# Volatile Constituents of the Solvent Extracts of Welsh Onions (*Allium fistulosum* L. Variety Maichuon) and Scallions (*A. fistulosum* L. Variety Caespitosum)

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Volatile components were isolated from Welsh onions and scallions by solvent extraction at ambient temperatures and analyzed by GC and GC-MS. There were 67 volatile components identified, including 12 novel polysulfides. Methyl methanethiosulfinate and 10 dialk(en)yl thiosulfonates were among those volatiles in Welsh onion and scallion extracts. These thiosulfinates and thiosulfonates were not previously identified in their distilled oils, probably due to their instability to heat.

## INTRODUCTION

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 and are commonly used in Chinese cuisine.

Recently, we reported the volatile constituents of the distilled oils of Welsh onions and scallions (Kuo and Ho, 1992). In addition to the sulfur compounds commonly reported in the genus *Allium* 41 novel volatile sulfurcontaining compounds were found in the distilled oils of Welsh onions and scallions. The novel compounds can be grouped as (1) 1-[alk(en)ylthio]alkyl alk(en)yl disulfides, (2) alkyl tetra- or pentathiaalkanes or -alkenes, and (3) thiaheterocycles. The purpose of this study was to investigate the volatile components of Welsh onions and scallions obtained by solvent extraction at ambient temperatures. It will be interesting to see whether those novel sulfur-containing volatiles identified in distilled oils can also be found in the solvent extracts.

### EXPERIMENTAL PROCEDURES

Materials. Welsh onions and scallions were purchased fresh from the local market. A standard of *n*-paraffins  $(C_5-C_{26})$  was purchased from Alltech Associates, Inc. (Deerfield, IL). cis- and trans-methyl 1-propenyl disulfides, syn- and anti-2-mercapto-3.4-dimethyl-2.3-dihydrothiophenes, cis- and trans-propyl 1-propenyl disulfides, dipropyl disulfide, syn- and anti-3,5-diethyl-1,2,4-trithiolanes, 6-ethyl-4,5,7-trithia-2,8-decadiene, methyl methanethiosulfonate, cis- and trans-1-propenyl methanethiosulfonates, methyl 1-propenethiosulfonate, propyl propanethiosulfonate, propyl 1-propenethiosulfonate, and 1-propenyl propanethiosulfonate were kindly 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 Solvent Extracts from Welsh Onions and Scallions. The solvent extracts of Welsh onions and scallions were obtained by glass-redistilled methylene chloride extraction of a freshly prepared slurry. The slurry was prepared by blending 500 g of samples with 500 mL of distilled water; 1000 mL of solvent was added to the slurry. The mixture was then stirred at room temperature for 12 h. The filtered methylene chloride extracts were dehydrated with Na<sub>2</sub>SO<sub>4</sub> and then passed through a silica gel column (60–200 mesh, 20 cm  $\times$  2 cm, Mallinckrodt, Inc., Paris, KY) to remove most of the chlorophyll. The solvent was then removed by nitrogen at ambient temperature to a final concentration of  $0.2 \,\text{mL}$ . The concentrated  $CH_2Cl_2$  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.

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  $\times$  0.32 mm (i.d.),  $d_{\rm f}$ =  $1.05 \,\mu$ m; Hewlett-Packard Co.) was used to analyze the isolated volatiles. Volatile concentrate  $(0.4 \,\mu\text{L})$  was injected with a 1:100 split ratio. 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 retention indices were calculated against  $C_5-C_{26}$  *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 and 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.

#### RESULTS AND DISCUSSION

In a previous paper, we reported the volatile components in the distilled oils from Welsh onions and scallions (Kuo and Ho, 1992). This study investigated the volatile compounds of solvent extracts from Welsh onions and scallions. The solvent extracts were obtained by glassredistilled methylene chloride extraction of a freshly prepared Welsh onion and scallion slurry kept at room temperature for 12 h. After the removal of excess solvents, the concentrated extracts 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 stationary phases (dimethyl polysiloxane) 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 in the solvent extracts of Welsh onions and scallions 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 the mass spectra. Table II lists the mass spectral data of some sulfurcontaining compounds identified in the present study.

