

Volatile Compounds Generated from Thermal Degradation of Alliin and Deoxyalliin in an Aqueous Solution

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Aqueous solutions of alliin, one of the major flavor precursors of garlic, and deoxyalliin, one of the thermal degradation products of γ -glutamyl-S-allylcysteine, which also is one of the major flavor precursors of garlic, were dissolved in water and heated in a closed system at 180 °C under different pH conditions. The volatile flavor compounds generated were isolated by Likens-Nickerson simultaneous distillation/solvent extraction and quantified and identified by GC and GC-MS. The major volatile compounds generated from the degradation of alliin at pH 3, 7, and 9 were allyl alcohol and acetaldehyde. At pH 5, the major volatile compounds generated from the degradation of alliin were acetaldehyde, 2-acetylthiazole, sulfur dioxide, ethyl acetate, and 1-propene. The major volatile compounds generated from the degradation of deoxyalliin at pH 5, 7, and 9 were diallyl sulfide, 2-methyl-1,4-dithiepane, (allylthio)acetic acid, diallyl disulfide, 2-ethyl-1,3-dithiane, 4,6-dimethyl-1,2,5-trithiepane, 3,6-dimethyl-1,4-dithiane, and allyl mercaptan. At pH 3, the major volatile compounds generated from the degradation of deoxyalliin were (allylthio)acetaldehyde, 3-(allylthio)propanal, 3,6-dimethyl-1,2,5-trithiepane, and (allylthio)acetic acid.

INTRODUCTION

It has been reported that intact garlic cloves contain alliin (S-allylcysteine S-oxide), a colorless and odorless compound (Stoll and Seeback, 1951). It is also well-known that the enzyme, alliinase, which is activated when the cellular tissue of garlic is disrupted, converts alliin to alliin (Stoll and Seeback, 1951). After the enzyme was deactivated by boiling the garlic bulb or homogenizing the garlic bulb with alcohol containing limited quantities of water, alliin was not converted to alliin and no more pungent odor was detected from the garlic samples (Stoll and Seeback, 1951; Ueda et al., 1990). Alliin was reported to be very unstable and was converted to allyl sulfides and dithiols and contributed to the flavor of garlic products (Stoll and Seeback, 1951; Sreenivasamurthy et al., 1961; Block, 1985; Yu and Wu, 1989a; Yu et al., 1989a).

Recent studies on the main sulfur compounds in intact garlic cloves by Lawson (1992) showed that alliin was the most predominant flavor precursor of garlic. The content of alliin in intact garlic cloves was high, up to 12-14 mg/g of fresh garlic. Besides alliin, two other cysteine sulfoxides, i.e., methyl- and *trans*-1-propenylcysteine sulfoxide, were also found in intact garlic cloves. However, the content of these two cysteine sulfoxides in garlic was lower when compared with that of alliin. Besides cysteine sulfoxides, some γ -glutamylcysteine dipeptides were also reported to be important flavor precursors of garlic (Lawson, 1992). γ -Glutamyl-S-allylcysteine, γ -glutamyl-S-*trans*-1-propenylcysteine, and γ -glutamyl-S-methylcysteine were found to be the major γ -glutamylcysteine dipeptides of garlic (Lawson, 1992). The content of these dipeptides in garlic was found to be 4-7, 4-8, and 0.5-1 mg/g of fresh garlic, respectively. The γ -glutamylcysteine dipeptides were thought only to be the "potential available" flavor pre-

cursors, because they cannot be cleaved by alliinase (Virtanen, 1965). The γ -glutamylcysteine dipeptides, however, have flavor themselves. Ueda et al. (1990) reported that γ -glutamyl-S-allylcysteine showed "characteristic kokumi flavor".

The pH and thermal effects on the formation of volatile compounds from the degradation of alliin, garlic homogenate, garlic oil, and diallyl disulfide have been well studied (Yu and Wu, 1988, 1989a,b; Yu et al., 1989b,c; Block et al., 1988). However, only a few papers reported the stability of garlic flavor precursors, and the results were not conclusive. The thermal generation of volatile compounds from the degradation of flavor precursors has not been studied yet. Stoll and Seeback (1951) reported that alliin was stable in an aqueous solution even at a high temperature. However, if it was heated in diluted methanol or ethanol to 100 °C, the solution immediately became a dark red color and ammonia and carbon dioxide were given off. Sreenivasamurthy et al. (1961) also reported that alliin remained stable during storage over a long time, either in an aqueous extract or in the dehydrated garlic powder. On the other hand, a recent study by Lawson (1992) concerning the effects of boiling on garlic's cysteine compounds showed that after being heated in boiling water, γ -glutamyl-S-allylcysteine was converted to S-allylcysteine, i.e., deoxyalliin (12% conversion in 20 min); γ -glutamyl-S-*trans*-1-propenylcysteine was converted to S-*trans*- and S-*cis*-1-propenylcysteine, and alliin was completely lost in 8 h to unknown compounds.

In the present paper, deoxyalliin (representing one of the thermally decomposed products of γ -glutamyl dipeptides) and alliin were synthesized and the volatile thermal degradation products of deoxyalliin and alliin in aqueous solution of different pHs were studied.

EXPERIMENTAL PROCEDURES

Synthesis of Deoxyalliin and Alliin. Deoxyalliin and alliin were synthesized according to the procedures of Iberl et al. (1990) with slight modifications as shown below.

