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Novel Polysulfides Identified in the Volatile Components from Welsh Onions (*Allium fistulosum* L. var. maichuon) and Scallions (*Allium fistulosum* L. var. caespitosum)

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Volatile components were isolated from Welsh onions (*Allium fistulosum* L. var. maichuon) and scallions (*A. fistulosum* L. var. caespitosum) by steam distillation and by dichloromethane extraction. The components of distilled oils and solvent extracts were analyzed by gas chromatography and gas chromatography-mass spectrometry (EI and CI). Sulfur-containing compounds accounted for 85% and 77% of the total volatiles in the distilled oils of Welsh onions and scallions, respectively. In addition to the sulfur compounds commonly reported in genus *Allium*, 25 novel volatile polysulfides were found in the distilled oils from both varieties of green onions. These compounds can be grouped as (a) alk(en)ylthioalkyl alk(en)yl disulfides, (b) alkyl tetra- or pentathiaalkanes or -alkene(s), and (c) thiaheterocycles. All these compounds are being reported in Welsh onions and scallions for the first time. Thermal reaction may be responsible for the formation of these volatile polysulfides.

INTRODUCTION

Onions, garlic, leeks, chives, and shallots are vegetables of the *Allium* species widely used to flavor foods. In addition to their flavoring application, medicinal properties of garlic and onions have been known for centuries. Recently, some biologically active sulfur compounds have been isolated from garlic and onions (Block et al., 1986; Bayer et al., 1989). The characteristic aromas of the *Allium* species are contributed to by the sulfur-containing volatiles. 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). It is known that the volatile components of the *Allium* genus are produced by enzymic splitting of the nonvolatile precursors, *S*-alk(en)ylcysteine sulfoxides, 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 *A. fistulosum* L. var. caespitosum (scallions), are used as vegetables or spices in many countries. They are important ingredients in Chinese cuisine (Ho et al., 1989). Kameoka et al. (1984) reported sulfides and furanones from steam volatile oils of Welsh onions and scallions. The reported sulfur-containing volatiles were only 40-48% in the neutral fraction of the total volatiles. The present study investigated the volatile components of distilled oils and solvent extracts from Welsh onions and scallions, with emphasis on the effect of heat on the formation of thermally generated polysulfides.

MATERIALS AND METHODS

Materials. Green onions were purchased from the local market. Methylene chloride was obtained from Fisher Scientific (Malvern, PA). Silica gel (60-200 mesh) was obtained from Mallinckrodt, Inc. (Paris, KY). A standard of *n*-paraffins (C₅-C₂₆) was purchased from Alltech Associates Inc. (Deerfield, IL).

Preparation of Distilled Oils and Solvent Extracts. Homogenized green onion samples were prepared by blending 1 kg of freshly cut stalks and foliage with 2 L of distilled water.

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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 solvent extracts of green onion samples were obtained by redistilled dichloromethane extraction of a freshly prepared slurry at room temperature for 12 h. The filtered methylene chloride extracts were passed through a silica gel column (60–200 mesh, 20 cm × 2 cm) to remove most of the chlorophyll. The solvent was then removed by nitrogen at ambient temperature. The concentrated CH₂Cl₂ extracts were treated with 1 mL of methanol to precipitate the wax and then filtered. The filtrate was used for GC and GC-MS analyses.

Room temperature solvent extraction was conducted for studying the effect of heat on the generation of volatiles in green onions.

GC and GC-MS Analysis. A Varian 3400 gas chromatograph equipped with an FID and a fused silica capillary column [HP-1 (100% dimethylpolysiloxane), 50 m × 0.32 mm (i.d.), *d_f* = 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 to 260 °C at 2 °C/min. Linear retention indices were calculated against C₅–C₂₆ *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, NH₃ was used as a reagent gas. The GC column was the same as described above.