## Table I. Volatile Compounds of the Solvent Extracts from Welsh Onions and Scallions

|             |   |                 | GC ar          | ea," % |                     |
|-------------|---|-----------------|----------------|--------|---------------------|
| peak no.    | compound  | retention index | A              | В      | ID                  |
|             |   |                 | 0.45           |        |                     |
| 1           |   |                 | 0.40           | 0.44   | GC, MS <sup>e</sup> |
| 2           | 1-propenetnioi<br>mothyl gylfhydryl gylfide                     | 696             | 20.20          | 0.10   | MS /                |
| 3           | methyl sunnyu yr sunnue<br>methyl sie-1-propenyl sulfide        | 716             |                | 20.78  | MS                  |
| 5           | methyl trans-1-propenyl sulfide <sup>c</sup>                    | 726             | _              | 0.01   | MS                  |
| 6           | dimethyl disulfide  | 731             | 0.04           | 0.01   | GC MS               |
| ž           | thiopropanal sulfoxide <sup>c</sup>                             | 740             | 4.87           | 1.83   | MS-18               |
| 8           | hexanal   | 778             | 0.04           | 0.26   | GC. MS              |
| 9           | 2.4-pentanedione <sup>c</sup>                                   | 795             | -              | 0.04   | MS                  |
| 10          | 2-methyl-2-pentenal   | 810             | 8.95           | 2.33   | GC. MS              |
| 11          | 2-hexenal <sup>c</sup>  | 839             | t <sup>h</sup> | 0.64   | MS                  |
| 12          | propyl 1-propenyl sulfide <sup>c</sup>                          |                 | 0.16           | _      | GC, MS              |
| 13          | 2,4-dimethylthiophene   | 880             | 0.13           | 0.15   | MS                  |
| 14          | 3,4-dimethylthiophene   | 898             | 0.74           | 0.10   | GC, MS              |
| 15          | di(1-propenyl) sulfide <sup>c</sup>                             | 904             | -              | 0.04   | MS                  |
| 16          | di(1-propenyl) sulfide <sup>c</sup>                             | 907             | 0.09           | 0.02   | MS                  |
| 17 <b>a</b> | methyl propyl disulfide   | 915             | 0.78           | 0.59   | MS                  |
| 17b         | methyl cis-1-propenyl disulfide                                 |                 |                |        | GC, MS              |
| 18          | methyl trans-1-propenyl disulfide                               | 922             | 0.43           | 0.60   | GC, MS              |
| 19          | methyl methanethiosulfinate <sup>c</sup>                        | 934             | 0.75           | 0.04   | MS-I                |
| 20          | dimethyl trisulfide   | 949             | 0.28           | 0.17   | MS                  |
| 21          | 2-pentylfuran   | 982             | t              | 0.02   | GC, MS              |
| 22          | methyl methanethiosulfonate                                     | 1009            | 0.14           | 0.04   | MS-I                |
| 23a         | dipropyl disulfide  | 1094            | 0.47           | 8.81   | GC, MS              |
| 23b         | propyl cis-1-propenyl disulfide                                 |                 |                |        | GC, MS              |
| 24          | propyl trans-1-propenyl disulfide                               | 1100            | 0.2            | 3.96   | GC, MS              |
| 25          | 3,4-dimethyl-2,5-dioxo-2,5-dinydrothiophene                     | 1104            | 1.38           | 0.08   | MS-I                |
| 26          | syn-2-mercapto-3,4-dimethyl-2,3-dinydrothiophene <sup>4,4</sup> | 1106            | 0.07           | 0.19   | GC, MS              |
| 27          | 3-metnyl-1,2,4-tritniolane                                      | 1121            | t<br>0.01      | 0.17   | MS                  |
| 20          | methyl propyl trisulfide  | 1134            | 0.91           | 0.28   | MS                  |
| 29          | methyl trans 1 propenyl trisulfide                              | 1145            | 0.11           | 0.30   | MS<br>MS            |
| 31          | anti-2-mercento-3 4-dimethyl-2 3-dihydrothionbene               | 1140            | 1.32           | 0.56   | CC MS               |
