# Volatile Flavor Compounds from Onion

Mans Boelens,* Pieter J. de Valois, Henk J. Wobben, and Arne van der Gen

The flavor complex from onion (*Allium cepa* L.) was studied by a combination of gas chromatographic and mass spectrometric techniques. The identification of 45 flavor constituents of steam-distilled onion oil will be described. Several oxygen compounds, thiols, thiophenes, monosulfides, disulfides, trisulfides, and a tetrasulfide have not been reported previously. The decomposition of alkyl propenyl disulfides in onion oil and the formation of dimethylthiophenes have been investigated. Headspace analysis of cut, boiled, and fried onions has been carried out. Several thiosulfonates could be identified in extracts of freshly cut onion. Compounds believed to make important contributions to onion flavor are: propyl thiosulfonates (freshly cut onion), propyl and propenyl di- and trisulfides (boiled onion), and dimethylthiophenes (fried onion).

Since Semmler (1892) investigated the essential oil of onion there have been several thorough studies on the flavor complex of onion. Carson (1967) gave a review about onion flavor research up to 1966. Bernhard (1969) presented a general view of Allium flavor chemistry. In 1969 Brodnitz *et al.* (1969) and coworkers examined the flavor components of onion oil and published a list of 17 onion oil constituents. Brodnitz and Pollock (1970) presented a gas chromatographic method for the analysis of onion oil. Bandyopadhyay *et al.* (1970) made studies on the flavoring constituents of onion by a combination of chromatographic and spectroscopic methods. Brodnitz and Pascale (1970a) prepared a synthetic onion oil, by either adding propenyl-containing polysulfides to a skeleton consisting of methyl and propyl sulfides or by heating propylalkane thiosulfinates. Brodnitz and Pascale (1970b) isolated the lachrymatory factor from a raw onion extract by means of preparative gas chromatography and identified the isolate as thiopropanal-*S*-oxide.

Methyl- and propylpropenyl disulfides have been recognized as important constituents of the oil from onions by Brodnitz *et al.* (1969) as well as in our laboratories. Wijers *et al.* (1969) developed a synthesis for this important class of natural products. Because $\alpha,\beta$-unsaturated disulfides were now available, the behavior of these compounds could be studied under a variety of conditions. During the search for the degradation products of propenyl-containing disulfides in onion oil, the presence of a relatively large number of unidentified components became evident. This led us to an analysis of onion oil by the combined glc–ms technique. Also the development and decomposition of the volatile components in the headspace of chopped, cooked, and fried onion was investigated. Alkyl alkane thiosulfonates were identified in extracts from freshly cut onions.

## EXPERIMENTAL

**Materials.** The onion oil used in this study was distilled at an Italian facility of NAARDEN during 1969. Details about Italian onion oils are described by Giusti (1968). Dutch onions (white type, family Victoria) and Egyptian onions (yellow type), harvested in 1969, were investigated during spring 1970. For the headspace analysis onions were cut in two. One part was chopped by hand and the other finely crushed in a whirlblender. Other onions were chopped by hand and analyzed either directly or after cooking for 45 min or after frying for 20 min. The prepared onions were put in glass-infusion bottles, from which the samples were taken. Onions (1 kg, Dutch or Egyptian) were chopped by hand and extracted with dichloromethane in a Soxhlet apparatus. The extraction of 100 g of freshly cut onions took about 3 hr. The combined extracts—about 1000 ml—were concentrated. The semisolid residue (1 g) was treated with 2 ml of methanol and filtered. The filtrate was used for mass spectrometric analysis.

The following reference samples were synthesized: monosulfides—methyl propenyl sulfide, propenyl propyl sulfide, and dipropenyl sulfide according to the method of Price and Snyder (1962); disulfides—methyl propenyl disulfide, propenyl propyl disulfide, and dipropenyl disulfide according to the methods of Wijers *et al.* (1969), isopropyl propyl disulfide and diisopropyl disulfide according to the method of Carson and Wong (1959); trisulfides—methyl propenyl trisulfide and propenyl propyl trisulfide, isopropyl propyl trisulfide, diisopropyl trisulfide, allyl propyl trisulfide, and diallyl trisulfide according to the method of Carson and Wong (1959); thiosulfonates—methyl methanethiosulfonate, propyl methanethiosulfonate, propenyl methanethiosulfonate, propyl propane thiosulfonate, propenyl propanethiosulfonate, and allyl prop-2-enethiosulfonate according to the methods of Boldyrev *et al.* (1956) and Wijers *et al.* (1969); thiophene derivatives—a mixture of 2,3-dimethyl- and 2,4-dimethylthiopene (1:4) according to the method of Sicé (1954); 3,4-dimethylthiophene according to the method of Linstead *et al.* (1937) and by heating dipropenyl disulfide (Boelens and Brandsma, 1971). 2,5-Dimethylthiophene was obtained commercially.

