

Sulfur-Containing Volatiles Arising by Thermal Degradation of Alliin and Deoxyalliin

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Alliin (*S*-allyl-L-cysteine sulfoxide) and its biochemical precursor deoxyalliin (*S*-allyl-L-cysteine) were heated in a closed model system at different temperatures (from 80 to 200 °C) in the presence of variable amounts of water (0–98%) for 1–60 min. The arising volatile compounds were isolated by extraction, analyzed, and identified by means of GC and GC/MS. The major volatile compounds generated by thermal degradation of these amino acids were diallyl sulfides (mono-, di-, tri-, and tetrasulfide) and allyl alcohol. Other important degradation products (arising especially at temperatures higher than 140 °C) were sulfur-containing cyclic compounds, namely 2,5-dimethyl-1,4-dithianes, 2-methyl-1,4-dithiepane, and dimethyl-1,2,5-trithiepanes. It was found that the typical garlic aroma can be formed nonenzymatically during the thermal treatment of either alliin or deoxyalliin. The major precursor of this aroma was alliin, while deoxyalliin was much more stable. The contribution of the individual volatiles to the resulting aroma with regard to their sensory properties is discussed.

Keywords: *Alliin; S-allylcysteine; deoxyalliin; garlic; sulfur volatiles; flavor precursor*

INTRODUCTION

Important natural constituents of many plants belonging to the genera *Allium* and *Brassica* are unique non-protein amino acids *S*-alk(en)yl-L-cysteines and their sulfoxides. The characteristic flavor arises in part due to the enzymatic degradation of these amino acids when the cellular tissue of these vegetables is disrupted by cutting, slicing, or chopping. The enzyme alliinase (EC 4.4.1.4) converts alliin (*S*-allyl-L-cysteine sulfoxide) and its methyl-, propyl-, and *trans*-1-propenyl analogues quickly into the corresponding alk(en)yl thiosulfinates, the pungent and antimicrobial principles of freshly crushed garlic and onion. These labile intermediates are subsequently transformed to a number of secondary products, namely alk(en)yl sulfides (Block, 1992). However, culinary processing causes thermal denaturation of alliinase, and thus some amount of aroma precursors remains unreleased and can participate in developing the characteristic flavor of processed vegetables. Along with alliin and other minor occurring cysteine sulfoxides (methyl and *trans*-1-propenyl derivatives), a considerable amount of γ -glutamyl-*S*-alk(en)yl-L-cysteine dipeptides was also found in intact garlic cloves (their content ranges between 0.1 and 0.8% of fresh weight). During the sprouting of garlic these are transformed to the corresponding *S*-alk(en)yl-L-cysteines by the action of enzyme γ -glutamyltranspeptidase and consequently oxidized to sulfoxides (Mütsch-Eckner *et al.*, 1992; Lawson *et al.*, 1991). Because they are not cleaved by alliinase, it can be assumed that they also participate in flavor generation of thermally processed garlic.

The volatile components of raw, dried, baked, fried, and boiled garlic and onion have been well documented, and the contributions of alk(en)yl thiosulfinates and their transformation products to the flavor of the processed vegetables have been thoroughly studied (Yu *et al.*, 1989, 1993). On the other hand, only a few papers

are focused on the contribution of alliin and its analogues to the flavor of thermally processed *Allium* vegetables.

The first serious studies relating to decomposition of cysteine sulfoxides were performed in the early 1970s by Nishimura *et al.* (Nishimura and Mizutani, 1972, 1973a,b; Nishimura *et al.*, 1970, 1971). These authors studied volatile products generated from cysteine sulfoxides after irradiation. They identified the corresponding alk(en)yl sulfoxides as the major volatile degradation products. Recently, Yu *et al.* (1994a–c) studied the volatile compounds arising from alliin and deoxyalliin either in an aqueous solution at different pH values or in propylene glycol, with or without the presence of glucose or 2,4-decadienal, respectively.

In the present study, the volatiles formed from thermally degraded alliin and deoxyalliin were identified and quantified to understand the formation mechanisms of sulfur-containing compounds developed during garlic processing. Formation of volatiles was observed to be influenced by temperature, time of heating, and water content.

EXPERIMENTAL PROCEDURES

Synthesis of Deoxyalliin and Alliin. Deoxyalliin was synthesized by alkylation of L-cysteine with allyl bromide according to the procedure of Yu *et al.* (1994c). L-(±)-Alliin was obtained by oxidation of deoxyalliin with hydrogen peroxide, and its naturally occurring (+)-stereoisomer was isolated by repeated crystallization from aqueous acetone according to the method of Stoll and Seebeck (1951). Structures of synthesized amino acids were confirmed by ¹H NMR, ¹³C NMR, and IR spectroscopy. Purity (>99%) was checked by means of HPLC after derivatization with *o*-phthalaldehyde in the presence of *tert*-butyl mercaptan (Velíšek *et al.*, 1993).

