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Received for review July 13, 1988. Accepted December 8, 1988.

## Volatile Compounds from Garlic

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Volatile components of crushed garlic were obtained by water distillation, steam distillation, and Likens-Nickerson (L-N) distillation/solvent extraction with or without steam, respectively. The volatile components were analyzed and identified by capillary gas chromatography (GC) and combined gas chromatography-mass spectrometry (GC-MS). The yield of garlic essential oils was  $0.22 \pm 0.01\%$  (w/w). Monosulfides, disulfides, and trisulfides were the major volatile components in garlic essential oils. Of 28 components, 13 were being reported for the first time as components of garlic. The essential oils obtained by L-N distillation/solvent extraction contained more 2,4-dimethylfuran, 2-propen-1-ol, aniline, and 3,5-diethyl-1,2,4-trithiolane than those from water distillation and steam distillation. Water layer of garlic distillate contained more 3,5-diethyl-1,2,4-trithiolane and 2-propen-1-ol than its oil layer. The essential oils obtained by steam distillations contained more high-volatility compounds and less low-volatility compounds than those by water distillations.

Garlic (*Allium sativum* Linn.) is one of the most important spices used in Chinese food. In some Chinese foods cooking, people put crushed garlic cloves into the wok

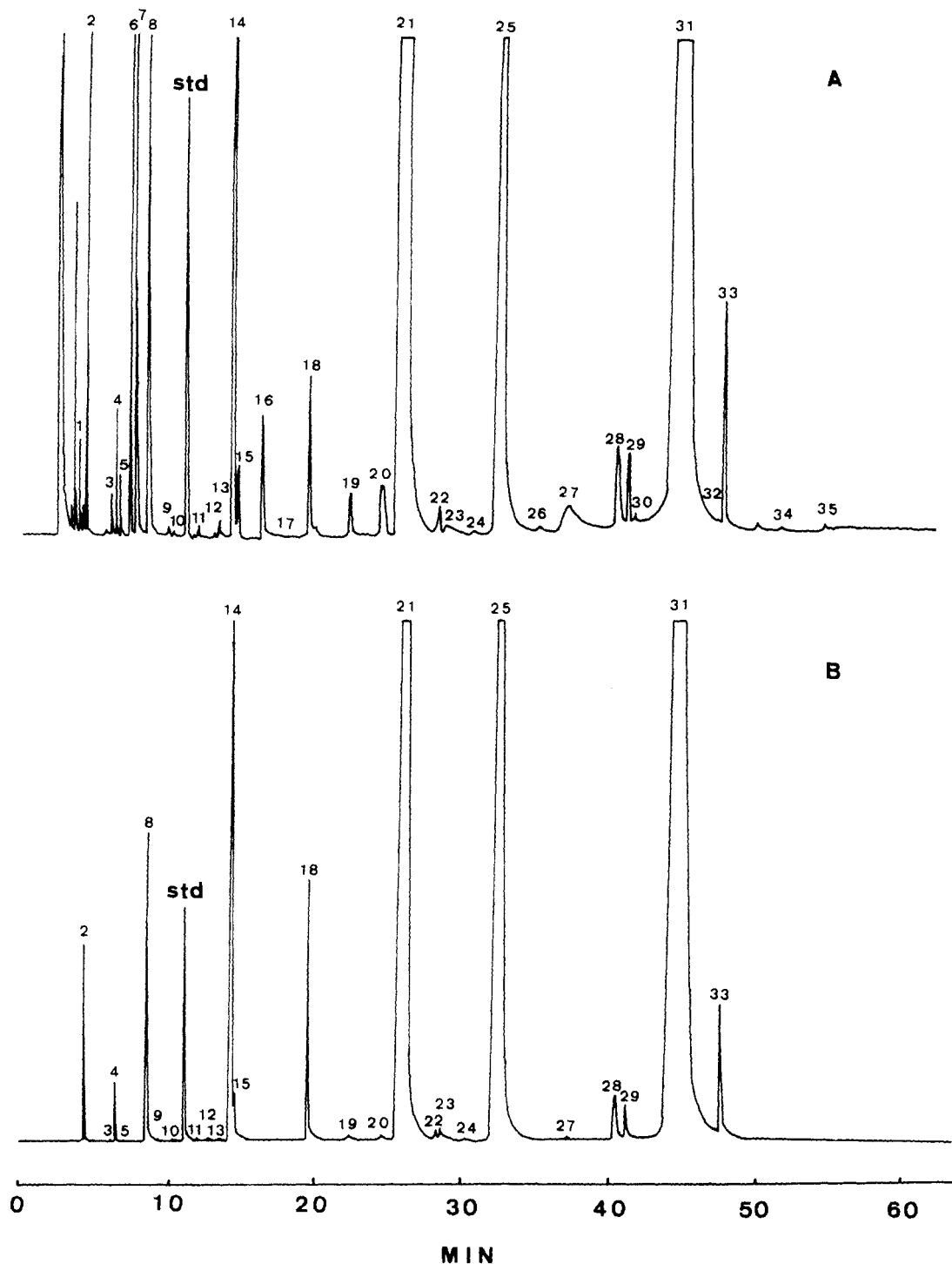
containing hot vegetable oil first and then put the vegetables and other foods or ingredients in and fry them.