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Table 1. Initial pH, Final pH, Final Appearance, and Flavor Description of Thermally Degraded Alliin and Deoxyalliin Aqueous Solution

initial pH	final pH	final appearance	flavor description (by odor)
Alliin Solution			
3.0	4.0	earthy yellow	sour, sulfury, black mushroom-like, and slightly roasted meaty
5.0	4.5	slightly dark-green	etheral, sour, sulfury, popcorn-like, roasted meaty
7.0	6.3	earthy, dark-yellow	sulfury, roasted nutty-meaty
9.0	8.0	slightly brown-yellow	sulfury, roasted nutty-meaty
Deoxyalliin Solution			
3.0	2.8	clear slightly yellow	pungent, cooked green garlic bush odor
5.0	6.9	cloudy slightly white-yellow	pungent, cooked garlic bush odor
7.0	7.1	very slightly white-yellow	pungent, cooked garlic bush with slightly fried garlic character
9.0	8.8	slightly black	pungent, cooked garlic bush-like with slightly fried garlic and phenolic character

Table 2. Volatile Compounds Identified from the Thermally Degraded Alliin Aqueous Solution

no.	compound identified	MW	RI ^a (DB-1)	mg/mol				mass spectrum ref
				pH 3	pH 5	pH 7	pH 9	
A1	1-propene	42	<500	1.1	39.9	nd ^b	1.3	d
A2	sulfur dioxide	64	<500	34.1	258.7	0.7	9.4	d
A3	acetaldehyde	44	<500	132.1	1199.6	364.0	131.3	d
A4	allyl alcohol	58	545	1452.9	93.3	1149.5	929.2	d
A5	ethyl acetate	88	601	83.5	232.3	0.8	33.4	d
A6	acetic acid	60	622	1.4	72.7	nd	nd	d
A7	2-butenal	70	629	nd	nd	nd	1.5	d
A8	2-pentenal	84	663	nd	nd	nd	10.1	f
A9	2-ethyl-4-methyl-1,3-dioxolane	116	666	nd	18.2	nd	nd	d
A10	2,6-dimethyl-1,4-dioxane	116	672	nd	10.4	nd	nd	e
A11	thiazole	85	716	9.8	9.9	25.6	1.8	e
A12	acetal	118	725	35.5	26.4	1.6	tr ^c	d
A13	dimethyl disulfide	94	748	nd	11.1	nd	nd	d
A14	2-methylthiazole	99	790	nd	7.5	4.5	1.2	f
A15	2-methylpyridine	93	797	13.4	nd	nd	nd	d
A16	ethanesulfonic acid methyl ester	108	798	nd	5.1	nd	nd	d
A17	methyl ethyl disulfide	108	821	nd	62.0	nd	nd	f
A18	2-ethyl-1,3-dioxane	116	824	nd	nd	0.9	tr	g
A19	methyl propyl disulfide	122	881	nd	7.5	nd	nd	d
A20	methyl allyl disulfide	120	900	nd	7.7	nd	nd	f
A21	3-methylthiane	116	953	nd	nd	nd	3.2	g
A22	dimethyl trisulfide	126	958	nd	11.5	nd	nd	d
A23	1,2-dithiacyclopentane	106	960	tr	1.7	nd	nd	f
A24	2-formylthiophene	112	962	4.8	nd	1.5	13.3	e
A25	3-formylthiophene	112	972	4.2	3.5	tr	5.6	f
A26	2-acetylthiazole	127	993	3.2	359.5	16.7	0.7	f
A27	1,2-bis(methylthio)ethane	122	1027	nd	nd	nd	0.5	e
A28	1,4-dithiepane	134	1091	nd	nd	nd	1.9	g
A29	2-ethylthiazole	113	1093	nd	nd	nd	3.0	d
A30	methyl propyl trisulfide	154	1097	nd	3.6	nd	nd	g
A31	1,3-dithiane	120	1099	2.6	nd	nd	nd	d
A32	3-formyl-2-methylthiophene	126	1107	tr	nd	nd	nd	g
A33	3,5-dimethyl-1,2,4-trithiolane	152	1127	nd	nd	8.9	2.1	e
A34	3,5-dimethyl-1,2,4-trithiolane	152	1133	nd	nd	10.2	1.7	e
A35	3,6-dimethyl-1,4-dithiane	148	1137	nd	nd	2.5	0.6	g
A36	3,6-dimethyl-1,4-dithiane	148	1145	nd	nd	2.0	tr	g
A37	methyl-1,2,3-trithiacyclopentane	138	1153	22.3	188.0	nd	5.3	h
A38	2,4,6-trimethylperhydro-1,3,5-dithiazine	163	1194	nd	nd	70.0	5.1	i
A39	1,2,3-trithiacyclohexane	138	1199	4.4	nd	nd	0.5	g
A40	dimethyl tetrasulfide	158	1202	nd	5.3	nd	nd	f
A41	dipropyl trisulfide	182	1225	tr	nd	nd	nd	f
A42	3,5-dimethyl-1,2,4-trithiane	166	1261	nd	nd	4.1	nd	g
A43	3,5-dimethyl-1,2,4-trithiane	166	1274	nd	nd	6.8	nd	g
A44	4-methyl-1,2,5-trithiepane	166	1293	nd	nd	13.4	nd	g
A45	methyl-1,2,3,4-tetrathiane	170	1335	nd	57.5	nd	nd	h
A46	1,2,3,4-tetrathiepane	170	1376	214.8	9.7	nd	0.8	g
A47	3,6-dimethyl-1,2,4,5-tetrathiane	184	1387	nd	nd	6.9	tr	j
A48	4,6-dimethyl-1,2,3,5-tetrathiane	184	1517	nd	20.9	nd	3.5	j
A49	4-ethyl-6-methyl-1,2,3,5-tetrathiane	198	1564	tr	tr	14.9	13.7	f
total				2020.1	2723.5	1705.5	1180.7	

^a RI, calculated Kovats retention indices. ^b nd, not detected. ^c Trace: <0.5 mg/mol. ^d Heller and Milne (1978). ^e Heller and Milne (1980). ^f TNO (1988). ^g Identified by mass spectrum interpretation. ^h Block et al. (1988). ⁱ Kawai and Ishida (1989). ^j Zhang et al. (1988).