RESULTS AND DISCUSSION

Sulfur-containing compounds account for 85% and 77% of the total volatiles in the distilled oils of Welsh onions and scallions, respectively. Carbonyl compounds (aldehydes, ketones, and 3-furanones) are 3.3% and 7.2% of the total volatiles of Welsh onions and scallion oils, respectively. The sulfur-containing volatiles in the neutral fraction of the distilled oils from Welsh onions and scallions were reported to be 40% and 47.5%, respectively, by Kameoka et al. (1984). Genetic and environmental factors could contribute to the quantitative variation in green onion volatiles (Freeman, 1979). The major volatiles identified in the distilled oils from Welsh onions and scallions were methyl propyl trisulfide, methyl 1-propenyl trisulfide, dipropyl disulfide, and propyl 1-propenyl disulfide, in decreasing order. The major volatile compounds identified in the CH₂Cl₂ extracts were propyl 1-propenyl disulfide, dipropyl disulfide, thiopropanal sulfoxide, and dialkyl thiosulfonates.

In addition to the sulfur compounds commonly reported in genus *Allium*, 25 novel volatile polysulfides were found in the distilled oils from both varieties of green onions. These novel volatile polysulfur compounds were either absent or of trace amounts in the solvent extracts. Shown in Figure 1 are the general chemical structures of these volatile polysulfides. The novel polysulfides shown in Figure 1 account for 16% and 5% of the total volatiles of Welsh onion and scallion oils, respectively. All these volatile compounds are being reported in Welsh onions and scallions for the first time, among which only compound 5 [1-(methylthio)propyl propyl disulfide] was reported in distilled oil from shallots (Chen and Wu, 1983). Boelens et al. (1974) also reported 1-(methylthio)propyl methyl disulfide and 1-(methylthio)propyl ethyl disulfide from heated 1-(alkylthio)-1-alkanethiols as main byproducts. The mass spectral data and retention indi-

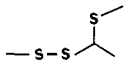
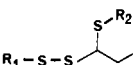


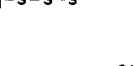
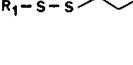
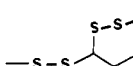
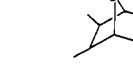
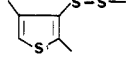
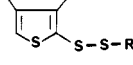
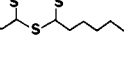
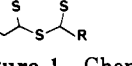
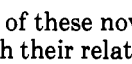
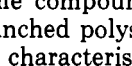
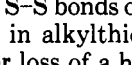
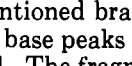

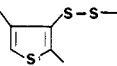
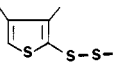
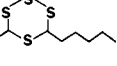
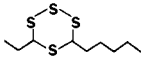
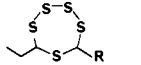
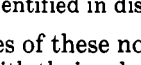
STRUCTURE	No.	SUBSTITUTION
	1	
	2	R ₁ = R ₂ = methyl
	4	R ₁ = methyl, R ₂ = propyl
	5	R ₁ = propyl, R ₂ = methyl
	6	R ₁ = methyl, R ₂ = 1-propenyl
	10	R ₁ = R ₂ = propyl
	11, 12	R ₁ = R ₂ = 1-propenyl
	13	R ₁ = 1-propenyl, R ₂ = propyl
	8a	R ₁ = R ₂ = methyl
	16	R ₁ = propyl, R ₂ = methyl
	8b	R ₁ = R ₂ = methyl
	14	R ₁ = methyl, R ₂ = propyl
	15	R ₁ = methyl, R ₂ = 1-propenyl
	19	R ₁ = R ₂ = propyl
	20, 21	R ₁ = 1-propenyl, R ₂ = propyl
	18	
	3	
	7	
	9	R = methyl
	17	R = propyl
	22, 23	
	24	R = ethyl
	25	R = pentyl

Figure 1. Chemical structures of novel volatile polysulfides identified in distilled oils from Welsh onions and scallions.

ces of these novel polysulfides are listed in Table I along with their relative percentages in the oils of Welsh onions and scallions. Representative fragmentation patterns of some compounds are shown in Figure 2. For all the branched polysulfides (1, 2, 4–6, 8a, 8b, 10–16, 18–21), the characteristic fragmentation resulted from the same cleavages b of compound 14 in Figure 2. Cleavages at the S–S bonds of the disulfide or trisulfide backbone resulting in alkylthio groups are also general patterns. Further loss of a hydrogen molecule from the alkylthio ions generated may also occur for some of the above-mentioned branched polysulfides. For compounds 7, 9, 17, base peaks were obtained by loss of an alkylthio radical. The fragmentation for compounds 3 and 22–25 can be characterized by cleavage of the ring structure and rearrangement of the fragments. Compounds 11, 12, and 22–25 have geometrical isomers. However, the exact configurations of these compounds have not been determined.