| 30          | nanhthalana <sup>c</sup>  | 1160            |                | 0.74   | GC, MS              |
| 33          | nronyl methanethiosulfonete                                     | 1175            | 0.49           | 0.20   | MS-I                |
| 34          | 1-property methanethiosulfonate                                 | 1179            | t.             | 0.00   | MS-I<br>MS-I        |
| 35          | dimethyl tetrasulfide   | 1186            | 0.36           | 0.54   | MS                  |
| 36          | methyl propanethiosulfonate                                     | 1188            | 0.08           | 0.95   | MS-I                |
| 37          | methyl 1-propenethiosulfonate                                   | 1220            | _              | 3.32   | MS-I                |
| 38          | 1-(methylthio)propyl methyl disulfide                           | 1241            | -              | 0.03   | MS                  |
| 39          | syn-3,5-diethyl-1,2,4-trithiolane                               | 1306            | 0.40           | -      | GC, MS              |
| 40a         | dipropyl trisulfide   | 1313            | 1.81           | 0.79   | GC, MS              |
| 40b         | anti-3,5-diethyl-1,2,4-trithiolane                              |                 |                |        | GC, MS              |
| 41          | propyl 1-propenyl trisulfide                                    | 1320            | 4.03           | 0.10   | MS                  |
| 42          | di(1-propenyl) trisulfide <sup>c</sup>                          | 1324            | 0.67           | 0.67   | MS                  |
| 43          | di(1-propenyl) trisulfide <sup>c</sup>                          | 1327            | 0.06           | 0.40   | MS                  |
| 44          | propyl propanethiosulfonate                                     | 1348            | 1.14           | 0.42   | MS-I                |
| 45          | 1-propenyl propanethiosulfonate <sup>c</sup>                    | 1356            | 0.41           | 0.57   | MS-I                |
| 46          | 3-ethyl-5-vinyl-1,2,4-trithiolane <sup>c,d</sup>                | 1366            | -              | 0.03   | MS-I                |
| 47          | methyl propyl tetrasulfide                                      | 1375            | 0.41           | 0.04   | MS                  |
| 48          | propyl cis-1-propenethiosulfonate                               | 1381            | 0.10           | 1.24   | MS-I                |
| 498         | propyl trans-1-propenethiosulfonate                             | 1383            | 0.81           | 0.57   | MS-I                |
| 49D         | 1-propenyl 1-propenetniosulionate                               | 1.405           | -              | t      | MS-1                |
| 50          |   | 1425            | -              | 0.40   | MS                  |
| 508<br>51   | 4-etnyi-2,3,5,5-tetratnianeptane                                | 1462            | 0.02           | 0.14   | MS NO               |
| 50          | dinaonyl totacylfide  | 1470            | 2.40           | 0.17   | GC, MS              |
| 53          | 4 fediethyl 1 2 3 5-tetrathiana                                 | 1000            | 2.00           | 0.10   | IVIO<br>MS          |
| 54          |   | 15/2            | 0.28           | 0.20   | MS-T                |
| 55          | 6-ethyl-4 5 7-trithig-9 8-decediene                             | 1600            | 0.28           | 0.17   | MS-1<br>MS          |
| 56          | 5-methyl-2-octyl-2H-furan-3-one                                 | 1691            | -              | 0.03   | MS                  |
| 57          | 1-propenyl dimethylthienyl disulfide <sup>c,d</sup>             | 1643            | 0.01           | 0.08   | MS.I                |
| 58          | propyl dimethylthienyl disulfide                                | 1648            | 0.91           | 0.00   | MS                  |
| 59          | 1-propenyl dimethylthienyl disulfide <sup>c,d</sup>             | 1653            | -              | 0.18   | MS-I                |
| 60          | 6-ethyl-4.5.7.8-tetrathianonane <sup>c,d</sup>                  | 1685            | 0.02           | 0.01   | MS-I                |
| 61          | 6-ethyl-4,5,7,8-tetrathia-2-nonene <sup>c,d</sup>               |                 | 0.01           | 0.02   | MS-I                |
|             |   |                 |                |        | -                   |

