500.0
final wt, g	1164.8	1163.1	1160.4	164.2	162.5
frying or baking time, min	6.9	16.8	36.4	60.2	29.8

^a A, fried garlic; B, oil-cooked garlic; C, microwave-fried garlic; D, baked garlic; E, microwave-baked garlic.

those used in the GC analysis described above. Mass spectra were obtained by electron ionization at 70 eV and an ion source temperature of 200 °C. The temperature of the transfer line was 200 °C.

RESULTS AND DISCUSSION

In this study, simultaneous steam distillation–solvent extraction (SDE) in a modified Likens–Nickerson apparatus was used for the flavor isolation of garlic samples. It is understood that SDE involved heating the samples; hence, some formation of artifacts probably was inevitable. Nevertheless, considering this experiment involved comparison of previously fried or baked garlic samples, being extracted under identical conditions, it was felt that interference from artifacts was minimal or at least occurred to a similar extent in all of the samples. Table I shows the weight changes and heat-treated time of garlic samples. During fried or baked treatments, it was determined that all samples were to have a similar weight loss, to represent the same extent of heat treatments. Since all garlic samples were fried, or heated, or baked at 180 °C, the extent of the heat treatment was thought to be greater than or at least similar to that in SDE; therefore, the formation of artifacts during SDE was thought to be negligible.

Alk(en)yl thiosulfates found in garlic were very unstable and could be transformed to polysulfides in water or to vinylidithiins in hexane, ether, or vegetable oil. The transformation rate of these thiosulfates to polysulfides in water was found to be proportional to the water temperature (Brodnitz et al., 1971; Block, 1985; Yu and Wu, 1989; Iberl et al., 1990a; Lawson, 1992). It was found that allyl alk(en)yl thiosulfates could be transformed to 2-vinyl-4*H*-1,3-dithiin and 3-vinyl-4*H*-1,2-dithiin during gas chromatography (GC) analysis with high injection port temperatures (Brodnitz et al., 1971; Block, 1985; Yu and Wu, 1989). Therefore, it was suggested that the contents of these two vinylidithiins by GC analysis could be used to represent the original content or relative content of allyl alk(en)yl thiosulfates (especially allicin) in the garlic products (Yu and Wu, 1989; Saito et al., 1989). To confirm that most of the thiosulfates in the garlic samples prepared in this study had been destroyed or transformed to other compounds before SDE, fresh garlic slices, baked garlic slices, and microwave-baked garlic slices were extracted by using methylene chloride, individually. After being concentrated under nitrogen flow, the concentrates were analyzed by using GC under the same conditions as shown under Experimental Procedures. The vinylidithiin content of the baked and microwave-baked garlic samples was only around 1 % of that found in the fresh-sliced garlic sample. These results showed that before SDE all of the allyl alk(en)yl thiosulfates in baked or microwave-baked garlic samples were almost destroyed or transformed to other compounds. The alk(en)yl thiosulfates in oil-treated (e.g., fried, oil-cooked, and microwave-fried) garlic samples were also thought to be almost totally destroyed or transformed before SDE. This proposal can be proved by checking the composition of volatile components in these oil-treated samples and will be discussed later.