Synthesis and Purification of L-Deoxyalliin (S-Allyl-L-cysteine). L-Cysteine (1 mol) was suspended in 3 L of absolute ethanol and kept in an ice bath; 1.1 mol of allyl bromide (99%, Aldrich Chemical Co., Milwaukee, WI) was added to the stirred suspension followed by the addition of 3.5 mol of NaOH as a 20 M aqueous solution. After 1 h of stirring, a solution of crude

deoxyalliin formed and was acidified to pH 5.3 by glacial acetic acid at 30 °C. After crystallization at 4 °C, the white needle-like crystals were filtered, washed twice with absolute ethanol, dried at 50 °C, and then recrystallized at 4 °C. This was done by dissolving the substance in a small portion of boiling water containing 1% glacial acetic acid. This solution was poured into

Table 3. Volatile Compounds Identified from the Thermally Degraded Deoxyalliin Aqueous Solution

no.	compound identified	MW	RI ^b (DB-1)	mg/mol				mass spectrum ref
				pH 3	pH 5	pH 7	pH 9	
D1	1-propene	42	<500	23.3	34.4	24.1	39.3	d
D2	acetaldehyde	44	<500	1.7	125.2	50.7	10.6	d
D3	allyl alcohol	58	540	1.2	28.0	24.4	11.1	d
D4	allyl mercaptan	74	583	9.4	137.9	142.6	143.7	f
D5	1-mercapto-2-propanol	92	761	47.9	37.1	21.3	2.2	f
D6	1-mercapto-3-propanol	92	776	8.0	12.5	8.0	0.8	g
D7	diallyl sulfide	114	852	4.2	835.6	399.5	294.0	e
D8	(allylthio)acetaldehyde	116	901	148.2	39.7	10.0	0.6	g
D9	1,2-dithiacyclopent-3-ene	104	941	1.1	3.7	3.9	3.4	g
D10	mercaptomethylcyclopentane	116	957	5.0	49.2	50.0	30.6	g
D11	2-formylthiophene	112	966	2.6	78.8	81.1	58.2	e
D12	3-formylthiophene	112	981	1.0	3.9	7.1	10.0	f
D13	4-methyl-1,3-dithiacyclopentane	120	1010	0.6	51.6	72.3	47.8	g
D14	(allylthio)acetic acid	132	1014	56.2	340.0	404.3	91.4	d
D15	2-methyl-1,3-dithiane	134	1029	nd	114.6	117.8	26.9	e
D16	3-(allylthio)propanol	132	1036	1.8	58.2	50.4	14.2	g
D17	3-(allylthio)propanal	130	1042	118.4	42.9	11.6	0.5	g
D18	diallyl disulfide	146	1075	39.5	324.4	281.8	326.3	e
D19	1,4-dithiepane	134	1098	nd ^c	53.0	70.2	18.5	g
D20	1,4-dithiacyclohept-5-ene	132	1107	3.3	nd	5.1	1.0	g
D21	2-(mercaptoethyl)tetrahydrothiophene	148	1110	7.8	40.3	13.2	24.4	g
D22	2-(mercaptomethyl)thiane	148	1119	6.1	17.4	7.3	3.2	g
D23	2-ethyl-1,3-dithiane	148	1131	7.1	275.6	237.0	166.2	g
D24	3,6-dimethyl-1,4-dithiane	148	1138	10.1	231.3	182.9	49.0	g
D25	methyl-1,2,3-trithiacyclopentane	138	1155	6.9	3.0	nd	nd	g
D26	2-methyl-1,4-dithiepane	148	1160	23.6	670.2	639.8	406.7	g
D27	4-methyl-1,2-dithiepane	148	1187	10.2	nd	nd	nd	g
D28	2,4,6-trimethylperhydro-1,3,5-dithiazine	163	1202	1.5	177.6	196.5	121.7	i
D29	1,5-dithiacyclooctane	148	1235	0.8	12.8	8.9	5.9	g
D30	5-hydroxy-1,2-dithiacyclooctane	164	1244	41.2	64.6	21.7	10.4	g
D31	unknown [152 (100), 142 (78), 59 (60), 41 (52), 101 (40), 92 (39), 65 (38), 60 (38), 67 (30), 73 (22), 79 (20), 113 (17)] ^a	152	1255	nd	15.4	16.9	25.8	g
D32	3,5-dimethyl-1,2,6-trithiane	166	1265	8.3	8.8	30.5	4.1	g
D33	4-(hydroxymethyl)-1,2-dithiepane	164	1274	4.4	30.8	6.9	2.6	g
D34	3,5-dimethyl-1,2,6-trithiane	166	1275	nd	20.8	45.5	4.6	g
D35	4-methyl-1,2,5-trithiepane	166	1298	nd	47.6	47.3	6.0	g
D36	1,2,5-trithiacyclooctane	166	1302	nd	25.1	22.4	4.0	g
D37	unknown [73 (100), 41 (98), 59 (60), 45 (45), 147 (44), 115 (44), 101 (38), 39 (40), 72 (32), 105 (22), 67 (21), 47 (13)]	147	1371	7.7	43.5	36.9	68.8	g
D38	1,2,3,4-tetrathiepane	170	1375	3.5	5.2	3.6	1.7	g
D39	3-ethyl-5-methyl-1,2,4-trithiolane	166	1407	nd	10.8	11.6	5.7	g
D40	3,6-dimethyl-1,2,5-trithiepane	180	1432	57.5	45.9	24.0	2.4	g
D41	3,6-dimethyl-1,2,5-trithiepane	180	1449	55.1	73.6	46.7	12.4	g
D42	4,6-dimethyl-1,2,5-trithiepane	180	1454	106.5	152.6	94.4	23.2	g
D43	4-ethyl-6-methyl-1,2,3,5-tetrathiane	198	1571	1.5	52.4	43.4	19.7	g
D44	7-methyl-4,5,8-trithiaundeca-1,10-diene	220	1593	3.1	9.4	10.5	4.7	h
D45	unknown [119 (100), 41 (14), 45 (13), 39 (12), 75 (10), 85 (8), 91 (6)]	206	1636	4.1	59.2	48.8	7.1	g
D46	unknown [160 (100), 159 (62), 127 (51), 202 (38), 128 (20), 97 (16), 161 (14), 39 (13), 204 (4)]	202	1674	11.1	14.4	11.6	17.2	g
D47	unknown [179 (100), 105 (65), 41 (38), 119 (30), 45 (28), 133 (20), 59 (13), 146 (10)]		1751	14.0	32.1	26.6	11.1	g
	total			865.5	4511.1	3671.1	2139.7	

^a MS, *m/z* (relative intensity). ^b RI, calculated Kovats retention indices. ^c nd, not detected. ^d Heller and Milne (1978). ^e Heller and Milne (1980). ^f TNO (1988). ^g Identified by mass spectrum interpretation. ^h Block et al. (1988). ⁱ Kawai and Ishida (1989).

a 15-fold amount of boiling ethanol. The solvent immediately turned turbid with the appearance of small plates of deoxyalliin. After cooling to room temperature, the solution was left to stand at 4 °C. Filtration was followed by washing with ethanol and drying at 50 °C. This product was the purified L-deoxyalliin. Its yield was 43.1%; the purity was higher than 99% when checked by high-performance silica gel thin-layer chromatography (Sigma Chemical Co., T-7395, 10 cm × 10 cm), using 1-butanol/acetic acid/water (2:1:1) as the developing solvent, and detected by 0.5% ninhydrin solution.