The major volatile compounds of garlic were sulfur-containing compounds. Semmler (1892) established the importance of diallyl disulfide and diallyl trisulfide in the flavor of garlic distillate. Stoll and Seebeck (1948) showed that garlic contains *S*-allylcysteine sulfoxide (alliin) and an enzyme, allinase. By the action of allinase on alliin, diallyl thiosulfinate (allicin) is formed, a volatile compound.

Diallyl thiosulfinate was found as a major constituent

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**Figure 1.** Capillary gas chromatograms of volatiles of garlic isolated in a Likens-Nickerson steam distillation/solvent extraction apparatus: (A) detected by FID; (B) detected by FPD.

of garlic solvent extract (Brodnitz et al., 1971). Upon gas chromatography, diallyl thiosulfinate undergoes dehydration, leading to the formation of two isomeric disulfides. At room temperature, diallyl thiosulfinate undergoes rearrangement reactions. After 24 h, sulfur dioxide and diallyl mono-, di-, and trisulfides are the major products of the reactions. Allyl tetrasulfides were also found present in garlic bush essential oil (Zoghbi et al., 1984).

Decomposition of diallyl thiosulfinate proceeds by several pathways (Block, 1985). In one, three molecules of diallyl thiosulfinate combine, producing two molecules of 4,5,9-trithiadodeca-1,6,11-triene 9-oxide (ajoene). Along another path, diallyl thiosulfinate self-decomposes to form two isomeric cyclic compounds: 2-vinyl-4*H*-1,3-dithiin and

3-vinyl-4*H*-1,2-dithiin. In this paper, the constituents of garlic oils were further identified and the constituents of essential oils obtained from distillations or distillations plus solvent extractions with direct heating or steam heating are compared.

#### EXPERIMENTAL SECTION

**Sample Preparation.** Garlic cloves were purchased in a local market, the type generally used in cooking. In each batch, 600 g of garlic cloves was blended with 1500 g of distilled water for 5 min in a Waring blender. Volatile constituents were extracted for 2 h at boiling temperature in the water distillation apparatus (sample A), steam distillation apparatus (sample B), Likens-Nickerson (L-N) water distillation/solvent extraction apparatus (sample E), and L-N steam distillation/solvent extraction ap-