Figure 3 shows the possible mechanism for the formation of some volatile compounds shown in Figure 1. The disulfide bonds of propyl 1-propenyl disulfide can be

Table I. Volatile Polysulfides of Distilled Oils from Welsh Onions (*A. fistulosum* L. var. *maichuon*) and Scallions (*A. fistulosum* L. var. *caespitosum*)

no. ^a	compd	<i>I</i> _k (HP-1)	mass spectral data ^b	GC area, ^c %	
				A ^d	B ^d
1	1-(methylthio)ethyl methyl disulfide	1145	79 (6), 77 (4), 76 (4), 75 (100), 60 (6), 59 (18), 58 (4), 49 (9), 47 (19), 41 (15)	0.27	0.23
2	1-(methylthio)propyl methyl disulfide	1235	89 (93), 79 (11), 73 (11), 61 (31), 49 (12), 47 (17), 46 (9), 45 (34), 41 (100), 39 (12)	6.07	0.85
3	5,6-dimethyl-2,3,7-trithiabicyclo[2.2.1]-heptane	1346	178 (63), 122 (49), 113 (89), 99 (100), 79 (33), 67 (37), 58 (35), 45 (86), 41 (83), 39 (71)	0.23	0.12
4	1-(propylthio)propyl methyl disulfide	1395	117 (96), 79 (10), 75 (89), 73 (19), 47 (39), 46 (9), 45 (38), 43 (81), 41 (100), 39 (18)	0.70	0.21
5	1-(methylthio)propyl propyl disulfide	1397	121 (1), 107 (1), 89 (100), 73 (10), 61 (22), 49 (6), 47 (12), 45 (18), 43 (11), 41 (71)	1.06	0.27
6	1-(1-propenylthio)propyl methyl disulfide	1407	121 (1), 115 (83), 89 (71), 81 (31), 79 (24), 73 (60), 61 (28), 59 (33), 45 (100), 41 (89), 39 (36)	0.76	0.43
7	methyl 2,4-dimethyl-3-thienyl disulfide	1440	190 (33), 143 (56), 142 (39), 111 (18), 99 (23), 73 (35), 71 (20), 59 (43), 45 (100), 39 (34)	0.02	0.02
8a	5-ethyl-2,3,4,6-tetrathiaheptane	1452	89 (100), 79 (9), 73 (6), 64 (4), 61 (20), 49 (6), 47 (13), 45 (21), 41 (56), 39 (6)	1.26	0.35
8b	4-ethyl-2,3,5,6-tetrathiaheptane	1452	121 (69), 79 (66), 73 (100), 47 (21), 46 (14), 45 (70), 41 (43)	1.28	0.33
9	methyl 3,4-dimethyl-2-thienyl disulfide	1460	190 (56), 143 (100), 111 (14), 99 (46), 67 (15), 65 (19), 59 (19), 45 (87), 41 (17), 39 (30)	0.11	0.08
10	1-(propylthio)propyl propyl disulfide	1557	150 (2), 128 (5), 118 (6), 117 (91), 77 (3), 75 (63), 61 (4), 47 (25), 43 (66), 42 (7), 41 (100)	0.33	0.86
11	6-ethyl-4,5,7-trithia-2,8-decadiene	1573	115 (100), 81 (43), 74 (10), 73 (54), 61 (11), 59 (23), 47 (9), 45 (36), 41 (33), 39 (16)	0.42	0.49
12	6-ethyl-4,5,7-trithia-2,8-decadiene	1584	115 (95), 105 (13), 81 (41), 74 (17), 73 (44), 61 (22), 59 (43), 47 (21), 45 (100), 41 (66)	0.12	0.31
13	1-(propylthio)propyl 1-propenyl disulfide	1603	117 (100), 75 (68), 74 (20), 73 (29), 47 (40), 46 (17), 45 (51), 43 (87), 41 (99), 39 (24)	0.24	0.04
14	4-ethyl-2,3,5,6-tetrathianonane	1616	149 (26), 121 (15), 107 (4), 79 (18), 75 (3), 73 (100), 47 (10), 45 (28), 43 (34), 41 (36)	0.76	0.28
15	4-ethyl-2,3,5,6-tetrathia-7-nonene	1620	147 (48), 121 (23), 105 (45), 79 (28), 73 (99), 61 (18), 47 (21), 45 (100), 41 (60), 39 (35)	0.16	0.17
16	3-ethyl-2,4,5,6-tetrathianonane	1627	89 (100), 79 (11), 74 (9), 73 (23), 61 (17), 47 (15), 45 (33), 43 (16), 41 (68), 39 (15)	0.79	<i>e</i>
17	propyl 3,4-dimethyl-2-thienyl disulfide	1635	144 (17), 143 (100), 142 (14), 112 (43), 111 (37), 99 (33), 97 (14), 67 (14), 65 (20), 43 (39)	0.25	0.17
18	4-ethyl-2,3,5,6,7-pentathiaoctane	1679	153 (37), 121 (30), 111 (29), 105 (24), 79 (58), 74 (29), 73 (78), 47 (43), 45 (100), 41 (60)	0.26	0.08
19	6-ethyl-4,5,7,8-tetrathiaundecane	1772	149 (30), 117 (12), 107 (7), 75 (21), 73 (100), 47 (13), 45 (29), 43 (81), 41 (63), 39 (18)	0.25	0.11
20	6-ethyl-4,5,7,8-tetrathia- <i>trans</i> -2-undecene	1779	149 (25), 147 (22), 105 (41), 75 (11), 73 (94), 71 (11), 47 (20), 45 (83), 43 (59), 41 (100)	0.07	0.01
21	6-ethyl-4,5,7,8-tetrathia- <i>cis</i> -2-undecene	1784	149 (26), 147 (24), 105 (47), 75 (12), 73 (100), 71 (11), 45 (83), 43 (50), 41 (97)	0.06	<i>e</i>
22	4-pentyl-6-ethyl-1,2,3,5-tetrathiane	1791	180 (20), 116 (23), 115 (38), 106 (25), 83 (15), 74 (57), 73 (29), 45 (67), 41 (100), 39 (31)	0.02	0.02
23	4-pentyl-6-ethyl-1,2,3,5-tetrathiane	1818	149 (21), 116 (15), 115 (23), 106 (19), 74 (36), 73 (100), 45 (31), 43 (85), 41 (89), 39 (26)	0.02	0.02
24	5,7-diethyl-1,2,3,4,6-pentathiepane	1822	180 (11), 170 (14), 106 (41), 74 (43), 73 (30), 47 (15), 46 (19), 45 (62), 41 (100), 39 (28)	0.11	<i>e</i>
25	5-pentyl-7-ethyl-1,2,3,4,6-pentathiepane	1923	138 (16), 74 (70), 73 (47), 59 (20), 58 (12), 47 (15), 46 (26), 45 (78), 41 (100), 39 (32)	0.02	0.04