Thermal Decomposition of Amino Acids. Amino acid (50 mg) was placed in a 5 mL glass tube, water was added, and the tube was sealed. After equilibration for 24 h, the tube was heated in an oven at the given temperature, then cooled in the freezer to –18 °C, and crushed under water (total volume of 2.45 mL). The resulting solution was immediately

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Table 1. Sulfur Volatiles Identified from Thermally Degraded Alliin^a

no.	compound identified	Kovats index		mg/g						
		HP-5	Wax	80 °C	100 °C	120 °C	140 °C	160 °C	180 °C	200 °C
1	1-mercapto-3-propanol ^b	798							0.06	0.64
2	allyl hydrogen disulfide ^d	844			0.35	0.21				
3	diallyl sulfide	861	1164	tr ^e	1.63	80.52	63.63	38.15	9.46	2.61
4	2,4-dimethylthiophene	878	1231				tr	tr	0.02	0.05
5	1,2-dithiolane	978	1523				0.12	0.13	0.16	0.50
6	2-methyl-1,3-dithiane	1033	1476				0.13	0.24	0.29	0.39
7	2-methyl-1,3-dithiane	1035	1480				0.12	0.23	0.27	0.37
8	2-ethyl-4-methyl-1,3-dithiolane ^d	1040						0.12	0.22	0.66
9	3-(allylthio)propanol ^b	1052	1745			0.07	0.27			
10	diallyl disulfide	1079	1500	0.09	13.28	23.36	3.43	0.63	tr	tr
11	1,4-dithiepane ^b	1099	1608		0.13	0.19	0.53	1.09	1.28	1.67
12	2-(mercaptoethyl)tetrahydrothiophene ^b	1117				0.20	0.42			
13	2,5-dimethyl-1,4-dithiane	1130	1584			0.23	5.14	9.85	10.11	10.93
14	2,5-dimethyl-1,4-dithiane	1136	1584			0.24	5.04	10.02	10.26	10.93
15	4-methyl-1,2,3-trithiolane ^c	1150				2.92	2.39	1.90	1.29	0.46
16	2-methyl-1,4-dithiepane ^b	1161	1635			0.58	12.69	24.08	24.55	25.57
17	2-vinyl-1,3-dithiane ^d	1183	1723						0.12	0.39
18	2-ethyl-1,3-dithiacyclohex-4-ene ^d	1195	1730							0.13
19	2-acetyl-5-methylthiophene	1197	1914			0.07	0.08	0.11	0.24	
20	1,5-dithiacyclooctane ^b	1225	1761				0.16	0.28	0.32	0.49
21	3,3,5,5-tetramethyl-1,2,4-trithiolane	1233	1651							0.50
22	unknown 1 (C ₈ H ₉ NS)	1280	2001			0.60				
23	diallyl trisulfide	1297	1822	2.24	38.78	10.96	0.69	0.16		
24	3-ethyl-5(or 6)-methyl-1,2,4-trithiane ^d	1300	1848							0.09
25	trans-3,5-diethyl-1,2,4-trithiolane	1333	1811							0.19
26	unknown 2 (C ₉ H ₁₁ NS)	1339	2015			0.89	0.19			
27	5-methyl-1,2,3,4-tetrathiane ^c	1359				1.03	0.45	0.33	0.26	0.20
28	5-methyl-4,7-dithia-1,9-decadiene ^c	1367	1871			0.73	1.29	0.20	0.13	0.12
29	cis-3,5-diethyl-1,2,4-trithiolane	1373	1832							0.07
30	unknown 3 (C ₉ H ₁₁ NS)	1379	2052			0.25	0.19	0.11	0.10	0.14
31	dimethyl-1,2,5-trithiepane ^b	1416	2105			0.08	0.73	0.90	0.86	0.78
32	dimethyl-1,2,5-trithiepane ^b	1430	2135			0.07	0.72	0.86	0.98	1.11
33	dimethyl-1,2,5-trithiepane ^b	1434	2135			0.20	1.82	2.11	2.38	2.62
34	diallyl tetrasulfide	1538			2.90	5.74	0.28			
35	3-(ethylthio)-1,2,4-trithiane ^d	1548							0.32	
36	7-methyl-4,5,8-trithia-1,10-undecadiene ^c	1581	2202			0.75	0.37			
37	6-methyl-4,5,8-trithia-1,10-undecadiene ^c	1591	2213			1.62	0.75	0.04		
38	6-methyl-1,2,3,4,5-pentathiepane ^d	1635				0.36	0.21	0.13	0.10	
39	dimethyl-1,2,3,6-tetrathiacyclooctane ^d	1647							0.28	0.09
40	8-methyl-4,5,6,9-tetrathia-1,11-dodecadiene ^d	1815				2.60	0.42	0.05		
41	7-methyl-4,5,6,9-tetrathia-1,11-dodecadiene ^d	1819				1.01	0.35			
42	9-methyl-4,5,6,7,10-pentathia-1,12-tridecadiene ^d	2056				0.37	0.03			
43	8-methyl-4,5,6,7,10-pentathia-1,12-tridecadiene ^d	2061				0.26				
44	allyl alcohol		1144	2.62	21.57	29.42	38.29	34.85	24.52	18.71
45	unknown 4 (C ₆ H ₁₂ S ₂)		1545					0.07	0.21	0.59
46	unknown 5 (C ₆ H ₁₂ S ₂)		1551					0.08	0.21	0.61
	total			4.95	78.64	165.53	140.93	126.72	93.00	81.61

