

# Volatile Constituents of the Distilled Oils of Welsh Onions (*Allium fistulosum* L. Variety Maichuon) and Scallions (*Allium fistulosum* L. Variety Caespitosum)

May-Chien Kuo and Chi-Tang Ho\*

Department of Food Science, Cook College, New Jersey Agricultural Experiment Station, Rutgers University, New Brunswick, New Jersey 08903

Volatile components were isolated from Welsh onions and scallions by steam distillation at atmospheric pressure and analyzed by GC and GC-MS. Sulfur-containing compounds account for 87% and 82% of the total volatiles in the distilled oils of Welsh onions and scallions, respectively. In addition to the sulfur compounds commonly reported in the genus *Allium*, 41 novel volatile sulfur-containing components were found in the distilled oils of green onions. The novel compounds can be grouped as (1) 1-[alk(en)ylthio]alkyl alk(en)yl disulfides, (2) alkyl tetra- or pentathiaalkanes or alkene(s), and (3) thiaheterocycles. Heat may be responsible for the formation of many of the sulfur-containing volatiles in green onion distilled oils. Some of the novel polysulfides identified have sweet, scallion-like or onion-like odors.

## INTRODUCTION

There are about 500 different species in the genus *Allium* of the family of Liliaceae, but only a few of them are considered to be important vegetables. Among them, onions, garlic, leeks, chives, scallions, and shallots are vegetables of the *Allium* species which have been widely used to flavor foods. In addition to their application as food flavors, the medicinal properties of garlic and onions have been recognized for centuries in some parts of the world (Whitaker, 1976; Fenwick and Hanley, 1985). Biologically active sulfur compounds responsible for these properties nevertheless have not been isolated from garlic and onions until very recently (Block et al., 1986; Bayer et al., 1989).

The characteristic aromas of the *Allium* species are attributed to the sulfur-containing volatiles in these plants. The composition and formation of volatiles in garlic and onion have been extensively studied and reviewed (Freeman and Whenham, 1975; Whitaker, 1976; Fenwick and Hanley, 1985; Carson, 1987; Whitefield and Last, 1991). It is known that the volatile components of the *Allium* genus are released from their nonvolatile precursors, *S*-alk(en)ylcysteine sulfoxides, by an enzyme-mediated degradation which takes place when the plants are crushed. The alk(en)yl groups are mainly a combination of propyl, 1-propenyl, allyl, and methyl groups, depending on the species.

Green onions, *Allium fistulosum* L. var. Maichuon (Welsh onions) and *Allium fistulosum* L. var. Caespitosum (scallions), are used as vegetables or spices in many countries. They are highly prized and extensively cultivated in China and Japan. They are especially important ingredients in Chinese cuisine (FIRDI, 1988; Ho et al., 1989). Volatiles of green onions were first studied by Kameoka et al. (1984), who reported sulfides and furanones as the major components in steam-distilled oils from Welsh onions and scallions. The sulfur-containing volatiles reported by these authors constituted only 40-48% of the total volatiles. This relatively low level of sulfurous volatiles in green onions is quite different from what was observed in onions.

Because of the thermally labile nature of the flavor compounds of the *Allium* species, considerable changes

in the volatile compositions may occur as a result of cooking and processing. In addition, the interactions of *Allium* flavor compounds with other food components during cooking or processing are of interest in pursuit of the generation of food flavor by thermal reactions. The present study investigated the volatile components in the distilled oils from Welsh onions and scallions. The purpose of using a harsh flavor isolation methodology, namely steam distillation, was to study the effect of heat on the thermal generation of volatile sulfur-containing components in green onions. Preliminary data on the qualitative identification of 25 novel polysulfides in these oils have been published (Kuo et al., 1990).

## EXPERIMENTAL PROCEDURES

**Materials.** Green onions were purchased fresh from a local market. A standard of *n*-paraffins (C<sub>5</sub>-C<sub>26</sub>) was purchased from Alltech Associates, Inc. (Deerfield, IL). *cis*- and *trans*-methyl 1-propenyl disulfides, 2-mercapto-3,4-dimethyl-2,3-dihydrothiophene, *cis*- and *trans*-propyl 1-propenyl disulfides, dipropyl disulfide, *syn*- and *anti*-3,5-diethyl-1,2,4-trithiolanes, and 6-ethyl-4,5,7-trithia-2,8-decadiene were provided by Dr. Eric Block of the Chemistry Department of the State University of New York at Albany. 2-Undecanone and 2-tridecanone were gifts from Givaudan Corp. (Clifton, NJ). Propanethiol and dimethyl disulfide were obtained from Pfaltz and Bauer, Inc. (Waterbury, CT).

**Preparation of Distilled Oils from Welsh Onions and Scallions.** Homogenized green onion samples were prepared by blending 1 kg of freshly cut stalks and foliage with 2 L of distilled water. Distilled oils were isolated from the slurry by steam distillation at atmospheric pressure for 2 h using a modified oil separator trap (AOAC, 1980). One milliliter of redistilled methylene chloride was then added to the two-layer phases of oil/water in the oil separator trap and left standing for 30 min. The recovery of oils was accomplished by complete drainage of the solvent layer. The excess solvent was removed by nitrogen at ambient temperature. The oils were then analyzed by GC and GC-MS.

**GC and GC-MS Analysis.** A Varian 3400 gas chromatograph equipped with an FID and a fused silica capillary column [HP-1, 100% dimethyl polysiloxane, 50 m × 0.32 mm (i.d.), *d*<sub>f</sub> = 1.05 μm; Hewlett-Packard Co.] was used to analyze the isolated volatiles. The operating conditions were as follows: injector temperature, 270 °C; detector temperature, 300 °C; He flow rate, 1 mL/min; oven temperature, 40-260 °C at 2 °C/min. Linear