^a Numbers refer to Figure 1. ^b *m/z* in decreasing values with intensity in parentheses. ^c Average of two experiments. ^d A, Welsh onions. B, scallions. ^e Not detected.

cleaved to produce propenylthio radicals. The radical then attaches to the double bond of another molecule of alkyl propenyl disulfide. The addition to the double bond can be at either C₁ or C₂ of the propenyl group. The adduct can either obtain a hydrogen atom to form branched polysulfides (I or II) or undergo ring closure. Loss of a hydrogen molecule and a hydrogen atom can give alkyl 3,4-dimethyl-2-thienyl disulfide or alkyl 2,4-dimethyl-3-thienyl disulfides. Loss of an alkylthio radical and hydrogen sulfide from the cyclized compounds may form 3,4- or 2,4-dimethylthiophenes. Both 2,4- and 3,4-dimethylthiophenes were observed in Welsh onion and scallion oils, with the latter 3–7 times more than the former. On the other hand, only trace amounts of dimethylthiophenes were detected in the methylene chloride extracts of both varieties. If the propenylthio radical attacks at the C₂ of the propenyl group, it then ends up with for-

mation of branched polysulfides (II) or 2,4-dimethylthiophene and alkyl 2,4-dimethyl-3-thienyl disulfides. On the other hand, the radical can attack the C₁ position to form branched polysulfides (I) or 3,4-dimethylthiophene and alkyl 3,4-dimethyl-2-thienyl disulfides. When R is a methyl group, we did observe the presence of two isomers of methyl dimethylthienyl disulfide with the methyl 3,4-dimethyl-2-thienyl disulfide predominating. However, when R is a propyl group, only propyl 3,4-dimethyl-2-thienyl disulfide was detected. With the observation of only the type I branched polysulfides in green onions, we think that the addition of the propenylthio radical to the C₁ position is more favored. In addition, the amount of branched polysulfides was more than that of dimethylthiophenes and alkyl dimethylthienyl disulfides in Welsh onions and scallion oils. In the solvent extracts, the result was the opposite. Therefore, when