^a Heated for 1 h in the presence of 10% water. ^b Yu *et al.* (1994c). ^c Block *et al.* (1988). ^d Tentatively identified by mass spectra interpretation. ^e tr, traces (<0.01 mg/g).

extracted with 5 mL of diethyl ether. The extract obtained was dried using anhydrous sodium sulfate and analyzed by GLC without any further treatment.

Gas Chromatographic Analysis. A Hewlett-Packard 5890 chromatograph fitted with a flame ionization detector and a HP-5 or HP-INNOWax fused silica capillary column (30 m × 0.25 mm i.d.; film thicknesses of 25 and 50 μm, respectively; Hewlett-Packard) was used. The operating conditions were as follows: injector temperature, 220 °C, detector temperature, 250 °C; nitrogen carrier gas flow rate, 2 mL/min; and temperature program (for HP-5 column), 40 °C (3 min), raised at 4 °C/min to 240 °C (10 min), and (for HP-INNOWax column), 40 °C (3 min), raised at 4 °C/min to 190 °C (10 min); 1 μL of sample was injected, using a split ratio of 1:5. The amount of volatiles was estimated by computing the areas against that of the internal standard (2,6-di-*tert*-butyl-4-hydroxytoluene, BHT). The response factor of all compounds to the FID was assumed to be the same.

Gas Chromatography/Mass Spectrometry (GC/MS) Analysis. GC/MS analyses were carried out using a Hewlett-Packard G1800A chromatograph. The operating conditions were the same as described above, with the exception of a helium carrier gas flow rate of 0.6 mL/min. Mass spectra were

obtained by EI ionization at 70 eV over the range of 15–300 mass units, with an ion source temperature of 250 °C.

Aroma Extract Dilution Analysis (AEDA). For AEDA experiments the effluent of the HP-5 column was split with a ratio of 1:1 to the FID and the sniffing port (SGE International, Australia) with addition of humidified air. The analyzed samples were diluted stepwise from 1:2 up to 1:1024 with diethyl ether. Odor description and aroma thresholds were evaluated by three trained assessors.

RESULTS AND DISCUSSION

Typical gas chromatograms of the volatiles formed from alliin heated at 120 and 180 °C for 1 h are shown in parts a and b of Figure 1, respectively. A total of 45 sulfur-containing volatile compounds were identified, as shown in Table 1. As can be seen, the predominant sulfur compounds arising from alliin at temperatures <140 °C are diallyl mono-, di-, and trisulfides. A considerable amount of allyl alcohol is also formed. At higher temperatures these quite labile sulfides decompose to form rather unusual sulfur-containing cyclic