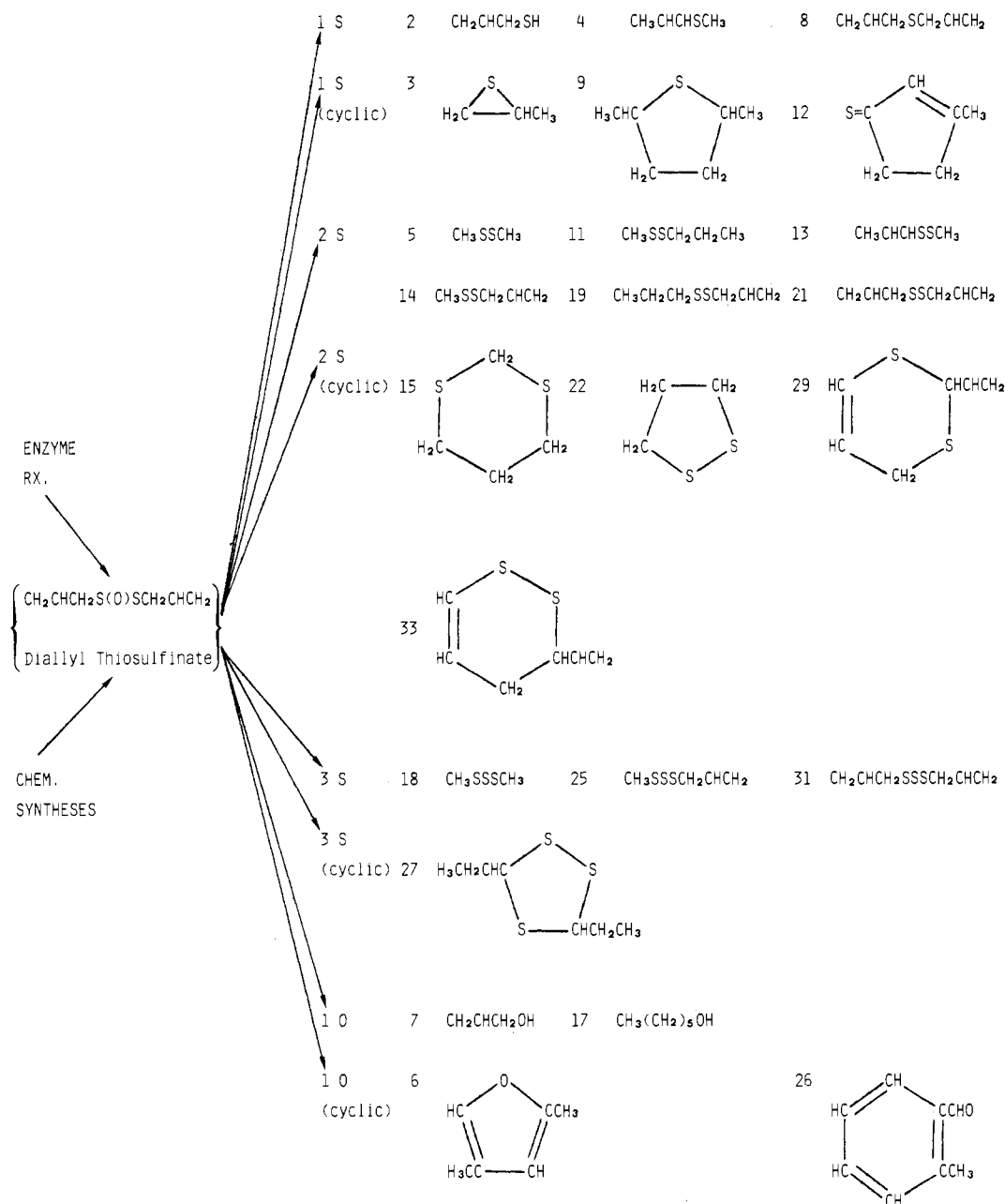


Figure 2. Structures of S-containing and O-containing compounds identified in garlic and the possible synthetic mechanism.

paratus (sample F) (Romer and Renner, 1974), respectively. In the L-N apparatus, redistilled diethyl ether (40 mL, 99.5%, E. Merck) was used as the extracting solvent. Volatiles in the water layer of the distillate of the water distillation and steam distillation were extracted two times by one volume of redistilled diethyl ether (samples C and D, respectively). Diethyl disulfide (Wako) stock solution (2 mL, 0.451 g in 50 mL of diethyl ether) was then added to the extract as an internal standard. The extracts were dried with anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated to minimum volume on a spinning band distillation apparatus (Kontes).

**Gas Chromatography.** Gas chromatography was conducted on a Shimadzu GC-9A equipped with both a flame ionization detector (FID) and a flame photometric detector (FPD). A 50 m  $\times$  0.22 mm fused silica column (Chrompack International, B.V.) coated with CP-Wax 52 CB was used. The column end was split into two columns to connect two detectors. The oven temperature was programmed from 50 to 200  $^\circ\text{C}$  at 2  $^\circ\text{C}/\text{min}$ . The injector and detector temperatures were 250  $^\circ\text{C}$ . The carrier gas was nitrogen at a flow rate of 0.75 mL/min. The data were recorded on a Shimadzu C-R3A and a C-R2AX integrator for FID and FPD, respectively. Values reported were from the average of two analyses. The linear retention indices of the volatile components were calculated with *n*-paraffins ( $\text{C}_8$ – $\text{C}_{25}$ , Alltech Associates) as

references (Majlat et al., 1974).

**Gas Chromatography–Mass Spectrometry.** GC–MS was conducted with a Hewlett-Packard 5985B system. The gas chromatograph was installed with a fused silica capillary (bonded CP-Wax 52 CB; 50 m  $\times$  0.32 mm). Operational parameters were as follows: carrier gas, helium; ionization voltage, 70 eV; ion source temperature, 200  $^\circ\text{C}$ .