Table I. Volatile Compounds of Distilled Oils from Welsh Onions and Scallions

peak no.	compound	$I_k$ (HP-1)	GC area, <sup>a</sup> %		ID
			A	B	
1	propanethiol <sup>d</sup>	587	0.69	0.27	GC, GC-MS
2	1-propenethiol <sup>d</sup>	595	0.18	0.44	GC-MS
3	methyl hydrodisulfide <sup>d</sup>	640	0.27	0.18	GC-MS
4	dimethyl disulfide <sup>d</sup>	722	0.78	0.24	GC, GC-MS
5	hexanal	749	0.11	0.35	GC, GC-MS
6	2-methyl-2-pentenal	773	0.16	0.32	GC, GC-MS
7	propyl hydrodisulfide <sup>d</sup>	808	0.58	1.49	GC-MS
8	<i>trans</i> -2-hexenal	825	<i>b</i>	2.45	GC, GC-MS
9	1-propenyl hydrodisulfide <sup>d</sup>	835	0.26	0.85	GC-MS
10	1-propenyl hydrodisulfide <sup>d</sup>	845	0.18	0.75	GC-MS
11	2,5-dimethylthiophene <sup>d</sup>	852	0.10	0.06	GC-MS
12	2,4-dimethylthiophene <sup>d</sup>	860	1.85	0.07	GC-MS
13	3,4-dimethylthiophene <sup>d</sup>	885	5.50	0.48	GC, GC-MS
14a	methyl propyl disulfide	912	2.76	1.41	GC-MS
14b	methyl <i>cis</i> -1-propenyl disulfide <sup>d</sup>				GC, GC-MS
15	methyl <i>trans</i> -1-propenyl disulfide <sup>d</sup>	918	5.91	1.51	GC, GC-MS
16	dimethyl trisulfide <sup>d</sup>	945	6.14	1.75	GC-MS
17	2-pentylfuran <sup>d</sup>	978	0.12	0.23	GC-MS
18a	dipropyl disulfide	1090	4.28	9.79	GC, GC-MS
18b	propyl <i>cis</i> -1-propenyl disulfide <sup>d</sup>				GC, GC-MS
19	propyl <i>trans</i> -1-propenyl disulfide <sup>d</sup>	1096	0.78	4.72	GC, GC-MS
20	3-methyl-1,2,4-trithiolane <sup>d</sup>	1115	0.21	0.86	GC-MS
21	methyl propyl trisulfide	1130	12.97	12.75	GC-MS
22	methyl <i>cis</i> -1-propenyl trisulfide <sup>d</sup>	1136	1.55	4.21	GC-MS
23	methyl <i>trans</i> -1-propenyl trisulfide <sup>d</sup>	1140	2.01	4.18	GC-MS
24	1-(methylthio)ethyl methyl disulfide <sup>c,d,e</sup>	1145	0.27	0.23	GC-MS
25	2-mercapto-3,4-dimethyl-2,3-dihydrothiophene <sup>d,e</sup>	1149	0.08	0.45	GC, GC-MS
26	dimethyl tetrasulfide <sup>d</sup>	1188	2.15	0.85	GC-MS
27	3-methyl-5-ethyl-1,2,4-trithiolane	1206	0.28	1.15	GC-MS
28	3-methyl-5-ethyl-1,2,4-trithiolane	1213	0.27	1.37	GC-MS
29	1-(methylthio)propyl methyl disulfide <sup>c,d,e</sup>	1235	6.07	0.85	GC-MS
30	2-undecanone	1269	0.42	0.72	GC, GC-MS
31	3,5-diethyl-1,2,4-trithiolane	1307	8.42	11.39	GC, GC-MS
32a	dipropyl disulfide	1314	3.86	2.44	GC, GC-MS
32b	3,5-diethyl-1,2,4-trithiolane				GC, GC-MS
33	propyl 1-propenyl trisulfide <sup>d</sup>	1318	2.94	6.59	GC-MS
34	di(1-propenyl) trisulfide <sup>d</sup>	1329	0.08	0.04	GC-MS
35	5,6-dimethyl-2,3,7-trithiabicyclo[2.2.1]heptane <sup>c,d,e</sup>	1346	0.23	0.12	GC-MS
36	methyl propyl tetrasulfide <sup>d</sup>	1362	0.15	0.27	GC-MS
37	methyl <i>cis</i> -1-propenyl tetrasulfide <sup>d</sup>	1366	0.17	0.21	GC-MS
38	methyl <i>trans</i> -1-propenyl tetrasulfide <sup>d</sup>	1369	0.13	0.14	GC-MS
39	1-(propylthio)propyl methyl disulfide <sup>c,d,e</sup>	1395	0.70	0.21	GC-MS
40	1-(methylthio)propyl propyl disulfide <sup>c,d</sup>	1397	1.06	0.27	GC-MS
41	1-(1-propenylthio)propyl methyl disulfide <sup>c,d,e</sup>	1407	0.76	0.43	GC-MS
42	1-(methylthio)propyl 1-propenyl disulfide <sup>c,d,e</sup>	1407	0.56	<i>t</i>	GC-MS
43	2,3-dimethyl-5,6-dithiabicyclo[2.1.1]hexane 5,5-dioxide <sup>c,d,e</sup>	1421	0.32	0.22	GC-MS
44	dimethyl pentasulfide <sup>d</sup>	1426	0.42	0.26	GC-MS
45	methyl dimethylthienyl disulfide <sup>c,d,e</sup>	1440	0.02	0.02	GC-MS
46	methyl dimethylthienyl disulfide <sup>c,d,e</sup>	1446	0.01	<i>t</i>	GC-MS
47a	5-ethyl-2,3,4,6-tetrathiaheptane <sup>c,d,e</sup>	1452	2.54	0.68	GC-MS
47b	4-ethyl-2,3,5,6-tetrathiaheptane <sup>c,d,e</sup>				
48	methyl dimethylthienyl disulfide <sup>c,d,e</sup>	1460	0.11	0.08	GC-MS
49	2-tridecanone	1476	1.63	3.10	GC, GC-MS
50	2,4-dimethyl-5,6-dithia-2,7-nonadienal <sup>d,e</sup>	1529	0.59	0.65	GC-MS
51	2,4-dimethyl-5,6-dithia-2,7-nonadienal <sup>d,e</sup>	1536	0.41	0.17	GC-MS
52	dipropyl tetrasulfide <sup>d</sup>	1544	0.82	1.11	GC-MS
53	propyl 1-propenyl tetrasulfide <sup>d</sup>	1550	0.24	0.49	GC-MS
54	1-(propylthio)propyl propyl disulfide <sup>c,d,e</sup>	1557	0.33	0.86	GC-MS
55a	2,4-dimethyl-5,6-dithia-2,7-nonadienal <sup>d,e</sup>	1563	0.24	0.57	GC-MS
55b	4,6-diethyl-1,2,3,5-tetrathiane <sup>d,e</sup>				GC-MS
55c	1-(propylthio)propyl 1-propenyl disulfide <sup>d,e</sup>				GC-MS
56	6-ethyl-4,5,7-trithia-2,8-decadiene <sup>c,d,e</sup>	1573	0.42	0.49	GC-MS
57	6-ethyl-4,5,7-trithia-2,8-decadiene <sup>c,d,e</sup>	1584	0.12	0.31	GC, GC-MS
58a	4,6-diethyl-1,2,3,5-tetrathiane <sup>d,e</sup>	1591	0.28	0.26	GC-MS
58b	3-ethyl-5-pentyl-1,2,4-trithiolane <sup>d,e</sup>				GC-MS
59	1-(propylthio)propyl 1-propenyl disulfide <sup>c,d,e</sup>	1603	0.24	0.04	GC-MS
60	4-ethyl-2,3,5,6-tetrathianonane <sup>c,d,e</sup>	1616	0.76	0.28	GC-MS
61	4-ethyl-2,3,5,6-tetrathia-7-nonene <sup>c,d,e</sup>	1620	0.16	0.17	GC-MS
62a	3-ethyl-2,4,5,6-tetrathiaheptane <sup>c,d,e</sup>	1627	0.79	<i>c</i>	GC-MS
62b	2,3-dihydro-2-octyl-5-methylfuran-3-one		0.84	0.11	GC-MS
63	propyl 3,4-dimethyl-2-thienyl disulfide <sup>c,d,e</sup>	1635	0.25	0.17	GC-MS
64	4-ethyl-2,3,5,6,7-pentathiaoctane <sup>c,d,e</sup>	1679	0.26	0.08	GC-MS
65	2-pentadecanone		0.02	0.01	GC-MS
66	5-ethyl-2,3,4,6,7-pentathiadecane <sup>d,e</sup>		0.09	0.01	GC-MS
67	2,4-dimethyl-5,6-dithia-2,7-nonadienal 5-oxide <sup>d,e</sup>	1723	0.31	0.06	GC-MS