Table 2. Sulfur Volatiles Identified from Thermally Degraded Deoxyalliin^a

no.	compound identified	Kovats index		mg/g						
		HP-5	Wax	80 °C	100 °C	120 °C	140 °C	160 °C	180 °C	200 °C
3	diallyl sulfide	861	1164		0.06	1.23	4.25	39.04	44.99	20.20
4	2,4-dimethylthiophene	878	1231							0.06
5	1,2-dithiolane	978	1523						0.12	0.17
6	2-methyl-1,3-dithiane	1033	1476						0.22	0.24
7	2-methyl-1,3-dithiane	1035	1480						0.18	0.18
8	2-ethyl-4-methyl-1,3-dithiolane ^d	1040							0.05	0.45
10	diallyl disulfide	1079	1500			1.56	7.49	20.52	2.62	0.14
11	1,4-dithiepane ^b	1099	1608					0.09	1.72	3.42
12	2-(mercaptoethyl)tetrahydrothiophene ^b	1117							0.06	tr ^e
13	2,5-dimethyl-1,4-dithiane	1130	1584					0.36	3.73	5.66
14	2,5-dimethyl-1,4-dithiane	1136	1584					0.38	4.05	6.73
15	4-methyl-1,2,3-trithiolane ^c	1150						tr	0.13	0.09
16	2-methyl-1,4-dithiepane ^b	1161	1635					1.04	9.99	13.95
20	1,5-dithiacyclooctane ^b	1225	1761						0.18	0.32
21	3,3,5,5-tetramethyl-1,2,4-trithiolane	1233	1651							0.21
23	diallyl trisulfide	1297	1822			0.52	0.68	0.87	0.21	0.14
26	unknown 2 (C ₉ H ₁₁ NS)	1339	2015					0.26		
28	5-methyl-4,7-dithia-1,9-decadiene ^c	1367	1871					1.30	0.35	
31	dimethyl-1,2,5-trithiepane ^b	1416	2105						0.20	0.40
32	dimethyl-1,2,5-trithiepane ^b	1430	2135						0.21	0.48
33	dimethyl-1,2,5-trithiepane ^b	1434	2135						0.51	1.07
34	diallyl tetrasulfide	1538						0.06		
36	7-methyl-4,5,8-trithia-1,10-undecadiene ^c	1581	2202					0.31		
37	6-methyl-4,5,8-trithia-1,10-undecadiene ^c	1591	2213					0.74	0.10	
39	dimethyl-1,2,3,6-tetrathiacyclooctane ^d	1647						0.89	0.14	
44	allyl alcohol		1144		tr	0.07	3.04	9.15	11.74	7.65
	total				0.06	3.38	15.46	75.01	81.50	61.56

^a Heated for 1 h in the presence of 10% water. ^b Yu *et al.* (1994c). ^c Block *et al.* (1988). ^d Tentatively identified by mass spectra interpretation. ^e tr, traces (<0.01 mg/g).

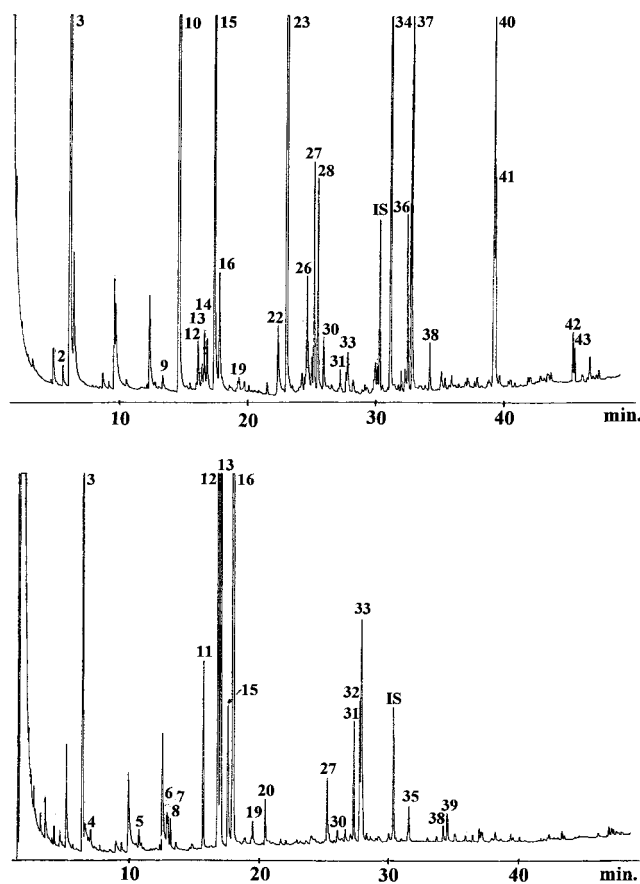


Figure 1. Gas chromatograms of volatiles obtained from thermally degraded alliin at (a, top) 120 and (b, bottom) 180 °C, respectively. (HP-5 column; heated for 60 min in the presence of 10% water; IS, internal standard; peak numbers correspond with those listed in Table 1; unlabeled peaks belong to non-sulfur compounds, namely alkyl-substituted pyridines.)