**Apparatus and Methods.** Distillation of onion oil was carried out in a Nester Faust NFA-100 spinning band distillation system.

Preparative scale gas chromatographic separations and headspace analysis were performed in a Becker 3810 gas chromatograph with a 100 to 2 splitter. Purified materials were obtained by gas chromatography on a 7-ft, $^1/_8$-in. (i.d.) glass column packed with 80/100 mesh acid-washed and silanized Embacel coated with 10% Carbowax 20M. A nitrogen flow rate of 10 ml/min was maintained while the temperature was programmed from 70 to 200° C at 1° C/min.

SCOT columns were prepared from widebore 200-ft, 0.03-in. (i.d.) glass tubing by coating with 40 ml of a 0.5% solution of UCON LB 550X in dichloromethane, with a flow of 2 cm/sec. A suspension of 6 g ANM rice (Neckar Chemie), 3 g UCON LB 550X, and 0.03 g Aerosil type R

Naarden Research Department, Postbox 2, Naarden, The Netherlands.

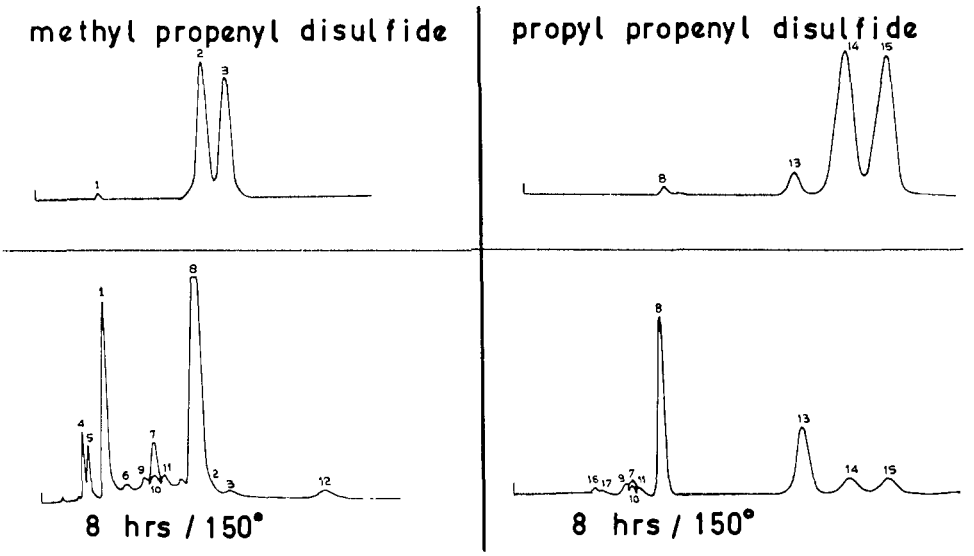



Figure 1. Gas chromatograms of heated alkyl propenyl disulfides. (For identification see Table I.)

972 (DEGUSSA) in 24 g of dichloromethane was brought into the column while a flow of 2 cm/sec was maintained. Subsequently a nitrogen flow rate of 1 ml/min was applied for 4 hr. The column was conditioned at a programmed temperature from 50 to 180° C at 1° C/min with a helium flow rate of 3 to 4 ml/min. SCOT columns were operated with a helium flow rate of 3.5 ml/min.

Mass spectra were recorded on a Varian MAT CH 5 mass spectrometer coupled with a Varian Aerograph model 1220 gas chromatograph. The separations were performed in an all-glass system from the point of the syringe to the center of the ion-source. The coupling was achieved by means of an interface specially developed to connect SCOT columns to a mass spectrometer. This interface consisted of an all-glass capillary restriction allowing a helium flow rate of 0.5 to 1.0 ml/min. The excess effluent was split off at atmospheric pressure. This is realized by inserting the capillary restriction partly into the SCOT column. The material admitted to the mass spectrometer is conducted to the heart of the ion-source by a glass capillary. The CH 5 mass spectrometer is equipped with an extra ion-source as a gas chromatographic detector operating at 20 eV to avoid ionization of helium. The main ion-source temperature was 210° C.

Infrared spectra were recorded on a Perkin-Elmer model 137 infrared spectrophotometer; cell thickness was 0.02 mm.