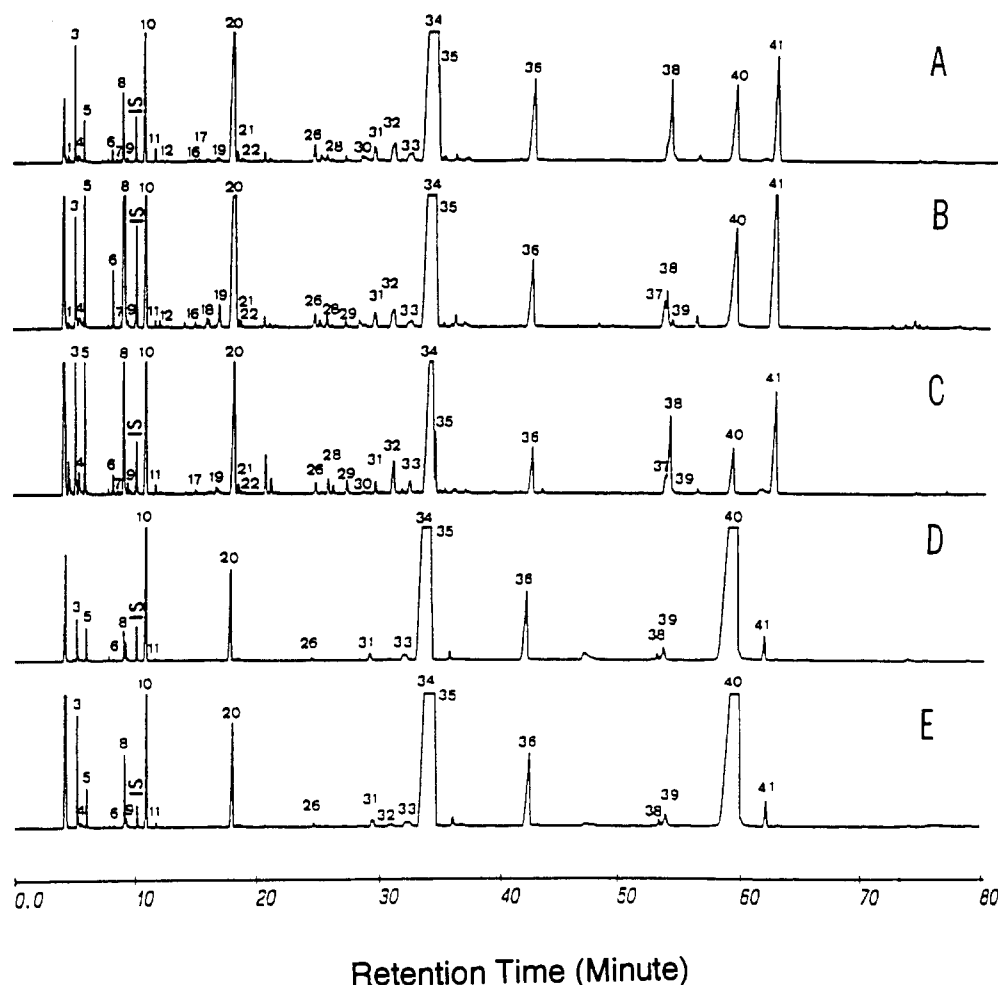


Figure 1. Capillary gas chromatograms of volatile compounds of fried garlic (A), oil-cooked garlic (B), microwave-fried garlic (C), baked garlic (D), and microwave-baked garlic (E).

Although HPLC has been suggested as the best method for the analysis of the alk(en)yl thiosulfates in *Allium* plants (Iberl et al., 1990b; Blania and Spangenberg, 1991; Lawson et al., 1991a,c; Block et al., 1992a), GC was used in this study because of the high sensitivity and high resolution power. Also, almost no thiosulfates were found in the garlic isolates, and the limitations of GC for the analysis of volatile compounds in fried and baked garlic were thought to be small. It was said that our objectives were to detect the transformation "volatile" compounds of alk(en)yl thiosulfates in garlic samples and probably the "trace" volatile compounds generated from the flavor precursors of garlic during the thermal treatments of garlic slices.

Figure 1 shows the capillary gas chromatographic separations of volatile compounds of garlic samples. The quantitative comparison of volatile compounds identified in this study is shown in Table II. A total of 41 volatile compounds were identified in this study. These volatile compounds can be separated into four groups: (1) acyclic sulfur-containing compounds, which can be further divided into thiol, monosulfide, disulfide, and trisulfide compounds with methyl, allyl, 1-propenyl, and propyl groups attached on the sulfur atoms; (2) cyclic sulfur-containing compounds, such as 2,5-dimethylthiophene, 2-vinylthiophene, 1,2-dithiacyclopentane, 3-vinyl-4*H*-1,2-dithiin, and 2-vinyl-4*H*-1,3-dithiin; (3) nitrogen-containing compounds, such as pyridine, 2-methylpyridine, and 2-methyl-5-ethylpyridine, which contain one nitrogen atom on the benzene ring, and 2,3-dimethyl-, 2,5-dimethyl-, 2,6-dimethyl-, ethyl-, and trimethylpyrazine, which contain two nitrogen

atoms on the benzene ring; (4) oxygen-containing compounds, such as acetaldehyde, allyl alcohol, 2-methyl-2-butenal, and 4-heptenal.