**Chemical Syntheses.** 2-Vinyl-4*H*-1,3-dithiin and 3-vinyl-4*H*-1,2-dithiin were synthesized by the method of Bock et al. (1982).

## RESULTS AND DISCUSSION

It is known that the major volatile components of garlic are not originally present in the intact cloves. It was found that a colorless, odorless, and water-soluble flavor precursor, alliin, is present in the intact cells of garlic. On injury of the cells, the enzyme allinase comes in contact with alliin and causes its breakdown into the sulfur-containing product allicin (Cavallito, 1944a; Jones and Mann, 1963). Allicin is unstable and will break down into the strong-smelling constituents of garlic oil.

The water layer of garlic distillate was found to be

Table I. Identity of Volatile Compounds of Garlic

peak no. <sup>a</sup>	compound <sup>b</sup>	I <sub>x</sub> <sup>c</sup> (CP-Wax 52 CB)	MW	ID	char MS data: m/e (rel intens) <sup>d</sup>			
1	propene* <sup>e</sup>		42	MS	41 (100) 27 (20)	39 (75) 37 (17)	42 (67) 38 (13)	40 (26)
2	propenethiol <sup>f</sup>		74	MS	74 (100) 49 (22)	41 (78) 46 (21)	39 (70) 38 (11)	45 (41) 40 (8)
3	1,2-epithiopropene* <sup>e</sup>	924	74	MS	74 (100) 59 (42)	41 (77) 39 (40)	46 (72) 32 (31)	45 (70) 26 (19)
4	methyl allyl sulfide <sup>j</sup>	956	88	MS, GC	88 (100) 39 (41)	45 (76) 47 (27)	73 (67) 46 (24)	41 (41) 61 (16)
5	dimethyl disulfide <sup>j</sup>	1077	94	MS, GC	94 (100) 47 (19)	45 (47) 48 (10)	79 (43) 61 (10)	46 (26) 96 (9)
6	2,4-dimethylfuran* <sup>g</sup>	1093	96	MS	95 (100) 53 (30)	41 (77) 65 (28)	67 (73) 40 (20)	39 (61) 66 (18)
7	2-propen-1-ol <sup>e</sup>	1125	58	MS	57 (100) 27 (18)	29 (40) 58 (17)	39 (38) 28 (12)	31 (31) 32 (10)
8	diallyl sulfide <sup>j</sup>	1148	114	MS, GC	45 (100) 99 (31)	39 (60) 72 (25)	41 (46) 47 (22)	114 (40) 71 (13)
9	tetrahydro-2,5-dimethylthiophene* <sup>e</sup>	1197	116	MS	101 (100) 74 (29)	116 (43) 67 (20)	41 (32) 55 (19)	59 (30) 46 (17)
10	C <sub>8</sub> H <sub>10</sub> S <sup>i</sup>	1233	114	MS	45 (100) 55 (64)	42 (86) 73 (48)	43 (86) 71 (28)	29 (86) 64 (28)
11	methyl propyl disulfide <sup>e</sup>	1252	122	MS	80 (100) 46 (19)	122 (99) 47 (18)	41 (43) 27 (16)	43 (35) 39 (15)
12	3-methyl-2-cyclopentene-1-thione* <sup>e</sup>	1261	112	MS	112 (100) 97 (40)	79 (86) 45 (39)	85 (45) 84 (27)	77 (42) 29 (30)
13	<i>trans</i> -1-propenyl methyl disulfide <sup>g</sup>	1270	120	MS	120 (100) 47 (25)	45 (91) 75 (24)	41 (42) 80 (17)	39 (41) 73 (17)