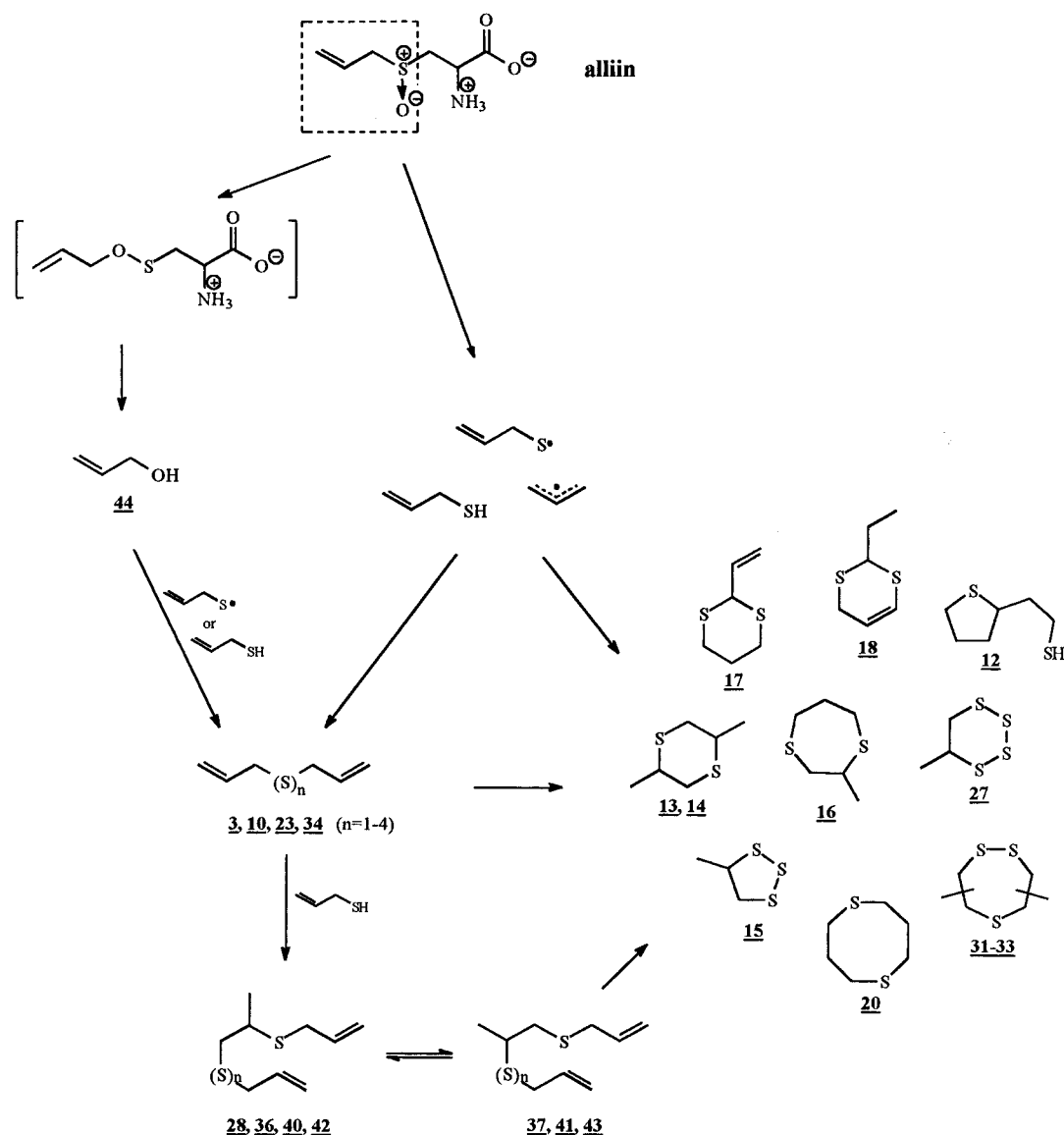
compounds, especially 2,5-dimethyl-1,4-dithianes, 2-methyl-1,4-dithiepane, and dimethyl-1,2,5-trithiepanes. It is possible that some of the compounds listed in Tables 1 and 2 could be artifacts that are produced in the gas chromatograph at high temperatures.