Recent studies on garlic flavor showed that only methyl, allyl, and 1-propenyl groups, but not a propyl group, were found in the flavor precursors, e.g., γ -glutamylalk(en)ylcysteines and alk(en)yl cysteine *S*-oxides, and the primary flavor compounds, e.g., alk(en)yl thiosulfates, of garlic (Lawson et al., 1991a-c; Lawson and Hughes, 1992; Lawson, 1992; Block, 1992; Block et al., 1992a,b). However, by using GC-MS or the combination of GC, GC-MS, and authentic compounds, four propyl sulfide compounds were indeed identified from the fried and baked garlic samples. They were propyl sulfide, allyl propyl sulfide, methyl propyl disulfide, and allyl propyl disulfide. It is possible that these propyl sulfide compounds could come from the hydrogenation of propenyl sulfides during the extreme thermal treatments of frying and baking of garlic.

Different yields of volatile compounds were found among these different thermally treated garlic samples, especially among oil-treated garlic samples and baked garlic samples. Besides the flavor generation process, frying and baking treatments were also thought to be the flavor loss process. The difference in the yields of volatile compounds among these garlic samples was thought to come from the difference in the type, the time, and the temperature of the heat treatments. Frying treatments were found to cause more loss of volatile compounds than baking treatments in this study.

Table II. Volatile Compounds Identified in Fried Garlic (A), Oil-Cooked Garlic (B), Microwave-Fried Garlic (C), Baked Garlic (D), and Microwave-Baked Garlic (E)

peak no. ^a	comps identified	RI ^b	MW	ID ^c	yield, mg				
					A	B	C	D	E
1	acetaldehyde	700	44	GC&MS	0.08	0.14	0.26	0.22	0.24
2	methanethiol	780	48	MS	0.18	0.15	1.00	nd ^d	0.26
3	allyl mercaptan	863	74	GC&MS	10.39	4.33	16.32	5.97	20.39
4	propyl sulfide	909	118	GC&MS	0.46	0.43	2.63	0.12	1.64
5	methyl allyl sulfide	932	88	GC&MS	4.14	8.38	11.79	4.05	7.33
6	dimethyl disulfide	1055	94	GC&MS	1.08	2.07	1.53	0.26	0.52
7	2-methyl-2-butenal	1063	84	MS	0.21	0.25	0.17	0.04	0.14
8	allyl alcohol	1071	58	GC&MS	7.23	30.61	16.32	4.05	14.44
9	allyl propyl sulfide	1086	116	MS	0.05	0.34	0.31	0.37	0.29
10	diallyl sulfide	1118	114	GC&MS	19.76	15.22	35.93	42.54	45.87
11	4-heptenal	1135	112	MS	1.48	0.32	0.95	0.54	1.10
12	pyridine	1145	79	GC&MS	0.29	0.32	0.29	nd	0.12
13	di(1-propenyl) sulfide	1154	114	MS	0.19	0.12	0.16	0.34	0.29
14	di(1-propenyl) sulfide	1162	114	MS	0.08	0.03	nd	0.14	0.20
15	2,5-dimethylthiophene	1188	112	MS	0.34	0.01	0.20	nd	0.05
16	2-methylpyridine	1200	93	MS	0.56	0.31	0.51	0.14	0.18
17	methyl propyl disulfide	1205	122	GC&MS	0.38	0.79	0.07	nd	0.04
18	C ₆ H ₉ S (cyclic)	1216	112	MS	0.08	0.48	0.29	0.27	0.29
19	methyl 1-propenyl disulfide	1225	120	MS	0.73	1.67	0.83	0.20	0.50
20	methyl allyl disulfide	1241	120	GC&MS	51.72	30.81	29.30	21.67	37.18
21	C ₄ H ₈ S ₂	1247	120	MS	1.24	0.33	0.95	0.37	0.60
22	2-vinylthiophene	1254	110	MS	0.79	0.33	0.29	0.53	0.72
23	2,5-dimethylpyrazine	1274	108	MS	0.40	0.17	0.13	nd	nd
24	2,6-dimethylpyrazine	1280	108	MS	1.45	0.66	4.73	nd	nd
25	ethylpyrazine	1286	108	MS	0.60	0.24	1.87	nd	nd
26	dimethyl trisulfide	1329	126	GC&MS	3.07	1.14	1.66	0.86	1.50
27	2,3-dimethylpyrazine	1337	108	MS	1.65	0.52	0.32	0.22	0.65
28	2-methyl-5-ethylpyridine	1342	121	MS	1.39	0.85	1.85	0.03	0.14
29	1,2-dithiacyclopentane	1347	106	MS	0.40	0.17	0.96	0.02	nd
30	trimethylpyrazine	1360	122	MS	0.98	0.49	1.95	0.05	0.14
31	allyl propyl disulfide	1386	148	MS	4.16	1.53	1.74	2.45	4.36
32	3-methyl-2-cyclopentene-1-thione	1403	112	MS	7.13	2.62	7.01	0.65	2.31
33	C ₆ H ₁₀ S ₂	1419	146	MS	4.18	1.26	2.88	3.99	3.67
34	diallyl disulfide	1441	146	GC&MS	250.77	89.70	90.24	335.53	566.78
35	C ₆ H ₁₀ S ₂	1444	146	MS	9.50	nd	7.49	6.21	7.40
36	methyl allyl trisulfide	1535	152	GC&MS	32.02	8.77	10.39	31.09	47.42
37	C ₄ H ₆ S ₂	1658	118	MS	2.00	2.34	2.99	0.47	0.38
38	3-vinyl-4H-1,2-dithiin	1663	144	GC&MS	23.76	2.68	17.03	1.74	2.50
39	C ₆ H ₁₀ S ₂	1670	146	MS	nd	0.60	0.08	5.43	7.09
40	diallyl trisulfide	1738	178	GC&MS	29.66	18.55	11.39	328.40	450.44
41	2-vinyl-4H-1,3-dithiin	1770	144	GC&MS	36.34	25.58	28.97	7.04	10.48
	total				510.92	255.31	313.78	805.98	1237.63