Table I. (Continued)

peak no.	compound	$I_k$ (HP-1)	GC area, <sup>a</sup> %		ID
			A	B	
68	2,4-dimethyl-5,6-dithia-2,7-nonadienal 5-oxide <sup>d,e</sup>	1734	0.13	0.17	GC-MS
69	6-ethyl-4,5,7,8-tetrathiaundecane <sup>c,d,e</sup>	1772	0.25	0.11	GC-MS
70	6-ethyl-4,5,7,8-tetrathia-2-undecene <sup>c,d,e</sup>	1779	0.07	0.01	GC-MS
71	6-ethyl-4,5,7,8-tetrathia-2-undecene <sup>c,d,e</sup>	1784	0.06	c	GC-MS
72	4-ethyl-6-pentyl-1,2,3,5-tetrathiane <sup>c,d,e</sup>	1791	0.02	0.02	GC-MS
73	4-ethyl-6-pentyl-1,2,3,5-tetrathiane <sup>c,d,e</sup>	1818	0.02	0.02	GC-MS
74	5,7-diethyl-1,2,3,4,6-pentathiepane <sup>c,d,e</sup>	1822	0.11	c	GC-MS
75	5,7-diethyl-1,2,3,4,6-pentathiepane <sup>d,e</sup>	1824	0.27	t	GC-MS
76	2,3-dihydro-2-decyl-5-methylfuran-3-one <sup>d,e</sup>	1838	0.02	0.04	GC-MS
77	5-ethyl-7-pentyl-1,2,3,4,6-pentathiepane <sup>d,e,f</sup>	2005	0.11	0.02	GC-MS

<sup>a</sup> Average of two experiments. A, Welsh onions; B, scallions. <sup>b</sup> Not detected. <sup>c</sup> Quantitative data and mass spectral data previously published (Kuo et al., 1990). <sup>d</sup> First reported in green onions. <sup>e</sup> Not previously identified in *Allium*. <sup>f</sup>  $I_k$  previously miscalculated as 1923 (Kuo et al., 1990). <sup>g</sup> t, trace (less than 0.01 %).

retention indices were calculated against C<sub>5</sub>-C<sub>26</sub> n-paraffins as references (Majlat et al., 1974). GC-MS analyses were conducted in a Varian 3600 GC directly coupled to a Finnigan 4500 mass spectrometer. Mass spectra were obtained by electron ionization (EI) and chemical ionization (CI). For EI-GC-MS, the ion source temperature was 140 °C; electron energy was 70 eV. For CI-GC-MS, NH<sub>3</sub> was used as a reagent gas. The GC column was the same as described above.

**Fractionation of Volatile Compounds by Gas Chromatography.** Volatiles of Welsh onion oil were fractionated by using a Varian 3600 GC equipped with an FID and a fused silica capillary column (30 m × 0.5 mm;  $d_f$  = 1.0 μm, DB-5, J&W Scientific Co.). The GC was modified to accommodate a sniffing port at the right wall of the GC. A splitter of a 1:10 ratio was put at the end of the separation column, and connected to it were two segments of an empty fused silica column. One segment of the column was connected to the FID, while the other was connected to the sniffing port, which was wrapped by a heating tape for controlling the temperature. The volatile fractions were collected by U-shaped glass tubing (20 cm × 0.25 mm) immersed in an iced water bath saturated with sodium chloride.

The operating conditions were as follows: injector temperature, 270 °C; detector temperature, 270 °C; He flow rate, 0.8 mL/min; oven temperature, 40–200 °C at 2 °C/min and 200–260 °C at 10 °C/min. The final oven temperature was held at 260 °C for 20 min.

**Sensory Evaluation of Volatile Sulfur-Containing Compounds.** The odor of volatile fractions collected by GC was dissolved in about 50–75 μL of absolute ethanol and evaluated by three experienced flavorists at a flavor company.

## RESULTS AND DISCUSSION

The volatile oils of Welsh onions and scallions were obtained by steam distillation at atmospheric pressure with a modified oil separator. The volatile components of the distilled oils were analyzed by gas chromatography and gas chromatography-mass spectrometry equipped with fused silica capillary columns. GC columns of both polar (Carbowax 20M) and nonpolar (dimethylpolysiloxane) stationary phases were examined. The latter was chosen for this study because it gave better resolution for the sulfur-containing compounds comprising a large number of isomers.