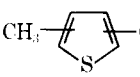
Nuclear magnetic resonance (nmr) spectra were determined on a Varian Associates A 60A instrument. Compounds were run in 10% v/v carbon tetrachloride solutions using tetramethylsilane as internal standard.

The presence of thiosulfonates in an onion extract was proved by means of a special method for the qualitative and quantitative determination of small amounts of known compounds in complicated mixtures. The working principle of this method dates from early attempts to couple a mass spectrometer with a gas chromatograph and is first described by Henneberg (1961). Of a compound that is to be traced, two properties have to be known: the mass spectrum, or at least some characteristic fragments with their relative abundance, and the glc retention time. The mass spectrometer is set to detect these ions and can be considered as a specific detector for those ions. If the particular compound is present, the detector has to produce a signal after elapse of the retention time. If a signal is found this is an indication the compound may be present. Proof is obtained by part reconstruction of the mass spectrum in this way. This method is very sensitive because the electron multiplier can be used at maximum sensitivity as contributions from all other components and instrument background are eliminated. The procedure can be accelerated by simultaneous detection of two selected ions, holding the magnetic field constant while switching the accelerating voltage between preselected values by use of the peak matching unit.

## RESULTS AND DISCUSSION

**Decomposition of Alkyl 1-Propenyl Disulfides.** By the action of heat or ultraviolet irradiation methyl propenyl disulfide and propyl propenyl disulfide are converted into dimethylthiophenes and saturated disulfides. Minor quantities of $\alpha,\beta$-unsaturated monosulfides and saturated trisulfides are also formed. A paper on the mechanistic aspects

$$CH_3CH{=}CH\text{-}S\text{-}S\text{-}R \longrightarrow$$



$$+ \text{ R-S-S-R } + H_2S$$

R = methyl or *n*-propyl

side reaction:

$$CH_3CH{=}CH\text{-}S\text{-}S\text{-}R \rightarrow \begin{cases} CH_3CH{=}CH\text{-}S\text{-}R + \\ CH_3CH{=}CH\text{-}S\text{-}CH{=}CH\text{-}CH_3 + \\ R\text{-}S\text{-}S\text{-}S\text{-}R \end{cases}$$

of these reactions will be published shortly (Boelens and Brandsma, 1971).

Figure 1 illustrates the effect of prolonged heating on samples of *cis*- and *trans*-propenyl methyl disulfide and of *cis*- and *trans*-propenyl propyl disulfide. Of the thiophenes formed the major product is 3,4-dimethylthiophene. Less than 10% of 2,4-dimethylthiophene is formed and only a trace (less than 1%) of the 2,5-dimethyl isomer is formed. The saturated disulfides formed are dimethyl disulfide and