^a Peak numbers refer to Figure 1. ^b RI, linear retention indices were obtained by using *n*-alkanes as standards in a polar fused silica capillary column [50 m × 0.32 mm (i.d.); 0.25- μ m thickness; CP-Wax 52 CB; Chrompack, Inc.]. ^c MS, identified by comparing the mass spectrum with that of the authentic compound. GC&MS, identified by comparing the mass spectrum and the retention index with those of the authentic compound. ^d nd, not detected.

Table III. Percent Composition of Some Important Volatile Compounds in Garlic Samples

compd	% composition				
	A ^a	B ^a	C ^a	D ^a	E ^a
diallyl sulfide	3.87	5.96	11.45	5.28	3.71
diallyl disulfide	49.08	35.13	28.76	41.63	45.81
diallyl trisulfide	5.81	7.27	3.63	40.75	36.41
methyl allyl sulfide	0.81	3.28	3.76	0.51	0.59
methyl allyl disulfide	10.12	12.07	9.34	2.69	3.01
methyl allyl trisulfide	6.27	3.44	3.31	3.85	3.83
allyl alcohol	1.42	11.99	5.21	0.51	1.17
vinylidithiins	11.88	11.07	14.66	1.09	1.05
nitrogen-containing compds	1.43	1.39	3.71	0.05	0.11
oxygen-containing compds ^b	0.35	0.28	0.44	0.11	0.12
other volatile compds	8.96	8.12	15.73	3.53	4.19

^a A-E represent samples as shown in Table I. ^b Allyl alcohol was not included.

The percentage composition of the major volatile compounds identified from garlic samples is shown in Table III. Diallyl disulfide and diallyl trisulfide were found to be the dominant compounds in baked and microwave-baked garlic samples. The content of diallyl disulfide in these baked garlic samples was very high (42–46%). The

content of diallyl trisulfide in these baked garlic samples was also very high (36–41%). Diallyl sulfide, methyl allyl trisulfide, and methyl allyl disulfide were found to be other major compounds in these baked garlic samples. Trace amounts of nitrogen-containing and oxygen-containing compounds (0.05–0.11% and 0.11–0.12%, individually) were identified in these baked garlic samples. The total content of vinylidithiins in baked garlic samples was low, only around 1%. The flavor compositions of baked and microwave-baked garlic samples were found to be very similar to those in the garlic oil prepared from garlic slices by using SDE (not shown here). However, the oxygen-containing and nitrogen-containing compounds were not found in the garlic oil. It is reasonable to assume, therefore, that in the early stages of the baking treatment the inner temperature of the garlic slices was thought to be similar to that of garlic slices heated in the SDE apparatus; therefore, the flavor generation patterns of baked garlic slices and garlic oil were thought to be similar. However, in the final stage, the temperature of garlic slices baked in the electric or the microwave oven could rise to higher than those in the SDE apparatus. Therefore, a different

flavor generation pattern could occur during the final stage of the baking treatment of the garlic slices.