<sup>a</sup> Average of two experiments. A, Welsh onions; B, scallions. <sup>b</sup> Not detected. <sup>c</sup> Volatiles not detected in distilled oils reported previously (Kuo and Ho, 1992). <sup>d</sup> Sulfur-containing volatile compounds newly found in food. <sup>e</sup> GC, MS indicates the identification by retention index and mass spectrum. <sup>f</sup> MS indicates the identification by mass spectrum only. <sup>g</sup> MS-I indicates mass spectral interpretation was used for structure assignment. <sup>h</sup> trace (less than 0.01%).

The most abundant volatile of Welsh onion extract was 1-propenethiol (2) (20.26%), followed by 2-methyl-2-pentenal (10) (8.95%). The most abundant volatile of scallion extract was methyl sulfhydryl sulfide (3) (26.78%), fol-

lowed by dipropyl disulfide (23a) (8.81%). Both qualitative and quantitative differences were observed among volatiles from Welsh onion and scallion extracts and distilled oils. Most of the novel branched polysulfides

| Table II.  | EI Mass Spectral | Data of Some Vo | olatile Sulfur-Containing | Compounds in t | the Solvent Extr | acts of Welsh ( | )nions |
|------------|------------------|-----------------|---------------------------|----------------|------------------|-----------------|--------|
| and Scalli | ons              |                 |                           |                |                  |                 |        |

| no.ª     | compound   | MW  | mass spectral data <sup>b</sup>   |
|----------|--|-----|---|
| 7        | thiopropanal sulfoxide   | 90  | 41 (100), 39 (47), 90 (26), 42 (30), 45 (22), 43 (14), 48 (10)  |
| 19       | $\sim s \rightarrow 0$<br>methyl methanethiosulfinate<br>$\sim s^{-s}$   | 110 | 47 (100), 64 (87), 45 (85), 46 (36), 110 (30), 63 (30), 95 (20)   |
| 22       | o<br>methyl methanethiosulfonate   | 126 | 47 (100), 45 (72), 63 (56), 81 (54), 79 (39), 44 (38), 64 (28),<br>126 (28)   |
| 25       | )<br>3,4-dimethyl-2,5-dioxo-2,5-dihydrothiophene   | 142 | 39 (100), 54 (64), 45 (63), 142 (43), 53 (30), 14 (18), 41 (19),<br>71 (15)   |
| 33       | orgonomic of the second   | 154 | 41 (100), 74 (68), 43 (46), 47 (41), 75 (33), 79 (31), 45 (31),<br>39 (25), 42 (21), 63 (18), 81 (15), 154 (11), 113 (7), 125 (5) |
| 34       | 1-propenyl methanethiosulfonate  | 152 | 45 (100), 72 (40), 73 (31), 39 (23), 71 (9), 152 (5), 119 (4),<br>89 (3)  |
| 36       | $ \frac{1}{2} $ methyl propanethiosulfonate $ \frac{1}{2} 1$ | 154 | 43 (100), 41 (71), 48 (66), 45 (40), 39 (27), 47 (23), 49 (17),<br>42 (17), 75 (8), 61 (8), 90 (7), 128 (4), 154 (3)              |
| 37       | methyl 1-propenethiosulfonate  | 152 | 41 (100), 39 (71), 45 (29), 105 (19), 47 (19), 73 (16), 88 (15),<br>152 (5)   |
| 44       | propyl propanethiosulfonate  | 182 | 41 (100), 74 (69), 45 (50), 39 (49), 105 (13), 47 (13), 43 (13),<br>116 (12)  |
| 45       | 1-propenyl propanethiosulfonate  | 180 | 43 (100), 41 (91), 45 (75), 74 (63), 39 (40), 73 (29), 72 (28),<br>58 (7), 180 (6), 89 (6)  |
| 46       | 3-ethyl-5-vinyl-1,2,4-trithiolane  | 178 | 59 (100), 45 (99), 41 (86), 72 (78), 178 (59), 104 (53), 71 (50),<br>39 (44)  |
| 48 + 49a | propyl 1-propenethiosulfonate  | 180 | 41 (100), 39 (47), 74 (26), 43 (25), 105 (23), 47 (16), 42 (12),<br>75 (12), 107 (7), 180 (3)                                     |
| 49b      | 1-propenyl 1-propenethiosulfonate  | 178 | 41 (100), 45 (91), 39 (71), 43 (25), 47 (21), 105 (20), 73 (19),<br>93 (16), 72 (14), 89 (13), 178 (5)                            |

Table II. (Continued)

| no.ª | compound                                    | MW  | mass spectral data <sup>b</sup>  |
|------|---|-----|--|
| 54   | 1-(1-propenylthio)propyl propyl disulfide   | 222 | 45 (100), 115 (86), 41 (55), 73 (45), 59 (38), 81 (35), 39 (33),<br>61 (20), 47 (18), 105 (13) |
| 57   | 1-propenyl dimethylthienyl disulfide        | 216 | 143 (100), 45 (64), 99 (26), 216 (21), 39 (22), 144 (13), 65 (12),<br>129 (3)                  |
| 59   | 1-propenyl dimethylthienyl disulfide        | 216 | 143 (100), 45 (89), 39 (33), 99 (30), 41 (26), 216 (19), 152 (19),<br>59 (16)                  |
| 60   | 6-ethyl-4,5,7,8-tetrathianonane<br>$s^{-s}$ | 228 | 73 (100), 41 (41), 43 (39), 45 (22), 149 (16), 39 (12), 121 (11),<br>79 (9), 107 (5)           |
| 61   | 6-ethyl-4,5,7,8-tetrathia-2-nonene          | 226 | 45 (100), 105 (85), 41 (83), 43 (52), 73 (48), 39 (44), 147 (37),<br>61 (25), 74 (24), 226 (1) |