14	methyl allyl disulfide <sup>e</sup>	1282	120	MS, GC	120 (100) 45 (36)	41 (69) 39 (30)	45 (36) 79 (10)	39 (31) 75 (27)
15	1,3-dithiane* <sup>e</sup>	1296	120	MS	120 (100) 39 (16)	45 (60) 73 (15)	72 (33) 47 (14)	71 (12) 71 (12)
16	aniline* <sup>e</sup>	1328	93	MS	93 (100) 65 (29)	39 (38) 40 (18)	92 (36) 41 (17)	66 (34) 45 (14)
17	1-hexanol* <sup>e</sup>	1337	102	MS	56 (100) 42 (24)	69 (54) 41 (21)	55 (44) 39 (15)	43 (36) 84 (12)
18	dimethyl trisulfide <sup>i</sup>	1380	126	MS, GC	126 (100) 46 (17)	45 (51) 64 (17)	79 (42) 111 (16)	45 (28) 80 (13)
19	propyl allyl disulfide <sup>g</sup>	1432	148	MS	41 (100) 39 (32)	148 (56) 45 (28)	106 (51) 64 (13)	43 (43) 75 (11)
20	C <sub>6</sub> H <sub>10</sub> S <sub>2</sub> <sup>i</sup>	1471	146	MS	73 (100) 45 (54)	146 (99) 105 (45)	81 (79) 39 (35)	41 (57) 71 (30)
21	diallyl disulfide <sup>i</sup>	1490	146	MS, GC	41 (100) 105 (27)	81 (53) 45 (35)	39 (52) 146 (35)	113 (39) 79 (24)
22	1,2-dimercaptocyclopentane* <sup>h</sup>	1519	106	MS	41 (100) 64 (31)	106 (88) 78 (21)	45 (60) 74 (20)	39 (40) 47 (20)
23	unknown	1532		MS	103 (100) 39 (15)	104 (64) 69 (11)	45 (39) 105 (11)	119 (16) 74 (8)
24	4-methyl-5-vinylthiazole* <sup>h</sup>	1560	125	MS	125 (100) 103 (18)	97 (65) 80 (17)	124 (60) 71 (16)	98 (38) 65 (12)
25	methyl allyl trisulfide <sup>g</sup>	1593	152	MS, GC	87 (100) 47 (51)	45 (95) 111 (21)	41 (72) 79 (20)	73 (72) 64 (16)
26	2-methylbenzaldehyde* <sup>e</sup>	1644	120	MS	91 (100) 89 (15)	120 (96) 63 (12)	119 (82) 92 (11)	65 (22) 39 (6)
27	3,5-diethyl-1,2,4-trithiolane* <sup>g</sup>	1682	180	MS	74 (100) 73 (15)	41 (31) 61 (13)	130 (18) 39 (12)	45 (17) 85 (10)
28	isobutyl isothiocyanate* <sup>h</sup>	1753	115	MS	115 (100) 45 (21)	73 (96) 43 (18)	41 (32) 39 (17)	74 (30) 105 (17)
29	3-vinyl-4 <i>H</i> -1,2-dithiin <sup>j</sup>	1761	144	MS, GC	45 (100) 97 (39)	111 (56) 103 (32)	39 (50) 71 (30)	144 (40) 72 (29)
30	unknown	1772		MS	146 (100) 72 (55)	74 (73) 71 (32)	73 (64) 138 (30)	117 (62) 45 (23)
31	diallyl trisulfide <sup>e</sup>	1806	178	MS	73 (100) 39 (19)	113 (94) 138 (18)	41 (33) 74 (17)	45 (26) 71 (14)
32	unknown	1851		MS	138 (100) 95 (60)	111 (92) 123 (50)	109 (64) 77 (48)	110 (62) 151 (36)
33	2-vinyl-4 <i>H</i> -1,3-dithiin <sup>j</sup>	1872	144	MS, GC	45 (100) 111 (38)	72 (61) 144 (37)	71 (53) 41 (21)	39 (45) 103 (17)
34	unknown	1943		MS	97 (100) 134 (32)	126 (51) 45 (18)	28 (41) 73 (23)	138 (34) 74 (21)
35	unknown	2003		MS	128 (100) 113 (21)	45 (37) 110 (21)	99 (35) 53 (16)	65 (26) 85 (15)