Synthesis and Purification of L-Alliin (S-Allyl-L-cysteine Sulfoxide). L-Deoxyalliin (0.3 mol) was dissolved in 500 mL of distilled water; 0.6 mol of hydrogen peroxide (30% w/w, Aldrich) was added slowly to the stirred solution, and stirring was continued for 24 h at room temperature. The solvent was evaporated at 60 °C under vacuum. The dry white residue was dissolved in a 500-mL mixture of acetone/water/glacial acetic acid (65:34:1) at boiling temperature. While cooling to room

temperature, long white needles started to grow. To complete precipitation of the oxidized amino acid, the solution was kept at 4 °C overnight. After filtration of the precipitate, it was washed with the solvent mentioned above, followed by washing with absolute ethanol. The precipitates were then dried at 50 °C. The product was pure L-(±)-alliin. The yield was 30.6%, and the purity was higher than 99% when checked by high-performance silica gel thin-layer chromatography (Sigma, T-7395, 10 cm × 10 cm), using 1-butanol/acetic acid/water (2:1:1) as the developing solvent, and detected by 0.5% ninhydrin solution.

Thermal Decomposition of Alliin and Deoxyalliin. Alliin or deoxyalliin (0.005 mol) as synthesized was dissolved in 100 mL of distilled water. The solution was adjusted to pH 3, 5, 7, and 9, individually, and added to a 0.3-L Hoke SS-DOT sample cylinder (Hoke, Inc., Clifton, NJ) and sealed. This cylinder was then heated at 180 °C in a GC oven for 1 h. After the cylinder was cooled to room temperature, a decomposed alliin or deoxyalliin reaction mass was obtained.

Isolation of the Volatile Compounds. The total reaction mass was simultaneously distilled and extracted into diethyl ether using a Likens-Nickerson (L-N) apparatus. After distillation, 5 mL of heptadecane stock solution (0.0770 g in 200 mL of diethyl ether) was added to the isolate as the internal standard; the results shown in the tables in this study were quantitative relative to the internal standard. After being dried over anhydrous sodium sulfate and filtered, the distillate was concentrated to about 5 mL using a Kuderna-Danish apparatus fitted with a Vigreux distillation column and then slowly concentrated further under a stream of nitrogen in a small sample vial to a final volume of 0.2 mL.

Gas Chromatographic Analysis. A Varian 3400 gas chromatograph equipped with a fused silica capillary column (60 m \times 0.25 mm i.d.; 1- μ m thickness, DB-1, J&W Inc.) and a flame ionization detector was used to analyze the volatile compounds. The operating conditions were as follows: injector temperature, 270 °C; detector temperature, 300 °C; helium carrier flow rate, 1 ml/min; temperature program, 40 °C (5 min), 2 °C/min, 260 °C (60 min). A split ratio of 50:1 was used.

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 used for the gas chromatography. The GC operating conditions were the same as described above. Mass spectra were obtained by electron ionization at 70 eV and an ion source temperature of 250 °C.

Identification of the Volatile Compounds. Identification of the volatile compounds in the isolate was mostly based on the gas chromatography-mass spectrometry (GC-MS), and information from the GC retention indices (I_k) used a C_6 - C_{25} mixture as the reference standard (Majlat et al., 1974). The structural assignment of volatile compounds was accomplished by comparing the mass spectral data from Heller and Milne (1978, 1980), TNO (1988), or previously published literature (Block et al., 1988; Zhang et al., 1988; Kawai and Ishida, 1989). Some of the compounds were identified only by mass spectral interpretation, and the identifications should be considered tentative. The retention indices were used for the confirmation of structural assignments.

Direct Probe Chemical Ionization Mass Spectrometry (DCI). DCI was conducted on a Finnigan MAT 8230 high-resolution mass spectrometer. Isobutane was used as the reagent gas at 1 Torr. The temperature of the probe was increased from 35 to 350 °C at 5 °C/s.

Positive Ion Liquid Secondary Ion Mass Spectrometry (LSIMS). LSIMS was conducted on a VG ZAB-T mass spectrometer (VG Instruments). The analysis conditions were listed as follows: Cs gun anode current, 2 μ A; Cs gun anode voltage, 30 kV; mass range, 200-2000 amu; instrument accelerating voltage, 8 kV; a magic bullet matrix [dithiothreitol/dithioerythritol (3:1) in methanol] was used.

RESULTS AND DISCUSSION

Confirmation of the Synthesized Compounds. Since their synthesis procedures were slightly modified from those reported by Iberl et al. (1990), deoxyalliin and alliin synthesized in this study were analyzed by DCI-MS for structural confirmation. Figure 1 shows the DCI mass spectrum of deoxyalliin. The chemical ionization properties of DCI, ion peak at m/z 162 ($M + 1$)⁺, confirmed the molecular weight of the synthesized deoxyalliin to be 161. The ion peak at m/z 145 came from the loss of the hydroxy radical or ammonia fragment; the ion peak at m/z 122 came from the loss of the allene ($\text{CH}_2=\text{C}=\text{CH}_2$) fragment, and the ion peak at m/z 90 came from the loss of the thioacrolein ($\text{CH}_2=\text{CH}-\text{CH}=\text{S}$) fragment from the molecular ion.