<sup>a</sup> Numbers refer to Table I. <sup>b</sup> m/z in decreasing values with intensity in parentheses.

identified in the distilled oils of Welsh onions and scallions were not detected in the solvent extracts. The significant differences were attributed to the thermally induced disulfide interchange (RSSR + R'SSR'  $\rightarrow$  2 RSSR') and disproportionation involved in sulfur volatiles of Welsh onions and scallions.

Including 7 novel sulfur-containing compounds reported in Table I, there were 30 components which exist only in the solvent extracts of Welsh onions and scallions. Including 5 novel sulfur-containing compounds, 37 of the 67 components listed in Table I were also identified in the distilled oils of Welsh onions and scallions (Kuo and Ho, 1992). The volatile sulfur-containing components identified only in the solvent extracts were thiopropanal sulfoxide, monosulfides, an isomer of di(1-propenyl) trisulfide, a thiosulfinate, thiosulfonates, and four novel sulfur-containing heterocyclics.

(A) Monosulfides and Trisulfides. Five dialkyl monosulfides were found in the solvent extracts of Welsh onions and scallions. Those monosulfides are methyl *cis*and *trans*-1-propenyl sulfides, propyl 1-propenyl sulfide, and two isomers of di(1-propenyl) sulfide. They are considered minor components of the volatiles of Welsh onion and scallion solvent extracts.

Three isomers of di(1-propenyl) trisulfides (41b, 42, 43) were identified in the Welsh onion and scallion extracts, and one of the isomers also occurred in the distilled oils of Welsh onions and scallions as described above. A tentative identification of three isomers of di(1-propenyl) disulfide was reported in onion oil by Boelens et al. (1971). The presence of di(1-propenyl) trisulfide, however, was not previously reported in *Allium*. Because of the presence of S-1-propenylcysteine sulfoxide, the theoretical presence of di(1-propenyl) disulfides in cut *Allium* plants is unquestionable.

(B) Thiopropanal Sulfoxide. Thiopropanal sulfoxide is a rather unstable compound. The presence of relatively high amounts of the onion lachrymatory factor (LF) of onions, thiopropanal sulfoxide, in the extracts of Welsh onions and scallions is therefore quite interesting. The amounts of LF, determined by the GC area percent in Welsh onions and scallions, were 4.87 and 1.83%; respectively. The EI-MS spectral data of thiopropanal sulfoxide are listed in Table II. The identification was achieved by comparing the mass spectrum with that reported by Brodnitz and Pascale (1971). The instability of the LF made identification difficult until the study by Brodnitz and Pascale (1971). They used GC to isolate the active LF, isolated from onions, and proved the structure by physical methods allied to chemical synthesis. According to Block et al. (1980), the LF of onion was found to possess a 19:1 mixture of Z and E configurations and to undergo a facile self-condensation. The thermally labile nature of LF makes its absence in Welsh onion and scallion distilled oils reasonable.

(C) Thiosulfinate and Thiosulfonates. (a) Thiosulfinate. Methyl methanethiosulfinate (19) was the only thiosulfinate found in Welsh onion and scallion extracts. It was reported to possess an unpleasant cabbage-like odor (Freeman and Whenham, 1975).

Alk(en)yl thiosulfinates are the transformation products of S-alk(en)yl-L-cysteine sulfoxide under the action of the enzyme aliinase. Thiosulfinates are pungent-smelling, thermal labile compounds which may undergo thermal disproportionation to form disulfides and thiosulfonates (Block et al., 1975; Fenwick and Hanley, 1985). It is not surprising that methyl methanethiosulfinate was not identified in the distilled oils but in solvent extracts.

(b) Thiosulfonates. Ten dialk(en)yl thiosulfonates were identified in extracts of Welsh onions and scallions. Their mass spectral data are listed in Table II. The identification of methyl methanethiosulfonate (22), propyl methanethiosulfonate (33), 1-propenyl methanethiosulfonate (34), methyl 1-propenethiosulfonate (37), propyl propanethiosulfonate (44), 1-propenyl propanethiosulfonate (45), and propyl 1-propenethiosulfonates (48, 49a) was based on mass spectra of synthesized authentic compounds provided by Dr. Eric Block or on the mass spectral data published by Boelens et al. (1971). The structural determination of thiosulfonates 36 and 49b was based on interpretation of mass fragments; therefore, they are considered tentatively identified.