The identities of volatile flavor components of Welsh onion and scallion oils are listed in Table I. The identifications were achieved by comparing their GC retention indices and mass spectra with either those of authentic compounds or published data (Bayer et al., 1989; Boelens et al., 1971, 1974; Heller and Milne, 1980; Ten Noever de Brauw et al., 1983; Wijers et al., 1969). When neither authentic sample nor published information was available, the identification was established by interpreting the fragmentation pattern of mass spectra. Table II lists the mass spectral data of the novel sulfur-containing compounds identified in the present study.

The flavor compounds found in green onions may be divided into the following categories: oxygenated compounds, thiols, disulfides, trisulfides, tetrasulfides, pentasulfides, tetrathia- and pentathiaalkanes (or alkene), and heterocyclics. Among the 77 compounds listed in Table I, 68 are sulfur-containing volatiles and the rest are carbonyl compounds.


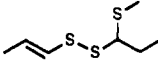
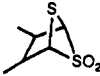
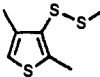
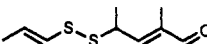
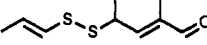
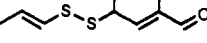
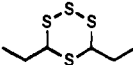
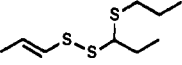
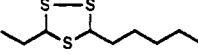
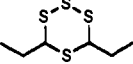
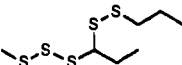
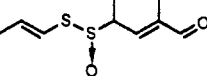
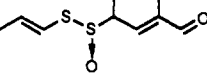
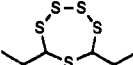
Sulfur-containing compounds account for 87% and 82% of the total volatiles in the distilled oils of Welsh onions and scallions, respectively. Carbonyl compounds (i.e., aldehydes and ketones) make up only 3.4% and 7.4% of the total volatiles in these two oils. Among all of the volatile compounds identified, methyl propyl trisulfide is the most abundant in the distilled oils of Welsh onions and scallions. According to Kameoka et al. (1984), the sulfur-containing compounds constitute 40% and 47.5% of total volatiles in the distilled oils from Welsh onions and scallions, respectively. The carbonyl compounds, on the other hand, made up 18.7% and 13.5%, respectively. In addition, these authors also reported a level of 4.3–6.4% fatty alcohols in green onions (Kameoka et al., 1984).

Except for di(1-propenyl) trisulfide (34), most of the thiols, monosulfides, disulfides, trisulfides, and tetrasulfides identified in the present study are common constituents of many *Allium* species such as onion, shallots, and chives. Including di(1-propenyl) trisulfide, 65 of the 77 components listed in Table I were not previously reported in green onions. Among them, 41 were novel volatile sulfur-containing compounds and were isolated and identified in *Allium* for the first time.

The previously reported major sulfur volatiles in Welsh onions and scallions were dipropyl disulfide, dipropyl trisulfide, methyl propyl disulfide, and methyl propyl trisulfide in decreasing order (Kameoka et al., 1984). An unusual methyl pentyl disulfide was also identified. Eighty-four components were identified in the distilled oils from green onions by Kameoka et al. (1984). Only 11 of them were sulfur-containing volatiles; among them, 7 were disulfides and trisulfides. Moreover, some fatty aldehydes (C<sub>6</sub>-C<sub>16</sub>), fatty alcohols (C<sub>6</sub>-C<sub>14</sub>), aliphatic hydrocarbons, and some methyl esters of long chain fatty acids were also reported. Genetic and environmental factors would contribute to the quantitative variation of volatiles of green onions obtained from different regions (Freeman, 1979).

Among the 41 novel volatile sulfur-containing compounds identified in the steam-distilled oils from Welsh onions and scallions, 26 have been previously reported by us (Kuo et al., 1990). These novel polysulfides make up 17% and 7% of the total volatiles of Welsh onion and scallion oils, respectively. Except for compound 40 [1-(methylthio)propyl propyl disulfide], all of these volatile

Table II. EI Mass Spectral Data of Novel Volatile Sulfur-Containing Compounds in Welsh Onions and Scallions

no. <sup>a</sup>	compound	MW	mass spectral data <sup>b</sup>
25	2-mercapto-3,4-dimethyl-2,3-dihydrothiophene <sup>c</sup> 	146	113 (100), 111 (88), 97 (72), 45 (63), 112 (62), 39 (47), 79 (22), 71 (19), 98 (19), 146 (18)
42	1-(methylthio)propyl 1-propenyl disulfide 	194	89 (100), 41 (71), 61 (24), 49 (6), 42 (3), 88 (1)
43	2,3-dimethyl-5,6-dithiabicyclo[2.1.1]hexane 5,5-dioxide 	178	113 (100), 99 (53), 45 (44), 79 (21), 39 (21), 79 (21), 41 (20), 114 (13), 178 (12), 97 (12)
46	methyl dimethylthienyl disulfide 	190	143 (100), 190 (59), 45 (49), 99 (31), 111 (21), 65 (15), 77 (10)
50	2,4-dimethyl-5,6-dithia-2,7-nonadienal 	202	69 (100), 45 (34), 41 (42), 129 (22), 59 (15), 67 (9), 55 (6), 47 (5), 128 (5), 70 (5)
51	2,4-dimethyl-5,6-dithia-2,7-nonadienal 	202	69 (100), 41 (50), 45 (39), 75 (36), 129 (20), 59 (19), 39 (19), 47 (10), 67 (9), 55 (6)
55a	2,4-dimethyl-5,6-dithia-2,7-nonadienal 	202	69 (100), 43 (37), 59 (26), 129 (22), 67 (10), 55 (7), 61 (6), 70 (6), 128 (6), 85 (5)
55b	4,6-diethyl-1,2,3,5-tetrathiane 	212	73 (100), 41 (46), 74 (44), 45 (36), 39 (15), 138 (12), 115 (10), 64 (8), 75 (7), 212 (6)
55c	1-(propylthio)propyl 1-propenyl disulfide 	222	117 (100), 43 (65), 75 (61), 41 (52), 73 (26), 47 (19), 39 (16), 74 (15), 76 (6), 105 (4)
58b	3-ethyl-5-pentyl-1,2,4-trithiolane 	222	74 (100), 41 (63), 45 (46), 75 (18), 83 (15), 47 (12), 115 (12), 59 (11), 106 (9), 157 (5)
58a	4,6-diethyl-1,2,3,5-tetrathiane 	212	73 (100), 41 (59), 74 (48), 45 (46), 39 (19), 138 (12), 115 (12), 69 (10), 59 (10), 46 (9)
66	5-ethyl-2,3,4,6,7-pentathiadecane 	260	89 (100), 41 (62), 45 (29), 61 (18), 73 (13), 74 (13), 47 (12), 39 (11), 46 (10), 79 (9)
67	2,4-dimethyl-5,6-dithia-2,7-nonadienal 5-oxide 	218	69 (100), 41 (42), 45 (27), 39 (15), 71 (8), 145 (7), 59 (6), 70 (6), 73 (5), 47 (5)
68	2,4-dimethyl-5,6-dithia-2,7-nonadienal 5-oxide 	218	69 (100), 41 (38), 45 (24), 39 (14), 71 (8), 218 (7), 145 (7), 111 (6), 59 (5), 72 (5)
75	5,7-diethyl-1,2,3,4,6-pentathiepane 	264	41 (100), 45 (73), 106 (71), 74 (58), 39 (32), 73 (30), 170 (25), 180 (21), 64 (20), 59 (16)