The proposed formation of sulfur volatiles from thermally degraded alliin is schematically shown in Figure 2. It can be assumed that allyl alcohol is formed from alliin through [2,3]-sigmatropic rearrangement according to the mechanism proposed by Yu *et al.* (1994c). This rearrangement of alliin might lead to the intermediate sulfenate. The reduction of sulfenate would yield allyl alcohol and cysteine. This pathway is favored in the presence of higher water amounts (the content of allyl alcohol formed from alliin increases with water content in the reaction system). Another important mechanism is probably a homolytic cleavage of labile C–S bonds, resulting in the formation of allylthio and propenyl radicals (this breakdown is probably the major mechanism involved in the thermal degradation of deoxyalliin). From these reactive fragments and other low molecular weight volatile compounds (particularly allyl mercaptan and hydrogen sulfide) are consequently formed diallyl sulfides and cyclic compounds, e.g. 2,5-dimethyl-1,4-dithianes (**13**, **14**), 4-methyl-1,2,3-trithiolane (**15**), 2-methyl-1,4-dithiepane (**16**), and dimethyl-1,2,5-trithiepanes (**31–33**). On the other hand, allyl alcohol can react with allyl mercaptan or hydrogen sulfide to form 3-(allylthio)propanol (**9**) and 1-mercapto-3-propanol (**1**), respectively. Allyl alcohol can also react with the allylthio radical, allyl mercaptan, or alliin/deoxyalliin to give diallyl sulfide (Rizzi, 1995). This assumption supports a decrease in the amount of allyl alcohol at prolonged heating. Unsaturated acyclic compounds **28**, **36**, **37**, and **40–43** are formed by addition of the allylthio radical or allyl mercaptan to the double bond of diallyl sulfides (Block, 1988).

Table 3. Dependence of Volatile Amounts on Time of Heating, Temperature, and Water Content

		time of heating ^b								
		1 min	2 min	4 min	8 min	15 min	30 min	60 min		
alliin	sulfur volatiles (mg/g)			1.99	105.61	168.73	161.61	136.11		
	conversion of sulfur ^a (%)			0.5	27.9	39.1	35.6	27.7		
deoxyalliin	sulfur volatiles (mg/g)				0.10	0.68	1.67	3.31		
	conversion of sulfur ^a (%)				0.01	0.1	0.3	0.7		
		temperature of heating ^c								
		80 °C	100 °C	120 °C	140 °C	160 °C	180 °C	200 °C		
alliin	sulfur volatiles (mg/g)	2.33	57.07	136.11	102.64	91.87	68.48	62.90		
	conversion of sulfur ^a (%)	0.7	16.1	27.7	19.8	19.4	15.8	15.3		
deoxyalliin	sulfur volatiles (mg/g)		0.06	3.31	12.42	65.86	69.76	53.91		
	conversion of sulfur ^a (%)		0.01	0.7	2.4	11.4	11.9	10.4		
		water content ^d								
		0%	5%	10%	20%	40%	80%	90%	95%	98%
alliin	sulfur volatiles (mg/g)	38.94	65.74	136.11	169.30	161.54	116.04	45.06	21.89	2.07
	conversion of sulfur ^a (%)	9.6	14.7	27.7	34.6	35.1	22.2	10.8	5.5	0.5
deoxyalliin	sulfur volatiles (mg/g)	0.43	1.10	3.31	3.44	3.51	3.23	1.89	0.78	0.51
	conversion of sulfur ^a (%)	0.1	0.2	0.7	0.6	0.6	0.5	0.3	0.1	0.1

^a Expressed as moles of sulfur bonded in volatiles per mole of alliin. ^b At 120 °C and 10% water. ^c For 60 min and 10% water. ^d At 120 °C for 60 min.

**Figure 2.** Formation of sulfur volatiles from thermally degraded alliin.

Total amounts of sulfur volatiles as influenced by time of heating, temperature, and water content are sum-

marized in Table 3. As can be seen, the total amount decreases somewhat with prolonged time of heating.

Table 4. Mass Spectra of Newly Tentatively Identified, Unknown, and Unusual Compounds Arising from Thermally Degraded Alliin and Deoxyalliin