Propyl propanethiosulfonate (44) and propyl 1-propenethiosulfonate (49a) are the two most abundant thiosulfonates detected in the Welsh onion extract. Among those thiosulfonates identified in scallion extract, the most abundant was methyl 1-propenethiosulfonate (37) (3.32%), followed by propyl 1-propenethiosulfonate (48) (1.24%). Although a trace component in scallion extract, the occurrence of 1-propenyl 1-propenethiosulfonate is rather interesting. In spite of the presence of 1-propenyl-L-cysteine sulfoxide in Allium plants being confirmed, the occurrence of di(1-propenyl) thiosulfinate and its products was once questioned (Fenwick and Hanley, 1985).

(D) Novel Sulfur-Containing Cyclics and Acyclics. Several novel volatile components were identified in the solvent extracts; some of them were also found in the distilled oils.

(a) Dihydrothiophenes. 3,4-Dimethyl-2,5-dioxo-2,5dihydrothiophene (25) was previously reported in freshly cut onion (Allium cepa) and leek (Allium porum) by Albrand et al. (1980) and Tokaska and Karwaska (1981). It was reported to have a smell like hydrogen sulfide and an odor threshold in water of 7 ppb (Albrand et al., 1980). The formation mechanism for this dihydrothiophene is not clear.

A similar component, namely 3,4-dimethyl-2,5-dihydrothiophen-2-one, was detected in onion oil (Boelens et al., 1971).

Block and Zhao (1990) first reported the formation of syn- and anti-2-mercapto-3,4-dimethyl-2,3-dihydrothiophene from pyrolysis of di(1-propenyl) disulfide. Subsequently, we reported the presence of anti-2-mercapto-3,4-dimethyl-2,3-dihydrothiophene in the distilled oils of Welsh onions and scallions (Kuo and Ho, 1992). Both syn- and anti-2-mercapto-3,4-dimethyl-2,3-dihydrothiophenes (26, 31) were identified in the solvent extracts of Welsh onions and scallions. For both Welsh onions and scallions, the amounts of anti isomers were higher than those of syn isomers.

(b) Trithiolane. In addition to syn- and anti-3,5-diethyl-1,2,4-trithiolanes which have been reported in the distilled oils of Welsh onions and scallions, 3-ethyl-5-vinyl-1,2,4trithiolane (46) was identified as a novel volatile in the extracts of scallion. The mass spectral data of compound 46 are listed in Table II.

Cyclic compounds containing four or more sulfur atoms such as 4,6-diethyl-1,2,3,5-tetrathianes and 5,7-diethyl-1,2,3,4,6-pentathiepanes identified in distilled oils of Welsh onions and scallions (Kuo and Ho, 1992) do not occur in the solvent extracts. Exposure of sulfur constituents in Welsh onions and scallions to heat during distillation should be responsible for the formation of these cyclic polysulfides in distilled oils of Welsh onions and scallions.

(c) Dimethylthienyl Disulfides. Four alk(en)yl dimethylthienyl disulfides were detected in solvent extracts of Welsh onions and scallions. Among them, methyl dimethylthienyl disulfide (50) and propyl dimethylthienyl disulfide (58) were also identified in the distilled oils of Welsh onions and scallions (Kuo and Ho, 1992). 1-Propenyl dimethylthienyl disulfides (57, 59) were only found in the solvent extracts. These novel volatile components were not previously reported in food flavors. Compounds 57 and 59 can either be positional or geometrical isomers.

(d) Branched Polysulfides. There were 21 branched polysulfides identified in distilled oils of Welsh onions and scallions, and only 6 of these compounds were detected in extracts of Welsh onions and scallions. Three of the six branched polysulfides detected in solvent extracts were newly identified components. They are 1-propenylthiopropyl propyl disulfide (54), 6-ethyl-4,5,7,8-tetrathianonane (60), and 6-ethyl-4,5,7,8-tetrathia-2-nonene (61).

The three new branched polysulfides identified in extracts of Welsh onions and scallions were not previously reported in *Allium* as volatile compounds. Also, these compounds were not previously reported in food flavors. ACKNOWLEDGMENT

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