<sup>a</sup> Numbers refer to Table I. <sup>b</sup>  $m/z$  in decreasing values with intensity in parentheses. <sup>c</sup> Mass spectral data previously reported by Block and Zhao (1990).

compounds are being reported in Welsh onions and scallions and in the genus *Allium* for the first time. Together with 1-(methylthio)propyl ethyl disulfide, 1-(me-

thylthio)propyl propyl disulfide was first reported by Boelens et al. (1974) as main byproducts of heated 1-(alkylthio)-1-alkanethiols, which were produced from the model

Table III. Odor Description of Some Novel Volatile Polysulfides Identified in Green Onion Distilled Oils

compound	odor description
1-(methylthio)propyl methyl disulfide	earthy, slightly green, slightly gassy, onion-like onion-like, dirty, gassy, thiazole-like, biting
1-(propylthio)propyl methyl disulfide and 1-(methylthio)propyl propyl disulfide (2.1:1)	
1-(propylthio)propyl methyl disulfide and 1-(methylthio)propyl propyl disulfide (3.1:1)	onion-like, fresh, sweet
1-(propylthio)propyl methyl disulfide, 1-(methylthio)propyl methyl disulfide, and 1-(methylthio)propyl 1-propenyl disulfide (1:5.8:1.26)	scallion-like, green

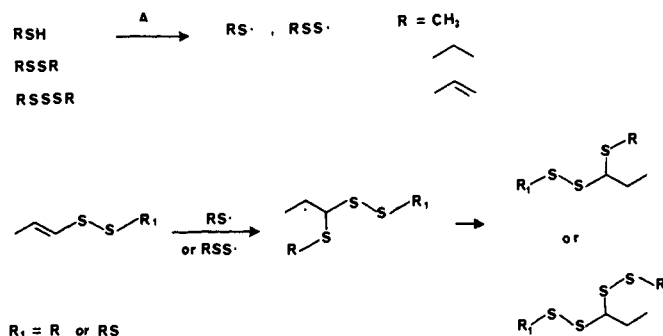


Figure 1. Mechanism proposed for the formation of branched polysulfides.

system of saturated aldehyde, hydrogen sulfide, and thiols. 1-(Methylthio)propyl propyl disulfide was also previously identified in the distilled oil from shallots (Chen and Wu, 1983). In addition, a similar polysulfide, namely ethyl 1-(ethylthio)ethyl disulfide, was generated from the reaction of mercaptoacetaldehyde and ammonium sulfide (Hwang et al., 1986).

**Nonaromatic Bicyclics.** Among the 41 novel volatile polysulfides reported in Table I, 15 are cyclic compounds including 2 bicycles. Those cyclic polysulfides account for 3.6% and 2.2% of total volatiles of Welsh onions and scallions, respectively.

Compound 35 (5,6-dimethyl-2,3,7-trithiabicyclo[2.2.1]heptane) has a similar structure to that of 5,6-dimethyl-2,7-dithia-3-oxabicyclo[2.2.1]heptane. The latter was proposed in the formation mechanism of the biologically active 2,3-dimethyl-5,6-dithiabicyclo[2.1.1]hexane 5-oxide from onion (Bayer et al., 1989). Compound 43 (2,3-dimethyl-5,6-dithiabicyclo[2.1.1]hexane 5,5-dioxide) has a structure similar to that of zwiebelane (2,3-dimethyl-5,6-dithiabicyclo[2.1.1]hexane 5-oxide), a biologically active compound from onion, reported by Bayer et al. (1989).

**Dimethyldihydrothiophene.** In addition to three isomers of dimethylthiophenes, several derivatives of thiophene were observed in the distilled oils of green onions. 2-Mercapto-3,4-dimethyl-2,3-dihydrothiophene (25) was not previously found in green onions or in other *Allium* species. Block and Zhao (1990) first reported the formation of *cis*- and *trans*-2-mercapto-3,4-dimethylthiophenes from pyrolysis of di(1-propenyl) disulfide. The identification of component 25 was accomplished by comparing the spectrum with that of an authentic sample. A molecular ion of  $m/z$  146 was observed from its EI-MS spectrum (see Table II for mass spectral data). A loss of SH radical from the molecular ion results in the fragment  $m/z$  113. Further loss of  $\text{H}_2$  results in the fragment  $m/z$  111. The rest of the fragmentation patterns are similar to that of 3,4-dimethylthiophene.

**Alkyl Dimethylthienyl Disulfides.** Among the novel cyclic polysulfides shown in Table I, alkyl dimethylthienyl disulfides, components 45, 46, 48 and 63, were reported for the first time in food flavors.