Due to the reducing property of DCI-MS (reaction with the isobutane plasma), the DCI mass spectrum of alliin was identical to that of deoxyalliin. Therefore, DCI-MS

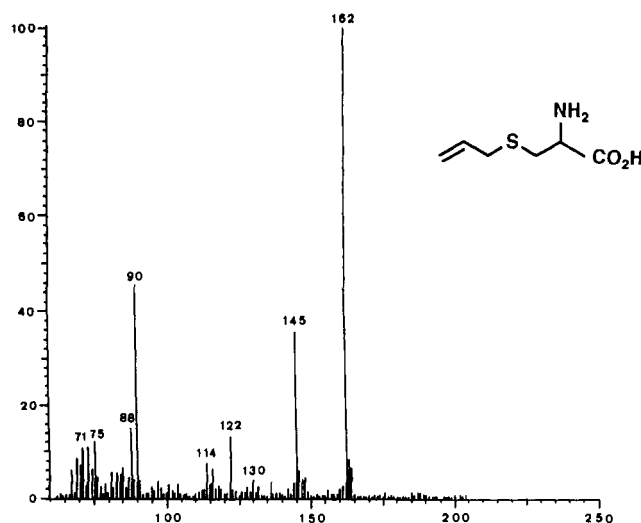


Figure 1. Mass spectrum of deoxyalliin by direct probe DCI-MS.

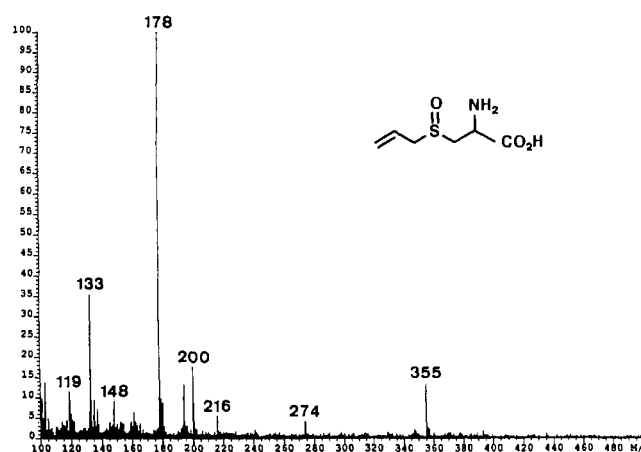


Figure 2. Mass spectrum of alliin by LSIMS in magic bullet.

was not suitable for alliin analysis. LSIMS was then used to analyze the synthesized alliin. Figure 2 shows the LSIMS spectrum of alliin. The ion peak at m/z 178 ($M + 1$)⁺ confirmed the molecular weight of the synthesized compound to be 177. The ion peak at m/z 355 came from a CI-generated dimer (artifact) of alliin which occurred during the LISMS analysis.

The structures of synthesized compounds were further confirmed by infrared (IR) spectrometry. Both of the synthesized compounds showed characteristic bands of amino acid around 2950 cm^{-1} ($-\text{NH}_3^+$) and around 1600 cm^{-1} ($-\text{COO}^-$, NH_3^+), and characteristic bands of an allyl double bond around 920 cm^{-1} . The synthesized alliin showed an extra characteristic band around 1100 cm^{-1} ($\text{S}=\text{O}$).

The purities of the synthesized compounds were checked by using high-performance silica gel thin-layer chromatography (TLC) using 1-butanol/acetic acid/water (2:1:1) as the developing solvent system and detected by spraying 0.5% ninhydrin solution. The synthesized deoxyalliin showed only one spot on the TLC plate ($R_f = 0.68$) and showed no spot from cysteine ($R_f = 0.56$), the starting material of the synthesis. The synthesized alliin showed two spots ($R_f = 0.58$ and 0.49) that represented two of the isomers, L-(+)- and L-(-)alliin, and showed no spot from deoxyalliin, the starting material of the synthesis.

Flavor Description of the Degraded Solutions. The pH changes, final appearance, and flavor description (by smelling only) of thermally degraded solutions of alliin

Table 4. Newly Tentatively Identified Volatile Compounds from the Thermally Degraded Alliin and Deoxyalliin Aqueous Solution