no.	compound	MS, <i>m/e</i> (relative intensity)
2	allyl hydrogen disulfide	106 (30, M ⁺), 74 (33), 73 (14), 64 (17), 59 (8), 46 (9), 45 (19), 41 (100), 39 (74)
8	2-ethyl-4-methyl-1,3-dithiolane	148 (68, M ⁺), 133 (51), 121 (4), 106 (79), 75 (14), 74 (26), 59 (100), 45 (17), 41 (40), 39 (18)
17	2-vinyl-1,3-dithiane	146 (82, M ⁺), 131 (15), 117 (8), 113 (11), 104 (59), 103 (21), 71 (13), 59 (100), 45 (23), 39 (17)
18	2-ethyl-1,3-dithiacyclohex-4-ene	146 (100, M ⁺), 104 (88), 103 (23), 76 (19), 72 (78), 71 (52), 59 (27), 45 (28), 41 (15), 39 (14)
22	unknown 1 (C ₈ H ₉ NS)	151 (54, M ⁺), 150 (14), 136 (22), 124 (3), 118 (10), 110 (8), 83 (13), 67 (7), 57 (9), 45 (12), 41 (100), 39 (66)
24	3-ethyl-5(or 6)-methyl-1,2,4-trithiane	180 (35, M ⁺), 147 (8), 138 (6), 115 (10), 106 (28), 74 (100), 59 (73), 41 (41), 39 (23)
26	unknown 2 (C ₉ H ₁₁ NS)	165 (99, M ⁺), 164 (14), 150 (28), 132 (24), 124 (29), 117 (13), 97 (22), 80 (17), 53 (37), 41 (100), 39 (41)
28	5-methyl-4,7-dithia-1,9-decadiene ^a	188 (0.6, M ⁺), 147 (35), 115 (37), 105 (14), 101 (24), 73 (63), 72 (23), 67 (16), 59 (40), 45 (30), 41 (100), 39 (43)
30	unknown 3 (C ₉ H ₁₁ NS)	165 (62, M ⁺), 164 (15), 150 (100), 134 (8), 117 (5), 106 (3), 97 (5), 77 (4), 69 (6), 53 (10), 45 (8), 41 (8), 39 (9)
35	3-(ethylthio)-1,2,4-trithiane	198 (3, M ⁺), 170 (0.6), 138 (100), 92 (12), 74 (33), 73 (55), 64 (15), 60 (30), 59 (38), 45 (29), 41 (33)
36	7-methyl-4,5,8-trithia-1,10-undecadiene ^a	179 (2), 147 (2), 146 (2), 138 (2), 115 (55), 101 (4), 81 (17), 73 (55), 59 (17), 45 (26), 41 (100), 39 (70)
37	6-methyl-4,5,8-trithia-1,10-undecadiene ^a	220 (0.4, M ⁺), 179 (3), 147 (3), 146 (2), 137 (2), 115 (70), 105 (4), 87 (5), 81 (23), 73 (73), 59 (14), 45 (33), 41 (100), 39 (47)
38	methyl-1,2,3,4,5-pentathiepane	202 (0.3, M ⁺), 170 (0.5), 138 (8), 129 (2), 106 (0.7), 96 (2), 74 (15), 73 (9), 59 (9), 42 (59), 41 (100), 39 (61)
39	dimethyl-1,2,3,6-tetrathia-cyclooctane	212 (2, M ⁺), 138 (70), 106 (4), 74 (86), 73 (54), 59 (21), 46 (21), 45 (58), 41 (100), 39 (43)
40	8-methyl-4,5,6,9-tetrathia-1,11-dodecadiene	252 (0.1, M ⁺), 211 (0.2), 179 (0.5), 147 (32), 138 (3), 113 (3), 105 (21), 81 (5), 74 (7), 73 (85), 59 (6), 45 (23), 41 (100), 39 (45)
41	7-methyl-4,5,6,9-tetrathia-1,11-dodecadiene	147 (3), 146 (4), 113 (5), 105 (6), 99 (3), 85 (4), 81 (12), 74 (12), 73 (18), 59 (4), 45 (23), 42 (11), 41 (100), 40 (13), 39 (70)
42	9-methyl-4,5,6,7,10-pentathia-1,12-tridecadiene	179 (2), 148 (3), 147 (4), 115 (60), 101 (5), 81 (17), 75 (14), 74 (15), 73 (45), 59 (17), 45 (24), 41 (100), 39 (75)
45, 46	unknowns 4 and 5 (C ₈ H ₁₂ S ₂) (identical spectra)	148 (35, M ⁺), 119 (100), 106 (3), 85 (7), 75 (13), 74 (9), 73 (15), 64 (5), 59 (11), 45 (25), 41 (37)

^a First reported by Block *et al.* (1988).

This can be explained by formation of brown pigments and other macromolecules (in part by self-condensation, in part by reaction with other small molecules, e.g. ammonia, hydrogen sulfide, and acetaldehyde). The amount of total volatiles also decreases with temperatures beyond 120 °C. This fact is rather related to increased formation of hydrogen sulfide and sulfur dioxide, typical thermal degradation products of all S-containing amino acids. The maximum amount of sulfur volatiles arises in the presence of 20–40% of water and decreases greatly at higher amounts of water, whereas the formation of allyl alcohol prevails. It can be expected that the amount of these volatiles formed from alliin when garlic cloves are cooked will be relatively small (about 0.5% of the alliin), since the water activity in the fresh garlic is about 98% (10 mg of alliin/650 mg of water in a 1 g clove). Higher amounts of volatiles probably arise in situations when the water activity of garlic decreases (on frying, roasting, baking, etc.).