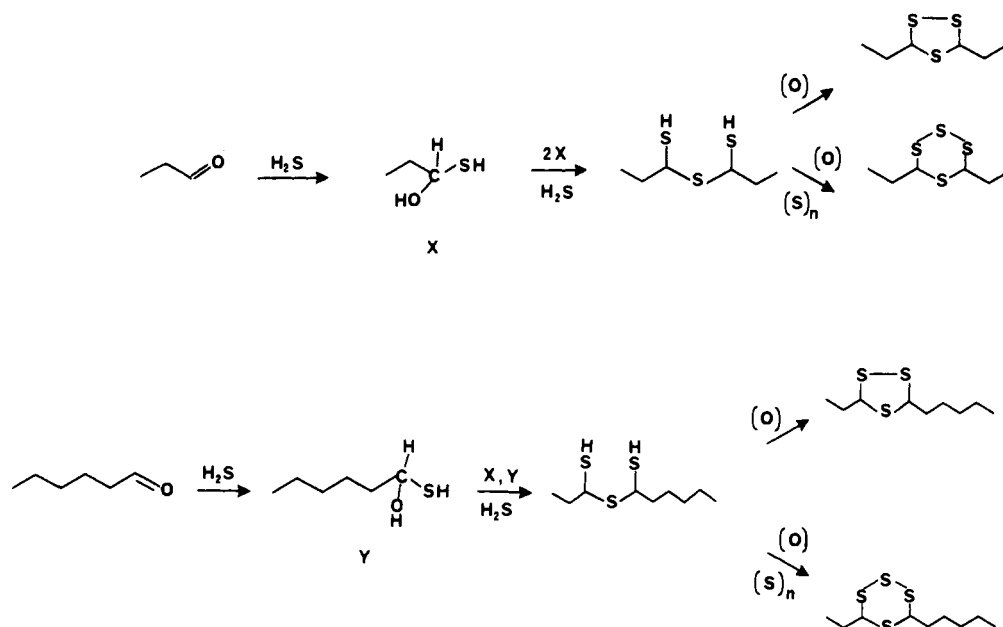
With the help of GC fractionation on a megabore capillary column (DB-5), two more isomers of propyl di-

methylthienyl disulfides were identified in green onion oils. Even after repetitive fractionation from a total amount of 100  $\mu\text{L}$  of Welsh onion oil, these two components were still present as trace volatiles. According to GC peak areas, the three isomers were estimated to have a ratio of 1:3.5:21. The most abundant isomer was proposed as propyl 3,4-dimethyl-2-thienyl disulfide (63). The mass spectral data of the additional identified isomers of propyl dimethylthienyl disulfides are as follows: (1) 142 (100%), 71 (80%), 218 ( $\text{M}^+$ , 74%), 143 (57%), 43 (55%), 112 (43%), 111 (32%), 45 (26%), 144 (21%); (2) 143 (100%), 218 ( $\text{M}^+$ , 52%), 41 (23%), 45 (21%), 111 (18%), 99 (17%), 144 (16%), 43 (16%), 144 (16%), 59 (13%).

**Nonaromatic Cyclic Polysulfides.** In addition to several commonly found 1,2,4-trithiolanes (compounds 20, 27, 28, 31, and 32b in Table I), several cyclic nonaromatic polysulfides were first reported in *Allium*. They are 3-ethyl-5-pentyl-1,2,4-trithiolane (58b), *syn*- and *anti*-4,6-diethyl-1,2,3,5-tetrathianes (55b, 58a), *syn*- and *anti*-4-ethyl-6-pentyl-1,2,3,5-tetrathianes (72, 73), 5,7-diethyl-1,2,3,4,6-pentathiepanes (74, 75), and 5-ethyl-7-pentyl-1,2,3,4,6-pentathiepane (77). By ring opening and rearrangement, the characteristic mass fragments of these cyclic polysulfides can be obtained through a similar mechanism proposed by Hwang et al. (1986). A homologue of compound 58b, namely 3-methyl-5-pentyl-1,2,4-trithiolane, was identified from the thermal reaction of 2,4-decadienal with cysteine and with glutathione (Zhang, 1991).

**Acyclics Containing Three Sulfur Atoms.** Ten of the 21 acyclic polysulfides listed in Table I are branched polysulfides containing 3 sulfur atoms in the structure. The presence of 1-(methylthio)ethyl methyl disulfide (24) indicates the possibility of unusual existence of vinyl-L-cysteine sulfoxide in green onions. Compound 24, 3-methyl-2,4,5-trithiahexane, was also identified as a flavor constituent in yeast extract of Werkhoff et al. (1991). It was reported to have a sulfury, onion, meaty aroma with strong impact. The amount of 1-(methylthio)propyl methyl disulfide (29) in Welsh onion oil was as high as 6%. It was actually the fourth most abundant volatile component of Welsh onion oil. All of the branched polysulfides identified in green onion oils have similar mass fragmentation patterns. The identification of 6-ethyl-4,5,7-trithia-2,8-decadiene (57) was confirmed by comparing its EI-MS spectrum with that of the authentic compound. The characteristic fragments of most acyclic polysulfides can be obtained by a general pathway as illustrated in the mass fragmentation pathways of 4-ethyl-2,3,5,6-tetrathianonane (60) (Kuo et al., 1990).

**Acyclics Containing Four and Five Sulfur Atoms.** There were eight branched polysulfide volatiles containing four sulfur atoms identified in green onions. Among them, 5-ethyl-2,3,4,6-tetrathiaheptane (47a) together with 4-ethyl-2,3,5,6-tetrathiaheptane (47b) constitutes 2.54% of the total volatiles of Welsh onion oil. 3-Ethyl-2,4,5,6-tetrathiaheptane (62a) and 6-ethyl-4,5,7,8-tetrathia-2-undecene (71) were not detected in the distilled oil of scallions. The EI-MS spectra of compounds 47a and 62a have



**Figure 2.** Mechanism proposed for the formation of nonaromatic cyclic polysulfides.

fragmentation patterns similar to those of branched polysulfides containing three sulfur atoms.

Two acyclic polysulfides containing five sulfur atoms were identified as volatiles in Welsh onions and scallions. The two polysulfides are 4-ethyl-2,3,5,6,7-pentathiooctane (64) and 5-ethyl-2,3,4,6,7-pentathiadecane (66). For the latter compound, the characteristic fragments of  $m/z$  111 and 153 result from cleavage at C-S bonds next to the trisulfide and disulfide backbone, respectively. Cleavage at the S-S bonds of the disulfide and trisulfide backbone result in the fragments of  $m/z$  45, 73, and 79.

**Sulfur-Containing Aldehydes.** There were three sulfur-containing aldehydes (50, 51, 55a) as well as two of their *S*-oxides (67, 68) identified in the distilled oils of green onions. Three geometrical isomers tentatively identified as 2,4-dimethyl-5,6-dithia-2,7-nonadienal (compounds 50, 51, and 55a) have similar mass spectral data as shown in Table II. The characteristic fragments of  $m/z$  69 and 129 were obtained from the cleavage at the bond between C<sub>3</sub> and C<sub>4</sub> and at the disulfide bond, respectively. The EI mass spectral data of two geometrical isomers tentatively identified as 2,4-dimethyl-5,6-dithia-2,7-nonadienal 5-oxide (67, 68) are shown in Table II. The characteristic ions of 69 and 145 resulted from the same fragmentation described above. Further loss of H<sub>2</sub>S and rearrangement of the oxygen atom from an ion of 145 could result in the fragment of  $m/z$  111.