no.	compound identified	MS, <i>m/e</i> (relative intensity)
D6	1-mercapto-3-propanol	92 (35), 61 (100), 60 (43), 31 (28), 59 (22), 74 (18), 41 (13), 27 (12), 29 (10), 94 (2)
D9	1,2-dithiacyclopent-3-ene	104 (53), 103 (100), 45 (22), 71 (11), 105 (11), 39 (10), 64 (10), 59 (9), 106 (5)
A21	3-methylthiane	116 (100), 46 (65), 74 (37), 41 (20), 42 (19), 60 (12), 88 (11), 29 (8), 117 (7), 106 (6), 118 (6)
D8	(allylthio)acetaldehyde	116 (41), 41 (100), 72 (76), 45 (71), 73 (53), 39 (50), 87 (49), 47 (28), 46 (21), 85 (20), 71 (17), 53 (13), 59 (12), 98 (10), 118 (2)
D10	mercaptomethylcyclopentane	116 (100), 46 (84), 74 (41), 41 (27), 45 (27), 39 (16), 42 (26), 47 (16), 60 (10), 88 (7), 118 (5)
D13	4-methyl-1,3-dithiacyclopentane	120 (100), 74 (72), 78 (46), 59 (19), 41 (12), 105 (10), 46 (9), 122 (8)
D17	3-(allylthio)propanal	130 (11), 74 (100), 41 (67), 45 (37), 61 (29), 39 (27), 73 (18), 47 (12), 59 (11), 29 (11), 46 (10), 105 (10), 132 (1)
D16	3-(allylthio)propanol	132 (37), 41 (100), 59 (87), 101 (74), 39 (28), 45 (26), 31 (22), 61 (19), 72 (18), 73 (16), 74 (15), 91 (14), 58 (13), 27 (8), 29 (8), 134 (2)
D20	1,4-dithiacyclohept-5-ene	132 (79), 72 (100), 45 (69), 59 (60), 60 (53), 71 (52), 41 (41), 73 (33), 74 (27), 75 (27), 39 (26), 61 (23), 99 (22), 103 (21), 47 (13), 87 (12), 27 (10), 134 (8)
A28, D19	1,4-dithiepane	134 (100), 60 (90), 74 (58), 75 (37), 61 (36), 59 (32), 46 (32), 41 (27), 45 (22), 91 (20), 39 (19), 119 (17), 105 (15), 136 (19)
A39	1,2,3-trithiacyclohexane	138 (100), 71 (63), 45 (36), 64 (23), 110 (20), 41 (19), 140 (14), 46 (13), 74 (13), 105 (11), 92 (10)
D25	methyl-1,2,3-trithiacyclopentane	138 (100), 73 (63), 74 (59), 41 (32), 64 (31), 45 (27), 59 (20), 96 (20), 140 (14), 39 (12), 46 (11)
A35, D24	3,6-dimethyl-1,4-dithiane	148 (55), 60 (100), 75 (44), 106 (37), 69 (31), 45 (25), 74 (24), 41 (21), 88 (18), 61 (16), 39 (14), 133 (8), 150 (6)
A36	3,6-dimethyl-1,4-dithiane	148 (90), 60 (100), 106 (66), 75 (47), 74 (31), 59 (30), 41 (21), 45 (20), 46 (17), 61 (17), 39 (10), 150 (10)
D21	2-(mercaptoethyl)-tetrahydrothiophene	148 (24), 41 (100), 75 (91), 61 (60), 74 (54), 73 (50), 45 (41), 87 (40), 39 (38), 47 (30), 59 (21), 106 (16), 88 (15), 85 (14), 27 (10), 150 (3)
D22	2-(mercaptomethyl)-thiane	148 (18), 41 (100), 59 (100), 75 (78), 101 (69), 74 (53), 45 (51), 39 (42), 47 (40), 73 (38), 61 (17), 150 (2)
D23	2-ethyl-1,3-dithiane	148 (85), 60 (100), 106 (74), 119 (43), 41 (40), 45 (40), 59 (35), 75 (32), 74 (30), 46 (29), 73 (23), 39 (20), 61 (19), 150 (8)
D26	2-methyl-1,4-dithiepane	148 (73), 60 (100), 106 (56), 75 (40), 45 (30), 59 (29), 41 (28), 74 (23), 46 (20), 61 (17), 39 (16), 73 (14), 47 (13), 91 (11), 150 (7)
D27	4-methyl-1,2-dithiepane	148 (82), 78 (100), 106 (100), 60 (41), 42 (38), 45 (27), 64 (26), 41 (22), 46 (18), 39 (15), 59 (13), 84 (10), 115 (10), 150 (8)
D29	1,5-dithiacyclooctane	148 (78), 106 (100), 41 (50), 45 (41), 60 (32), 73 (31), 87 (29), 74 (26), 46 (21), 39 (19), 47 (19), 108 (13), 150 (8)
A30	methyl propyl trisulfide	154 (90), 112 (100), 43 (43), 47 (32), 64 (25), 41 (21), 79 (17), 45 (15), 39 (13), 156 (10)
D30	5-hydroxy-1,2-dithiacyclooctane	164 (100), 45 (78), 59 (74), 106 (37), 74 (35), 39 (33), 73 (31), 43 (28), 64 (20), 31 (18), 79 (18), 90 (17), 47 (16), 89 (14), 29 (9), 166 (3)
D33	4-(hydroxymethyl)-1,2-dithiepane	164 (53), 41 (100), 106 (99), 59 (50), 31 (42), 64 (34), 73 (30), 45 (29), 78 (14), 72 (11), 60 (10), 61 (10), 108 (10), 29 (9), 166 (5)
A42, D32	3,5-dimethyl-1,2,4-trithiane	166 (34), 59 (100), 60 (47), 101 (38), 64 (23), 106 (23), 41 (21), 45 (20), 61 (20), 124 (15), 39 (9), 92 (9), 168 (6)
A43, D34	3,5-dimethyl-1,2,4-trithiane	166 (62), 60 (100), 59 (96), 101 (42), 64 (33), 106 (30), 45 (29), 61 (26), 41 (24), 124 (12), 168 (8)
A44, D35	4-methyl-1,2,5-trithiepane	166 (47), 59 (100), 60 (80), 101 (42), 41 (23), 45 (21), 106 (20), 61 (20), 64 (19), 39 (11), 58 (11), 168 (7)
D36	1,2,5-trithiacyclooctane	166 (53), 59 (100), 60 (48), 101 (43), 64 (32), 41 (27), 45 (26), 61 (25), 106 (24), 124 (17), 73 (12), 58 (11), 92 (10), 168 (9)
D39	3-ethyl-5-methyl-1,2,4-trithiolane	166 (100), 124 (63), 59 (50), 60 (41), 45 (34), 64 (31), 101 (31), 74 (27), 41 (25), 73 (21), 106 (21), 105 (19), 70 (15), 126 (14), 168 (13)
A46, D38	1,2,3,4-tetrathiepane	170 (100), 64 (82), 41 (65), 128 (59), 106 (58), 59 (36), 45 (35), 73 (31), 39 (30), 74 (22), 172 (18), 130 (16), 115 (12), 138 (11)
D40	3,6-dimethyl-1,2,5-trithiepane	180 (100), 119 (86), 74 (82), 41 (58), 73 (58), 45 (53), 59 (46), 92 (41), 64 (36), 39 (28), 138 (27), 106 (25), 134 (24), 69 (23), 46 (17), 75 (16), 182 (14), 27 (9)
D41	3,6-dimethyl-1,2,5-trithiepane	180 (92), 74 (100), 73 (76), 41 (65), 45 (46), 59 (37), 106 (37), 119 (36), 64 (35), 39 (31), 38 (31), 92 (23), 75 (20), 147 (17), 46 (15), 182 (13), 47 (11), 78 (11), 115 (10), 27 (8)
D42	4,6-dimethyl-1,2,5-trithiepane	180 (100), 74 (94), 73 (87), 41 (60), 138 (58), 45 (40), 115 (32), 59 (31), 64 (30), 39 (20), 75 (19), 106 (18), 182 (15), 119 (13), 120 (12), 46 (12), 47 (11), 147 (11)
D43	4-ethyl-6-methyl-1,2,3,5-tetrathiane	198 (4), 138 (100), 73 (46), 74 (32), 64 (24), 59 (21), 45 (17), 92 (17), 41 (14), 60 (13), 140 (12), 139 (10)

and deoxyalliin are listed in Table 1. The odor of the degraded solutions of alliin can be described as roasted meaty and popcorn-like. On the other hand, the odor of degraded solutions of deoxyalliin had more garlic (actually more garlic bush or young garlic clove-like) character. Color formation after the thermal degradation of both of alliin and deoxyalliin was very impressive. It indicated that besides the formation of volatile compounds (actually, as shown in Tables 2 and 3, the conversion rate of alliin and deoxyalliin to the volatile compounds was low), some high molecular weight nonvolatile polymers or colorants should also be generated. However, efforts were focused only on the formation of volatile compounds from the thermal degradation of alliin and deoxyalliin in this study.