<sup>a</sup>Number refers to Figure 1. <sup>b</sup>Compounds with asterisks indicate those newly identified in garlic. <sup>c</sup>Calculated value using *n*-paraffins (C<sub>6</sub>-C<sub>25</sub>; Alltech Associates) as references. <sup>d</sup>Number in parentheses indicates relative percentage. <sup>e</sup>EPA/NIH, 1980. <sup>f</sup>Wu and Wu, 1983. <sup>g</sup>MSDC, 1983. <sup>h</sup>TNO, 1981. <sup>i</sup>Tentatively identified. <sup>j</sup>Identified by authentic compound.

cloudy. There were some volatile components suspended or dissolved in the water layer. In this study, these components were identified; the difference of volatile components in various garlic oils was also studied.

Figure 1 shows the capillary gas chromatographic separations of volatile compounds of garlic essential oil isolated by L-N steam distillation/solvent extraction and detected by FID and FPD, respectively.

The volatile compounds of garlic identified in this study are shown in Table I. The GC analyses of volatile compounds from different extraction methods are shown in Table II. Identifications were accomplished by comparing

the retention indices and/or mass spectra with those of authentic compounds and the published data (Wu and Wu, 1983; EPA/NIH, 1980; TNO, 1981; MSDC, 1983; Jennings and Shibamoto, 1980). The structure assignments of some of the novel S compounds were based solely on the interpretation of mass spectral data; therefore, these compounds are considered tentative. Of the 28 compounds reported in this study, 13 are new to the volatiles of garlic (compounds with an asterisk in Table I).

Figure 1B shows the capillary gas chromatograph of S compounds (detected by FPD) isolated by L-N steam distillation/solvent extraction. The S compounds could

Table II. Composition of Volatiles Isolated from Garlic

peak no. <sup>a</sup>	compound	yield, <sup>b</sup> ×10 <sup>-6</sup> g/g garlic bulb					
		A <sup>c</sup>	B <sup>c</sup>	C <sup>c</sup>	D <sup>c</sup>	E <sup>c</sup>	F <sup>c</sup>
1	propene	0.10	0.01	0.27	0.15	5.99	4.04
2	propenethiol	5.77	10.85	1.38	4.65	11.53	41.07
3	1,2-epithiopropene	0.10	0.17	0.14	0.47	0.15	1.66
4	methyl allyl sulfide	1.71	1.93	0.53	0.63	3.82	4.64
5	dimethyl disulfide	1.25	0.82	0.77	0.64	2.37	2.51
6	2,4-dimethylfuran	5.12	5.89	14.07	14.93	29.60	27.67
7	2-propen-1-ol	0.44	0.11	23.09	36.14	121.22	81.04
8	diallyl sulfide	29.60	49.39	2.05	3.40	30.86	98.71
9	2,5-dimethyl-tetrahydrothiophene	0.31	0.41	tr <sup>d</sup>	tr	0.17	0.62
10	C <sub>6</sub> H <sub>10</sub> S	0.26	0.25	tr	tr	0.12	0.35
11	methyl propyl disulfide	0.44	0.47	0.03	0.08	0.66	0.76
12	3-methyl-2-cyclopentene-1-thione	1.03	1.10	0.20	0.16	1.60	1.42
13	<i>trans</i> -1-propenyl methyl disulfide	tr	tr	0.26	0.24	0.92	tr
14	methyl allyl disulfide	87.62	82.88	8.17	5.56	99.95	103.91
15	1,3-dithiane	2.02	1.64	0.11	0.08	2.95	2.75
16	aniline	tr	tr	6.11	5.74	10.52	6.83
17	1-hexanol	tr	tr	0.23	0.08	tr	0.08
18	dimethyl trisulfide	14.50	18.23	1.30	0.82	18.96	15.04
19	propyl allyl disulfide	6.02	5.53	0.27	0.10	6.36	6.77
20	C <sub>6</sub> H <sub>10</sub> S <sub>2</sub>	16.15	14.33	0.82	0.26	16.03	11.10
21	diallyl disulfide	548.11	530.44	33.51	16.74	537.18	612.63
22	1,2-dimercaptocyclopentane	2.16	2.15	0.13	tr	2.42	2.09
23	unknown	5.09	4.62	2.46	2.39	4.58	0.94
24	4-methyl-5-vinylthiazole	0.18	0.07	0.10	0.15	tr	0.75
25	methyl allyl trisulfide	270.91	278.59	17.51	5.79	272.17	250.61
26	2-methylbenzaldehyde	tr	tr	0.10	0.03	tr	0.09
27	3,5-diethyl-1,2,4-trithiolane	3.52	0.15	43.00	41.55	15.94	16.75
28	isobutyl isothiocyanate	19.93	20.17	1.06	0.14	25.29	18.48
29	3-vinyl-4 <i>H</i> -1,2-dithiin	8.75	5.79	0.87	0.34	10.65	6.29
30	unknown	1.30	0.89	1.52	1.03	3.04	1.71
31	diallyl trisulfide	1010.83	1024.90	51.31	10.09	1060.89	903.44
32	unknown	0.21	tr	1.05	tr	tr	tr
33	2-vinyl-4 <i>H</i> -1,3-dithiin	21.82	14.79	2.71	2.16	29.33	16.37
34	unknown	tr	tr	0.54	0.51	2.27	0.09
35	unknown	tr	tr	2.22	1.57	3.88	0.32
	total	2065.25	2076.57	217.88	156.52	2331.42	2241.53