These sulfur-containing aldehydes were speculated to be the addition product of 2-methyl-2-pentenal and 1-propenyldithio radical through free-radical reactions. 2-Methyl-2-pentenal is the aldol condensation product of propanal.

**Odor Description of Some Novel Polysulfides.** Fractionated by GC with a megabore fused silica capillary column, some branched polysulfides listed in Table I were purified from Welsh onion oil. The odor of those isolated novel polysulfides was evaluated by three professional flavorists. Some components were described as having onion-like and scallion-like odors. Their odor descriptions are listed in Table III.

**Formation Mechanism of Branched and Nonaromatic Cyclic Polysulfides.** A possible mechanism for the formation of some volatile polysulfides through free-radical addition was proposed by Kuo et al. (1990). The

proposed mechanism can be summarized as the equations in Figure 1. In the proposed mechanism, alk(en)ylthiyl (RS<sup>•</sup>) or alk(en)ylthio radical (RSS<sup>•</sup>) can be derived from alk(en)ylthiol, alk(en)yl sulfhydryl sulfide, or alk(en)yl di- or trisulfide. The radical may then attach to the double bond of a molecule of alk(en)yl propenyl disulfide (or trisulfide).

There was evidence that in the disulfide molecule the C-S bond is weaker than the S-S bond, which suggests that the cleavage of the C-S bond in disulfide may be favored (Block et al., 1988). This further suggests that the formation of the dithio radical (RSS<sup>•</sup>) from disulfide is preferred to the formation of the thiyl radical (RS<sup>•</sup>). The estimated S-S bond energy in trisulfide, however, is similar to C-S bond energy; therefore, both S-S and C-S homolysis should occur (Block et al., 1988). This indicates that both thiyl and dithio radicals can be obtained from a trisulfide molecule. Radicals centered at sulfur (i.e., RS<sup>•</sup>) are most highly reactive and are encountered only as fleeting intermediates in chemical reactions (Block, 1978). The detection of a thiyl radical and/or polysulfur radicals (R(S)<sub>n</sub><sup>•</sup>) was reported by using an ESR method (Block, 1978; Nishimura and Mizutani, 1975; Nishimura et al., 1973).

Figure 2 illustrates the mechanism proposed for the formation of alkyl-substituted 1,2,4-trithiolanes, 1,2,3,5-tetrathianes, and 1,2,3,4,6-pentathiepanes. The addition of H<sub>2</sub>S to propanal or hexanal results in hemimercaptals (compound X or Y). They are normally unstable and can further react with H<sub>2</sub>S to form dimers or even trimers. Oxidation of the mercapto groups with or without the presence of sulfur will form the ring structure as shown in Figure 2. Accordingly, acetaldehyde is responsible for the methyl groups in 3-methyl-1,2,4-trithiolane and *syn*- and *anti*-3-methyl-5-ethyl-1,2,4-trithiolanes.

In cut *Allium* plants, the most important oxygen-containing compounds are acetaldehyde and propanal. The former is derived from pyruvate, while the latter is derived from thiopropanal *S*-oxide when alk(en)yl-L-cysteine sulf-oxides are decomposed by alliinase. With regard to hexanal, it is a well-known enzymic oxidative decomposition product from linoleic acid. Hydrogen sulfide can be readily available from thiols or alk(en)yl sulphydryl sulfides or from mercaptodihydrothiophenes when thiophenes are

formed. Sulfur atoms are readily available through desulfurization of alk(en)ylsulfenic acids.

#### ACKNOWLEDGMENT

New Jersey Agricultural Experiment Station Publication No. D-10205-3-91 supported by state funds and Hatch Regional Project NE-116. We thank Dr. Mingjien Chien for Givaudan Corp. for technical advice and assistance and Mr. Jorome Lombarda, Dr. James La Marta, and Dr. Ellen Lauber of Givaudan Corp. for sensory evaluation. We also thank Ms. Joan Shumsky for secretarial aid.