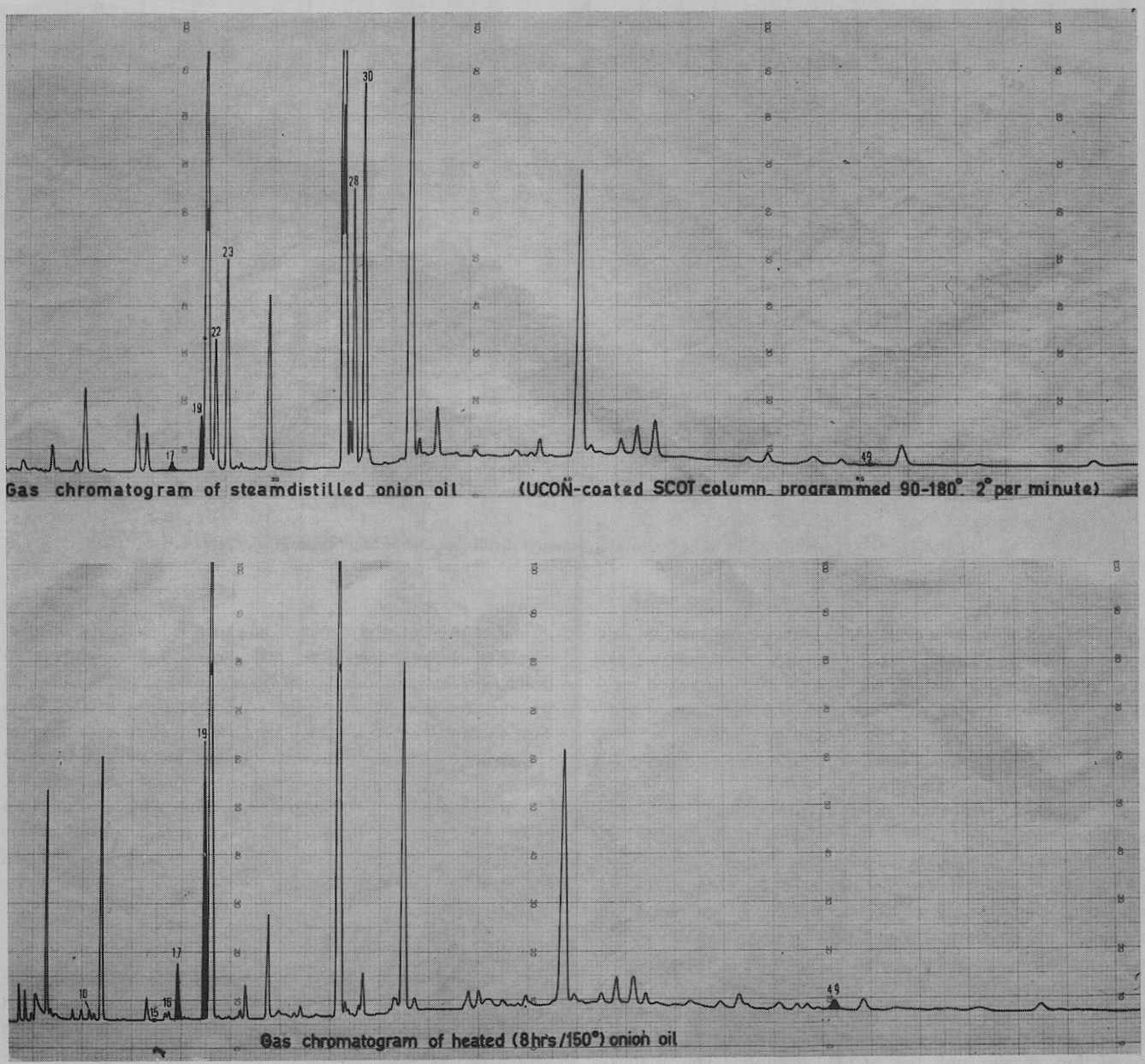



**Figure 2.** Gas chromatograms of steam-distilled and heated onion oil. (For identification see Table III.)

**Table I. Identification of Compounds from Heated Alkyl Propenyl Disulfides**

| | |
|---|---|
| 1 | Dimethyl disulfide |
| 2 | Methyl *cis*-propenyl disulfide |
| 3 | Methyl *trans*-propenyl disulfide |
| 4 | Methyl *cis*-propenyl monosulfide |
| 5 | Methyl *trans*-propenyl monosulfide |
| 6 | 2,5-Dimethylthiophene |
| 7 | 2,4-Dimethylthiophene |
| 8 | 3,4-Dimethylthiophene |
| 9 | Di-*cis*-propenyl monosulfide |
| 10 | *cis*-Propenyl *trans*-propenyl monosulfide |
| 11 | Di-*trans*-propenyl monosulfide |
| 12 | Dimethyl trisulfide |
| 13 | Dipropyl disulfide |
| 14 | Propyl *cis*-propyl disulfide |
| 15 | Propyl *trans*-propenyl disulfide |
| 16 | Propyl *cis*-propenyl monosulfide |
| 17 | Propyl *trans*-propenyl monosulfide |

**Table II. Identification of Compounds in Headspace of Cut Onion**

| Peak no. | |
|---|---|
| 1 | Ethanal |
| 2 | Propanal |
| 3 | 2-Methylbutanal |
| 4 | 2-Methylpentanal |
| 5 | Dimethyl disulfide |
| 6 | 2-Methylpent-2-enal |
| 7 | 2,4-Dimethylthiophene |
| 8 | Methyl propyl disulfide |
| 9 | 3,4-Dimethylthiophene |
| 10 | Methyl *cis*-propenyl disulfide |
| 11 | Methyl *trans*-propenyl disulfide |
| 12 | Dipropyl disulfide |
| 13 | Propyl *cis*-propenyl disulfide |
| 14 | Propyl *trans*-propenyl disulfide |

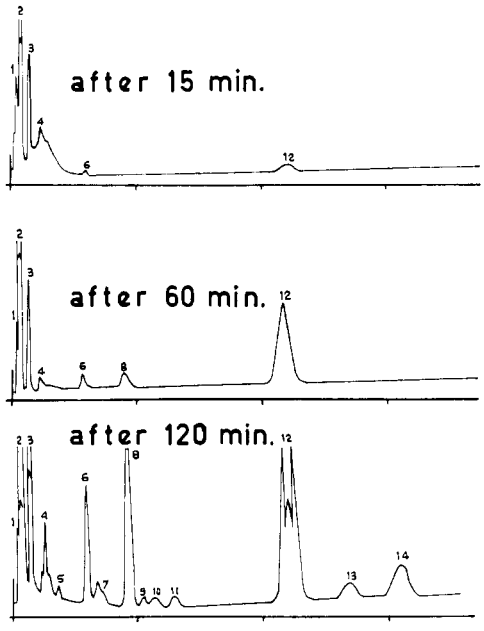



Figure 3. Headspace analysis of cut onion. (For identification see Table III.)