<sup>a</sup> Number refers to Figure 1. <sup>b</sup> Average of two experiments; yields were calculated with diethyl disulfide as internal standard. <sup>c</sup> Key: A and B, essential oil obtained by water distillation and steam distillation, respectively; C and D, volatiles in the water layer of the distillate of water distillation and steam distillation, respectively; E and F, volatiles isolated in the Likens-Nickerson water distillation/solvent extraction and steam distillation/solvent extraction apparatus, respectively. <sup>d</sup> Less than 0.005 ppm.

be confirmed by using FPD as the detector; the number of S atoms in each S compound could be confirmed by the ratio of  $M^+ + 2/M$  (4.4% for one S atom). Figure 2 shows the structures of garlic volatile compounds. The major compounds of garlic can be classified into sulfur-containing compounds and oxygen-containing compounds. The S compounds can be further classified into three major groups containing one, two, and three sulfurs. The sulfur-containing and oxygen-containing compounds were thought to arise from the decomposition and rearrangement of diallyl thiosulfinate (Boelens et al., 1971; Block and Ahmad, 1984). It is worth noting that most of the compounds list in Figure 2 could also be detected in the decomposed or rearranged products of synthetic allicin or diallyl thiosulfinate. It is therefore reasonable to assume that chemical reactions, such as decomposition and rearrangement of diallyl thiosulfinate, may be the dominant forces in the final stages of formation of sulfur-containing compounds and oxygen-containing compounds.

Brodnitz et al. (1971) found that diallyl thiosulfinate decomposes into two cyclic sulfur-containing compounds during gas chromatographic analysis. These two compounds were identified to be 3-vinyl-1,2-dithi-5-ene and 3-vinyl-1,2-dithi-4-ene, respectively. Block (1985) found that diallyl thiosulfinate will self-decompose, giving 2-propenesulfenic acid and thioacrolein. The self-condensation of two molecules of 2-propenesulfenic acid regenerates a molecule of diallyl thiosulfinate; the self-condensation of two molecules of thioacrolein yields two types of

cyclic compound by Diels-Alder reaction. These two cyclic compounds were identified to be 2-vinyl-4*H*-1,3-dithiin and 3-vinyl-4*H*-1,2-dithiin. In this study, peaks 29 and 33 of Figure 1 were identified as 2-vinyl-4*H*-1,3-dithiin and 3-vinyl-4*H*-1,2-dithiin, respectively, by using authentic compounds. These two compounds may be artifacts from diallyl thiosulfinate during the gas chromatographic analysis. However, the result obtained from gas chromatographic analysis cannot tell whether they are originally present in the sample or are artifacts in the analysis.

In this study, the yields of garlic essential oils ranged from 0.21% to 0.23%. The yields of garlic essential oils isolated from distillation had lower values because of losing some components in the water layer as shown in Table I. The essential oils obtained by steam distillation (samples B and F) contained more high-volatility components such as propenethiol (peak 2), 1,2-epithiopropene (peak 3), methyl allyl sulfide (peak 4), diallyl sulfide (peak 8), tetrahydro-2,5-dimethylthiophene (peak 9), and methyl propyl disulfide (peak 11) and fewer low-volatility components such as diallyl disulfide (peak 21), 1,2-dimercaptocyclopentane (peak 22), 3-vinyl-4*H*-1,2-dithiin (peak 29), and 2-vinyl-4*H*-1,3-dithiin (peak 33) than those obtained by water distillation. The water layer of garlic distillate (samples C and D) contained more 2,4-dimethylfuran (peak 6), 2-propen-1-ol (peak 7), aniline (peak 16), and 3,5-diethyl-1,2,4-trithiolane than its oil layer (samples A and B). The essential oils obtained by L-N distillation/solvent extraction contained more of these

compounds than those from water distillation and steam distillation (samples A and B) too. These differences are partially due to the fact that these components are dissolved or suspended in the water layer easier than in the oil layer of the distillate; when distilled in the L-N apparatus, these components could easily be extracted by the solvent.

#### ACKNOWLEDGMENT

Grateful acknowledgment is made for financial support from the Council for Agricultural Planning and Development of the Republic of China. The technical assistance of Ming-Chin Wang and Shu-Er Liou, Food Industry Research and Development Institute, is appreciated.