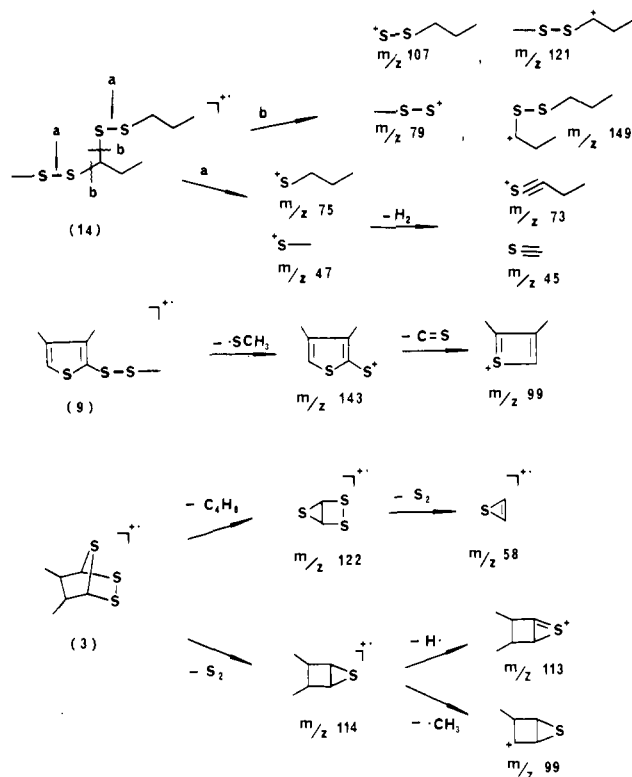


Figure 2. Mass fragmentation pathways of some volatile polysulfides.

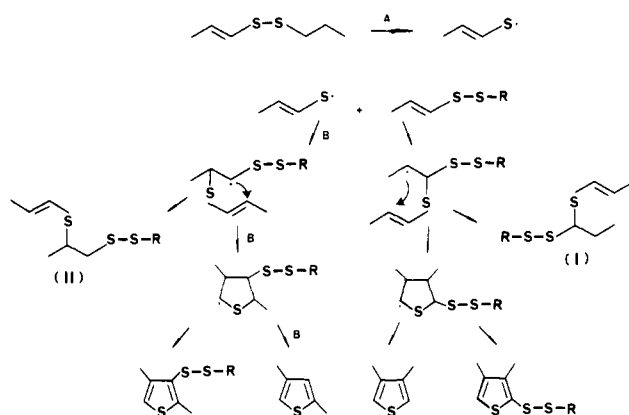


Figure 3. Proposed mechanism for the formation of some volatile polysulfides in distilled oils of Welsh onions and scallions.

thermal energy is concerned, the reaction toward ring closure is more favored than reaction toward formation of branched polysulfides. Boelens and Brandsma (1972) have proposed a free-radical mechanism for the formation of 2,4-dimethylthiophene. Reaction route B in Figure 3 was proposed by Boelens and Brandsma (1972) for the formation of 2,4-dimethylthiophene when alkyl 1-propenyl disulfide was heated at 150 °C for 8–16 h. However, they did not report the presence of alkyl 2,4-dimethyl-3-thienyl disulfide. They have also proposed a different mechanism for the formation of 3,4-dimethylthiophene. However, we believe the mechanism we proposed is more likely. Compound 3 (5,6-dimethyl-2,3,7-trithiacyclo[2.2.1]heptane) shown in Figure 1 has a structure similar 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).

The sulfur chemistry of genus *Allium* is rather complicated. The exact mechanism for the formation of these novel polysulfides is not known. Thermal reaction may play an important role in the formation of these compounds because most of the branched polysulfides were absent in the volatiles of solvent extracts.

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