Major Volatile Compounds Generated from the Thermal Degradation of Alliin. Volatile compounds identified from the thermal degradation of alliin in aqueous solution of different pHs are listed in Table 2. Allyl alcohol (A4) and acetaldehyde (A3) were the predominant volatile compounds found in the degraded solution of alliin at pH 3, 7, and 9. Allyl alcohol was proposed to be generated from alliin through [2,3]-sigmatropic rearrangement. [2,3]-Sigmatropic rearrangement of alliin might lead to the intermediate sulfenate. The reduction of sulfenate would 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. Acetaldehyde identified was proposed to be one of the

Table 5. Volatile Compounds Probably Generated from the Self-Interaction of Allyl Mercaptan

no.	name	structure
A35, A36, D24	3,6-dimethyl-1,4-dithiane	
D26	2-methyl-1,4-dithiepane	
D29	1,5-dithiacyclooctane	
D21	2-(mercaptoethyl)-tetrahydrothiophene	
D22	2-(mercaptomethyl)thiane	
D27	4-methyl-1,2-dithiepane	
D7	diallyl sulfide	
D18	diallyl disulfide	
D44	7-methyl-4,5,8-trithiaundeca-1,10-diene	

main degradation products of cysteine which degraded from alliin.

Among the volatile compounds identified in the degraded solution of alliin, acetaldehyde, ethyl acetate (A5), thiazole (A11), 2-methylthiazole (A14), 2-methylpyridine (A15), 3-formylthiophene (A25), 2-acetylthiazole (A26), 3,5-dimethyl-1,2,4-trithiolane (A33, A34), 2,4,6-trimethylperhydro-1,3,5-dithiazine (A38), 3,6-dimethyl-1,2,4,5-tetrathiane (A47), and 4,6-dimethyl-1,2,3,5-tetrathiane (A48) had been identified from the thermal degradation products of cysteine (Shu et al., 1985; Zhang et al., 1988). It is reasonable to assume that these compounds were also generated from the decomposition of cysteine which was formed as the result of thermal decomposition of alliin. The presence of these volatile compounds also can be used to support the proposed mechanisms presented to trace the formation of allyl alcohol from alliin through [2,3]-sigmatropic rearrangement.

pH Effects on the Yields of Several Volatile Compounds Degraded from Alliin. Similar to the degradation of cysteine (Shu et al., 1985), the volatile profiles of the degradation of alliin were found to be highly pH-dependent. At pH 3, 7, and 9, allyl alcohol and acetaldehyde were the predominant compounds. The formation of acetal, 2-methylpyridine, and 1,2,3,4-tetrathiepane (A46) was favored at a lower pH (pH 3). On the other hand, the formation of 3,5-dimethyl-1,2,4-trithiolane, 2,4,6-trimethylperhydro-1,3,5-dithiazine, and 4-ethyl-6-methyl-1,2,3,5-tetrathiane (A49) was favored under neutral or alkaline pH (pH 7 and 9) conditions. At pH 5, a degradation occurred and produced predominantly acetaldehyde, sulfur dioxide, 2-acetylthiazole, ethyl acetate, methyl sulfides, methyl-1,2,3-trithiacyclopentane, and methyl-1,2,3,4-tetrathiane.

Major Volatile Compounds Generated from the Thermal Degradation of Deoxyalliin. Volatile compounds identified from the thermal degradation of deoxyalliin in aqueous solution of different pHs are listed in Table 3. Since the standard mass spectra of the authentic compounds are lacking, parts of the compounds listed in Table 3 were tentatively identified by the interpretation of the fragmentation of the mass spectra. The mass spec-

Table 6. Volatile Compounds Probably Generated from the Interaction of Allyl Mercaptan and Other Small Molecular Volatile Compounds










no.	name	structure
A21	3-methylthiane	
A23	1,2-dithiacyclopentane	
A37, D25	methyl-1,2,3-trithia-cyclopentane	
A39	1,2,3-trithiacyclohexane	
A45	methyl-1,2,3,4-tetra-thiane	
A46, D38	1,2,3,4-tetrathiepane	
D9	1,2-dithiacyclopent-3-ene	
D10	(mercaptomethyl)-cyclopentane	
D30	5-hydroxy-1,2-dithia-cyclooctane	
D33	4-(hydroxymethyl)-1,2-dithiepane	
D40, D41	3,6-dimethyl-1,2,5-trithiepane	
D42	4,6-dimethyl-1,2,5-trithiepane	
D5	1-mercapto-2-propanol	
D6	1-mercapto-3-propanol	
D16	3-(allylthio)propanol	
D17	3-(allylthio)propanal	

tral data of the volatile compounds tentatively identified are shown in Table 4.

As shown in Table 3, diallyl sulfide (D7), 2-methyl-1,4-dithiepane (D26), diallyl disulfide (D18), (allylthio)acetic acid (D14), and 3,6-dimethyl-1,4-dithiane (D24), 2,4,6-trimethylperhydro-1,3,5-dithiazine (D28), and allyl mercaptan (D4) were the predominant volatile compounds found in the degraded solution of deoxyalliin at pH 5, 7, and 9. (Allylthio)acetaldehyde (D8), 3-(allylthio)propanal (D17), 4,6-dimethyl-1,2,5-trithiepane (D42), and (allylthio)acetic acid (D14) were the predominant volatile compounds found in the degraded solution of deoxyalliin at pH 3.