**Registry No.** CH<sub>2</sub>CHCH<sub>2</sub>SH, 870-23-5; CH<sub>2</sub>CHCH<sub>2</sub>SCH<sub>3</sub>, 10152-76-8; CH<sub>3</sub>SSCH<sub>3</sub>, 624-92-0; CH<sub>2</sub>CHCH<sub>2</sub>OH, 107-18-6; CH<sub>2</sub>CHCH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>, 592-88-1; CH<sub>3</sub>SSCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 2179-60-4; CH<sub>3</sub>CHCHSSCH<sub>3</sub>, 23838-19-9; CH<sub>3</sub>SSCH<sub>2</sub>CH<sub>2</sub>, 2179-58-0; CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>OH, 111-27-3; CH<sub>3</sub>SSSCH<sub>3</sub>, 3658-80-8; CH<sub>3</sub>C-H<sub>2</sub>CH<sub>2</sub>SSCH<sub>2</sub>CH<sub>2</sub>, 2179-59-1; CH<sub>2</sub>CHCH<sub>2</sub>SSCH<sub>2</sub>CH<sub>2</sub>, 2179-57-9; CH<sub>3</sub>SSSCH<sub>2</sub>CH<sub>2</sub>, 34135-85-8; CH<sub>2</sub>CHCH<sub>2</sub>SSSCH<sub>2</sub>CH<sub>2</sub>, 2050-87-5; propene, 115-07-1; 1,2-epithiopropene, 1072-43-1; 2,4-dimethylfuran, 3710-43-8; tetrahydro-2,5-dimethylthiophene, 1551-31-1; 3-methyl-2-cyclopentene-1-thione, 30221-52-4; 1,3-dithiane, 505-23-7; aniline, 62-53-3; 1,2-dimercaptocyclopentane, 89211-39-2; 4-methyl-5-vinylthiazole, 1759-28-0; 2-methylbenzaldehyde, 529-20-4; 3,5-diethyl-1,2,4-trithiolane, 54644-28-9; isobutyl isothiocyanate, 591-82-2; 3-vinyl-4H-1,2-dithiin, 62488-53-3; 2-vinyl-4H-1,3-dithiin, 80028-57-5.

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Received for review May 18, 1988. Accepted September 13, 1988.

## Effects of pH Adjustment and Heat Treatment on the Stability and the Formation of Volatile Compounds of Garlic

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Effects of pH adjustment after blending, 30-min standing, and heat treatment of garlic cloves on the stability and the formation of volatile compounds of garlic were studied with GC in this study. It was found that the amount of the two isomeric cyclic compounds 3-vinyl-4H-1,2-dithiin and 2-vinyl-4H-1,3-dithiin, which were artifacts from alliin, decreased with increasing pH values, whereas the amount of diallyl disulfide, propenethiol, propyl allyl disulfide, and diallyl sulfide increased with increasing pH values. Formation of diallyl trisulfide, methyl allyl trisulfide, 1,3-dithiane, 2,4-dimethylfuran, aniline, and *trans*-1-propenyl methyl disulfide were favored in neutral conditions, whereas formation of methyl allyl disulfide, methyl allyl sulfide, 1,2-epithiopropene, and methyl propyl disulfide were favored around pH 9.0.

Garlic (*Allium sativum* Linn.) has been known since ancient times as a flavoring agent and for its medicinal properties. Semmler (1892) established the importance of diallyl disulfide and diallyl trisulfide in the flavor of garlic distillate. It was also evident at an early stage that the odorous compounds of interest were not present in the plant as such but were formed (enzymically) when the cellular tissue was disrupted. Cavallito and Bailey (1944) described the isolation of the odoriferous antibacterial substance alliin (diallyl thiosulfinate) from extraction of

garlic with ethanol at room temperature. Stoll and Seebeck (1948) reported that intact garlic cloves contain 0.24% by weight *S*-allylcysteine *S*-oxide (alliin), a colorless odorless solid, and the enzyme allinase, which converts alliin into alliin. In addition to alliin, three (possibly four)  $\gamma$ -L-glutamyl derivatives of *S*-alk(en)ylcysteine sulfoxides were identified in garlic (Virtanen, 1965). These compounds are not cleaved by allinase; they represent only "potentially available" flavor. Consequently, peptidases and transpeptidases, which "release" these secondary flavor precursors to first precursors, thiosulfonates, are important enhancers of the aroma of garlic and its products (Virtanen, 1965).

The crude cell-free garlic enzyme solution, of unspecified purity, utilized by Stoll and Seebeck (1947, 1948) showed a broad pH optimum (5-8) and a temperature optimum (37 °C) under the conditions used. With use of protamine and ammonium sulfate as precipitation agents followed

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