It is not easy to compare our results with those of Yu *et al.* (1994c), because they carried out their experiments under different conditions (at a temperature of 180 °C for 1 h, 99% water, isolation of volatiles by Likens–Nickerson simultaneous distillation/solvent extraction). They identified along with allyl alcohol acetaldehyde, thiazole, and 2-acetylthiazole as the major degradation products arising from alliin. These compounds (typical degradation products of cysteine) are probably formed via [2,3]-sigmatropic rearrangement of alliin. This degradation mechanism is favored in the presence of higher water amounts. Thus, it is not surprising that we were not able to detect the above-mentioned compounds in our experiments carried out in the presence

of 10% water. However, efforts were focused only on the formation of sulfur volatile compounds arising from thermally degraded alliin and deoxyalliin. Most of the major sulfur-containing compounds identified in the work of Yu *et al.* (1994c) were also found in the present study. In good agreement with our results is their finding of small amounts of sulfides because these decompose at the higher temperatures used by them.

The resulting aroma of degraded alliin samples is strongly dependent on the temperature of heating. At lower temperatures it can be described as garlic-like and biting, with ammonia and pyridine-like notes. At higher temperatures sulfury, burnt, gummy, mushroom-like, and biting odors prevail. The contribution of individual components to the resulting aroma as determined by aroma extract dilution analysis (Grosch, 1993; Etiévant *et al.*, 1994) is shown in Figure 3. Compounds **2**, **3**, **10**, **23**, and **34** possess a typical garlic-like odor. On the other hand, the odor of compounds **12**, **15**, **16**, **27**, and **31–33** can be described as garlic-like with sulfury, burnt, and biting notes. Very interesting sensory properties were observed with the isomeric pair of 2,5-dimethyl-1,4-dithiepane. The first isomer (**13**) smells unpleasant, and the second one (**14**) possesses mushroom-like odor with a considerably lower threshold value than the former isomer.

In summary, garlic-like aroma can be formed from alliin and deoxyalliin also nonenzymatically at temperatures >100 °C. Alliin is much more labile than deoxyalliin, especially at temperatures <160 °C. The chemical behaviors of the naturally occurring (+)-stereoisomer of alliin and a mixture of both isomers were identical (not shown). The types of compounds formed from alliin and/or deoxyalliin depend mainly on

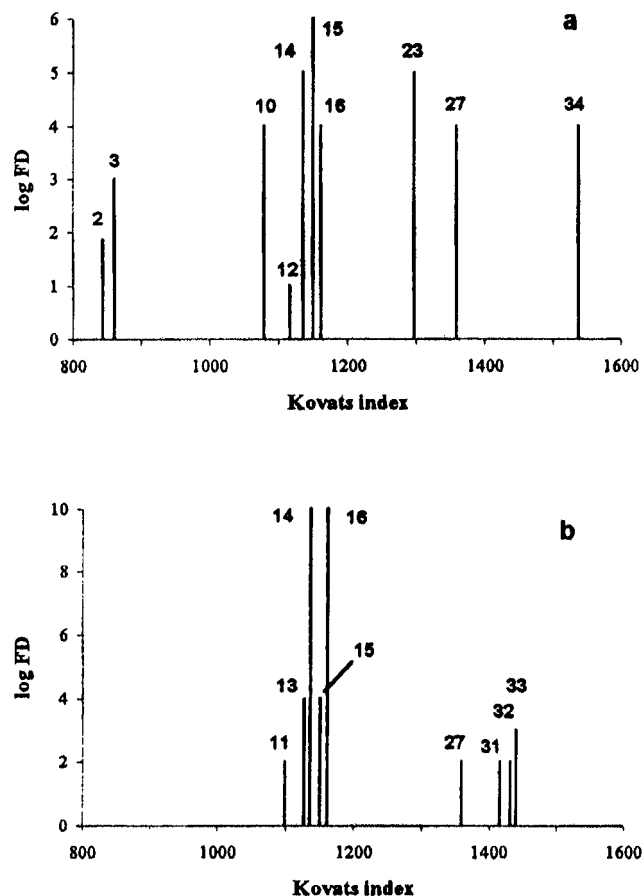


Figure 3. Flavor dilution chromatograms of the odorants formed from heated alliin at (a) 120 and (b) 180 °C, respectively. (Peak numbers correspond with those listed in Table 1.)

temperature of heating. Water activity and time of heating influence the total amount of volatiles formed rather than their structures.

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