Volatile Compounds Probably Derived from Allyl Mercaptan and Found in the Degraded Solution of Deoxyalliin or Alliin. Several volatile compounds identified from the degradation of alliin or deoxyalliin were found to be closely related to the self-interaction of allyl mercaptan or the interactions of allyl mercaptan with other degradation products of alliin or deoxyalliin. It is reasonable to assume that allyl mercaptan was generated from alliin and deoxyalliin through a hydrolysis process or free-radical rearrangement.

Table 7. Volatile Compounds Probably Generated from the Interaction of Allyl Mercaptan, Hydrogen Sulfide, and Aldehydes

no.	name	structure
A28, D19	1,4-dithiepane	
A31	1,3-dithiane	
A42, A43, D32, D34	3,5-dimethyl-1,2,4-trithiane	
A44, D35	4-methyl-1,2,5-trithiepane	
D13	4-methyl-1,3-dithiacyclopentane	
D15	2-methyl-1,3-dithiane	
D20	1,4-dithiacyclohept-5-ene	
D23	2-ethyl-1,3-dithiane	
D36	1,2,5-trithiacyclooctane	

(1) *Volatile Compounds Probably Generated from the Self-Interaction of Allyl Mercaptan.* Table 5 shows the structures of some of the volatile compounds that were probably generated from the self-interaction of allyl mercaptan. In view of this, we propose the following: (1) 3,6-dimethyl-1,4-dithiane (A35, A36, D24), 2-methyl-1,4-dithiepane (D26), 1,5-dithiacyclooctane (D29), 2-(mercaptoethyl)tetrahydrothiophene (D21), and 2-(mercaptomethyl)thiane (D22) are the cyclization products of two allyl mercaptan molecules; (2) 4-methyl-1,2-dithiepane (D27) and 4-(hydroxymethyl)-1,2-dithiepane (D33) result from the cyclization of two allyl mercaptan molecules followed by either hydrogenation or hydration; (3) 4,6-dimethyl-1,2,5-trithiepane (D42) and 3,6-dimethyl-1,2,5-trithiepane (D40, D41) occur from the interactions of two molecules of allyl mercaptan and one molecule of hydrogen sulfide; (4) diallyl sulfide (D7) and diallyl disulfide (D18) result from the oxidation of allyl mercaptan; (5) 3-(allylthio)propanol (D16) comes from the hydration of diallyl sulfide; (6) 3-(allylthio)propanal (D17) comes from the oxidation of 3-(allylthio)propanol; and (7) 7-methyl-4,5,8-trithiaundeca-1,10-diene (D44) occurs from the addition of one molecule of allyl mercaptan to one molecule of diallyl disulfide. 7-Methyl-4,5,8-trithiaundeca-1,10-diene also was identified from the pyrolysis of diallyl disulfide by Block et al. (1988).

(2) *Volatile Compounds Probably Generated from the Interactions of Allyl Mercaptan and Other Small Molecular Volatile Compounds.* Table 6 shows the structures of some of the volatile compounds that were probably generated through the interactions of allyl mercaptan and other low molecular weight volatile compounds as follows: (1) 1,2-dithiacyclopentane (A23) comes from the interactions of one molecule of allyl mercaptan and one molecule of hydrogen sulfide; (2) 1,2-dithiacyclopent-3-ene (D9) results from the oxidation of 1,2-dithiacyclopentane; (3) methyl-1,2,3-trithiacyclopentane (A37, D25) and 1,2,3-trithiacyclohexane (A39) occur from the inter-

action of one molecule of allyl mercaptan and two molecules of hydrogen sulfide; (4) methyl-1,2,3,4-tetrathiane (A45) and 1,2,3,4-tetrathiepane (A46, D38) come from the interactions of one molecule of allyl mercaptan and three molecules of hydrogen sulfide; (5) 1-mercapto-2-propanol (D5) and 1-mercapto-3-propanol (D6) result from the interactions of one molecule of allyl mercaptan and one molecule of water; and (6) (mercaptomethyl)cyclopentane (D10) and 3-methylthiane (A21) occur from the interactions of one molecule of allyl mercaptan and one molecule of 1-propene.

(3) *Volatile Compounds Probably Generated from the Interactions of Allyl Mercaptan, Hydrogen Sulfide, and Aldehydes.* Table 7 shows the structures of some of the volatile compounds that were probably generated through the interactions of allyl mercaptan, hydrogen sulfide, and aldehydes as follows: (1) 4-methyl-1,3-dithiacyclopentane (D13) and 1,3-dithiane (A31) result from the interactions of one molecule of allyl mercaptan, one molecule of formaldehyde, and one molecule of hydrogen sulfide; (2) 2-methyl-1,3-dithiane (D15) and 1,4-dithiepane (A28, D19) occur from the interactions of one molecule of allyl mercaptan, one molecule of acetaldehyde, and one molecule of hydrogen sulfide; (3) 1,4-dithiacyclohept-5-ene (D20) comes from the oxidation of 1,4-dithiepane; (4) 3,5-dimethyl-1,2,6-trithiane (A42, A43, D32, D34), 1,2,5-trithiacyclooctane (D36), and 4-methyl-1,2,5-trithiepane (A44, D35) result from the interactions of one molecule of allyl mercaptan, one molecule of acetaldehyde, and two molecules of hydrogen sulfide; and (5) 2-ethyl-1,3-dithiane (D23) occurs from the interactions of one molecule of allyl mercaptan, one molecule of propanal, and one molecule of hydrogen sulfide.

pH Effects on the Yields of Several Volatile Compounds Degraded from Deoxyalliin. As shown in Table 3, the degraded solution of deoxyalliin at pH 5 had the highest yields of volatile compounds. The degraded solution of deoxyalliin at pH 3 had the lowest yields of volatile compounds. (Allylthio)acetaldehyde and (allylthio)propanal were more stable in the degraded solution at pH 3. Except for 1-mercapto-2-propanol, 3-(allylthio)acetaldehyde, and 3-(allylthio)propanal, the formation of most of the volatile compounds generated from the thermal degradation of deoxyalliin was favored at either pH 5 or 7.

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