Diallyl disulfide was again found to be the dominant volatile compound in fried, oil-cooked, and microwave-fried garlic samples. Its content in these garlic samples was around 29–49%. The content of diallyl trisulfide in these oil-treated garlic samples, however, was found to be very low, only around 4–7%. Besides diallyl sulfide, methyl allyl disulfide, and methyl allyl trisulfide, vinylidithiins and allyl alcohol were also found to be other major volatile compounds in these oil-treated garlic samples. The content of allyl alcohol in the oil-cooked garlic sample was found as high as 12%. The total content of vinylidithiins in these oil-treated garlic samples was found to be 11–15%. Significant amounts of oxygen containing and nitrogen-containing compounds were found in these oil-treated garlic samples. The content of these nitrogen-containing volatile compounds was 4%. Since the composition of volatile compounds in oil-treated garlic samples was found to be so different from that in baked garlic samples or garlic oil, most of the volatile compounds of these oil-treated garlic samples were thought to be formed before the SDE. This means that almost all of the alk(en)yl thiosulfonates had been destroyed or had been transformed to other compounds before SDE.

The generation mechanisms of diallyl trisulfide from alliin were reported (Block, 1992). The interactions of two molecules of alliin to form the sulfonium ion and then the addition of water to the allyl double bond followed by the electron rearrangements in this sulfonium ion were thought to be the key steps for the formation of diallyl trisulfide. Only a small amount of diallyl trisulfide was found in oil-treated garlic samples. This probably resulted from the inhibition of the interaction of alliin molecules and the inhibition of the addition of water to the allyl double bond in the sulfonium ion in the oil system.

Vinylidithiins were found to be generated from allyl alk(en)yl thiosulfonates when these thiosulfonates were put in hexane, ether, or vegetable oil or were heated in the neat state at very high temperatures (Brodnitz et al., 1971; Block, 1985, 1992; Yu and Wu, 1989; Lawson et al., 1991c; Lawson, 1992). A very high content of these vinylidithiins was found in oil-treated garlic samples in this study. Both high-heat treatment of garlic slices and the nonpolar property of vegetable oil were thought to be the reasons the content of these vinylidithiins was so high in the oil-treated garlic samples.

A significant amount of allyl alcohol was found in the oil-treated garlic samples, especially in the oil-cooked garlic sample. Alliin, one of the flavor precursors of garlic, was thought to contribute to the formation of allyl alcohol during the fried or oil-cooked treatment of garlic slices. Allyl alcohol was found to be the major degradation volatile compound when the synthesized alliin was heated in water in a closed reaction cylinder at 180 °C, and some other cysteine degradation volatile compounds (Shu et al., 1985) were also found (Yu and Ho, unpublished results, 1993). It was proposed that allyl alcohol could be generated from alliin through [2,3]-sigmatropic rearrangement. [2,3]-Sigmatropic rearrangement of alliin may lead to intermediate sulfenate. The reduction of sulfenate will yield allyl alcohol and cysteine. A similar mechanism has been proposed by Park et al. (1992) to explain the formation of acrolein from S-(3-chloro-2-propenyl)cysteine.

The sulfur-containing volatile compounds identified from garlic samples in this study are postulated mainly to be the decomposed and/or rearranged products of alk(en)yl thiosulfonates. Significant amounts of nitrogen-

containing volatile compounds, e.g., pyridines and pyrazines, were found in baked and oil-treated garlic samples. These compounds have been widely found in some thermally treated foods and also from the model reaction system of amino compounds and reducing sugars. These compounds were proved to be generated from the interactions of amino compounds and reducing sugars. It has been said that these compounds belong to some of the Maillard reaction products (Kato et al., 1973; Mulders, 1973; Zhang, 1991; Whitfield, 1992). It is proposed that nitrogen-containing volatile compounds found in this study were mainly generated from the interactions of reducing sugars and flavor precursors, e.g., γ -glutamylalk(en)ylcysteine and alk(en)ylcysteine S-oxides, in the garlic or that the flavor precursors of garlic could contribute to the formation of these nitrogen-containing volatile compounds during frying or baking treatment of garlic slices. This is because the total content of these flavor precursors was found higher than those of amino acids (Raghavan et al., 1983; Fenwick and Hanley, 1985; Lawson, 1992) and these flavor precursors all contain amino groups. When alliin or allylcysteine was heated with glucose in water in a closed reaction cylinder at 180 °C, these nitrogen-containing compounds were found in this model system (Yu and Ho, unpublished results, 1993). The presence of these nitrogen-containing volatiles in fried or baked garlic slices, but not in the garlic oil, indicated that high-temperature thermal treatment of frying or baking of garlic slices favored the Maillard reaction for the formation of these compounds.

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