#### LITERATURE CITED

- AOAC. *Official Methods of Analysis of the Association of Official Analytical Chemists*, 13th ed.; Horwitz, E., Ed.; Association of Official Analytical Chemists: Washington, DC, 1980; p 320.
- Bayer, T.; Wanger, H.; Block, E.; Grisoni, S.; Zhao, S. H.; Neszmelyi, A. Zwiebelanes: Novel biologically active 2,3-dimethyl-5,6-dithiabicyclo[2.1.1]hexane 5-oxides from onion. *J. Am. Chem. Soc.* 1989, 111, 3085-3086.
- Block E. *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978; pp 176-216.
- Block, E.; Zhao, S. H. Onion essential oil chemistry. Cis and trans-2-mercapto-3,4-dimethyl-2,3-dihydrothiophene from pyrolysis of bis(1-propenyl) disulfide. *Tetrahedron Lett.* 1990, 31, 4999-5002.
- Block, E.; Ahmad, S.; Catalfamo, J. L.; Jain, M. K.; Apitz-Castro, R. Antithrombic organosulfur compounds from garlic: Structural, mechanistic, and synthetic studies. *J. Am. Chem. Soc.* 1986, 108, 7045-7055.
- Boelens, H.; de Volois, P. J.; Wobben, H. J.; van der Gen, A. Volatile components from onion. *J. Agric. Food Chem.* 1971, 19, 984-991.
- Boelens, M.; van der Linde, L. M.; de Valois, P. J.; van Dort, H. M.; Takken, H. J. Organic sulfur compounds from fatty aldehydes, hydrogen sulfides, thiols and ammonia as flavor constituents. *J. Agric. Food Chem.* 1974, 22, 1071-1076.
- Carson, J. F. Chemistry and biological properties of onions and garlic. *Food Rev. Int.* 1987, 3, 71-103.
- Chen, J. W.; Wu, C. M. Effect of heating on shallot essential oils. Presented at the 9th International Congress of Essential Oil, Singapore, 1983.
- Fenwick, G. R.; Hanley, A. B. The genus *Allium* part 2. *CRC Crit. Rev. Food Sci. Nutr.* 1985, 22, 273-377.
- FIRDI. 1987 Annual Report; Food Industry Research and Development Institute: Taiwan, 1988; pp 44-51.
- Freeman, G. G. Factors affecting flavor during growth, storage and processing of vegetables. In *Process in Flavor Research*; Land, D. G., Nursten, H. E., Eds.; Applied Science Publishers: London, 1979; pp 225-243.
- Freeman, G. G.; Whenham, R. J. A survey of volatile compounds of some *Allium* species in terms of S-alk(en)yl-L-cysteine sulfoxides present as flavor precursors. *J. Sci. Food Agric.* 1975, 26, 1869-1886.
- Heller, S. R.; Milne, G. W. A. *EPA/NIH Mass Spectral Data Base*; U.S. Department of Commerce: Washington, DC, 1980.
- Ho, C.-T.; Zhang, Y.; Shi, H.; Tang, J. Flavor chemistry of Chinese foods. *Food Rev. Int.* 1989, 5, 253-287.
- Hwang, S.-S.; Carlin, J. T.; Bao, Y.; Hartman, G. J.; Ho, C.-T. Characterization of volatile compounds generated from the reactions of aldehydes with ammonium sulfide. *J. Agric. Food Chem.* 1986, 34, 538-542.
- Kameoka, H.; Iida, H.; Hashimoto, S.; Miyazawa, M. Sulphides and furanones from steam volatile oils of *Allium fistulosum* and *Allium chinense*. *Phytochemistry* 1984, 23, 155-158.
- Kuo, M.-C.; Chien, M.; Ho, C.-T. Novel polysulfides identified in the volatile components from Welsh onions (*Allium fistulosum* L. var maichuon) and scallions (*Allium fistulosum* L. var caespitosum). *J. Agric. Food Chem.* 1990, 38, 1378-1381.
- Majlat, P.; Erdos, Z.; Takacs, J. Calculation and application of retention indices in programmed temperature gas chromatography. *J. Chromatogr.* 1974, 91, 89-110.
- Nishimura, H.; Mizutani, J. Phytochemistry and radiation chemistry of sulfur-containing amino acids. A new reaction of the 1-propenylthiyl radicals. *J. Org. Chem.* 1975, 40, 1567-1575.
- Nishimura, H.; Hanzawa, T.; Mizutani, J. Photochemistry of sulfur-containing amino acids. Formation of thiophene derivatives. *Tetrahedron Lett.* 1973, 4, 343-344.
- Ten Noever de Brauw, M. C.; Bouwman, J.; Tas, A. C.; La Vos, G. F. *Compilation of Mass Spectra of Volatile Components in Foods*; Central Institute for Nutrition and Food Research: Zeist, The Netherlands; 1983.
- Werhoff, P.; Bruning, J.; Emberger, R.; Guntert, M.; Kopsel, M.; Kuhn, W. Studies on volatile sulphur-containing flavor components in yeast extract. In *Proceedings of the 11th International Conference of Essential Oils, Fragrances and Flavors*; Bhattacharyya, S. C., Sen, N., Sothi, K. L., Eds.; Aspect Publishing: London, 1990; Vol. 4, pp 215-243.
- Whitaker, J. R. Development of flavor, odor, and pungency in onion and garlic. *Adv. Food Res.* 1976, 22, 73-13.
- Whitefield, F. B.; Last, J. H. Vegetables. In *Volatile Compounds in Foods and Beverages*; Maarse, H., Ed.; Dekker: New York, 1991; pp 203-281.
- Wijers, H. E.; Boelens, H.; Van Der Gen, A. Synthesis and some properties of 1-alkenyl alkyl disulfides and di(1-alkenyl) disulfides. *Recl. Trav. Chim. Pays-Bas* 1969, 88, 519-529.
- Zhang, Y. Thermal Generation of Food Flavors from Cysteine and Glutathione. Ph.D. Dissertation, Rutgers University, New Brunswick, NJ, 1991.

Received for review July 12, 1991. Accepted October 9, 1991.

**Registry No.** 1, 79869-58-2; 2, 925-89-3; 3, 6251-26-9; 4, 624-92-0; 5, 66-25-1; 6, 623-36-9; 7, 137363-84-9; 8, 6728-26-3; (Z)-9, 137393-33-0; (E)-10, 137363-85-0; 11, 638-02-8; 12, 638-00-6; 13, 632-15-5; 14a, 2179-60-4; 14b, 23838-18-8; 15, 23838-19-9; 16, 3658-80-8; 17, 3777-69-3; 18a, 629-19-6; 18b, 23838-20-2; 19, 23838-21-3; 20, 51647-38-2; 21, 17619-36-2; 22, 23838-24-6; 23, 23838-25-7; 24, 4413-29-0; 25, 137363-86-1; 26, 5756-24-1; cis-27, 69098-45-9; trans-28, 69098-44-8; 29, 53897-66-8; 30, 112-12-9; cis-31, 38348-25-3; 32a, 629-19-6; trans-32b, 38348-26-4; 33, 33368-79-5; 34, 115868-72-9; 35, 126898-39-3; 36, 87148-08-1; 37, 137363-87-2; 38, 123136-50-5; 39, 126876-21-9; 40, 126876-22-0; 41, 126876-23-1; 42, 37399-26-1; 43, 137363-88-3; 44, 7330-31-6; 45, 137364-00-2; 46, 126876-24-2; 47a, 126876-25-3; 47b, 126876-42-4; 49, 593-08-8; 50, 137363-89-4; 52, 52687-98-6; 53, 137363-90-7; 54, 126876-27-5; cis-55b, 137363-91-8; (Z)-55c, 137363-92-9; 56, 126876-28-6; trans-58a, 137363-93-0; 58b, 137363-94-1; (E)-59, 137363-95-2; 60, 126876-30-0; 61, 126876-31-1; 62a, 126876-25-3; 62b, 57877-72-2; 63, 126876-33-3; 64, 126876-34-4; 65, 2345-28-0; 66, 137363-96-3; 67, 137363-97-4; 69, 126876-35-5; 70, 137363-82-7; 71, 137363-82-7; cis-72, 126876-38-8; trans-73, 126876-39-9; trans-74, 137363-83-8; cis-75, 137363-98-5; 76, 137363-99-6; 77, 126876-41-3.