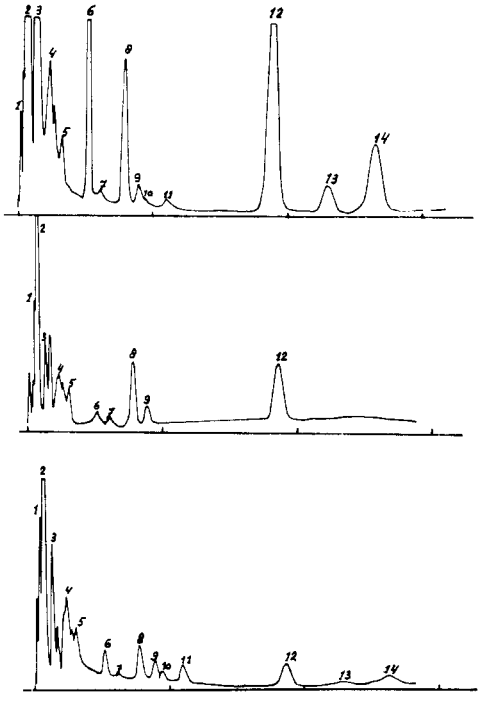


Figure 4. Headspace analysis of (top) freshly cut, (middle) boiled, and (bottom) fried onions. (For identification see Table II.)

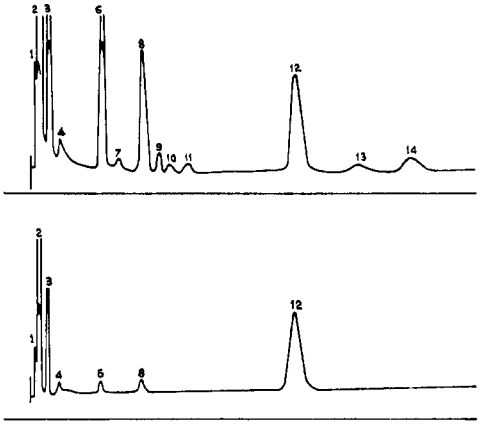


Figure 5. Headspace analysis of (bottom) chopped and (top) finely crushed onions. (For identification see Table II.)

dipropyl disulfide, respectively. See Table I for other by-products.

**Decomposition of Alkyl 1-Propenyl Disulfides in Onion Oil.** Alkyl propenyl disulfides, as well as 3,4-dimethylthiophene, have been demonstrated to be present in onion oil by Brodnitz *et al.* (1969), but no relationship has been suggested to exist between the two. The presence of 3,4-dimethylthiophene in onion oil was confirmed as was also the presence of the 2,4 and 2,5 isomers.

After heating a steam-distilled onion oil a sharp increase in the amount of dimethylthiophenes was observed and the alkyl propenyl disulfides had disappeared (Figure 2).

**Analysis of Headspace Volatiles from Onions.** The question can be raised whether dimethylthiophenes are already present in freshly cut onions or whether they are formed during the processing. Figure 3 shows the development of the volatile components in the headspace of cut onions. The first compounds to appear are oxygen derivatives, mostly carbonyl compounds. They are listed in Table II. The difference in headspace between onions that have been chopped by hand and those that have been crushed by a whirlblender is illustrated in Figure 4. The concentration of oxygen compounds in the headspace of finely crushed onions is appreciably higher than in chopped onions.

Second to appear are the saturated disulfides, and only after 2 hr were the unsaturated disulfides found. At the same time the 2,4- and 3,4-dimethylthiophenes were observed. There are indications that this time span may be appreciably shorter when freshly harvested onions are used. The onions used for this investigation were at least 6 months old.

In Figure 5 headspace gas chromatograms of raw and prepared onions are compared. Although the absolute quantities of the dimethylthiophenes (peaks 7 and 9) remain about the same, their relative importance is much larger in the boiled and even more in the fried onion.

**Analysis of Steam-Distilled Onion Oil.** A gas chromatogram of steam-distilled onion oil on a UCON coated glass SCOT column is shown in Figure 6. The identified compounds are listed in Table III.

The flavor components of onion oil can be classified in the following categories: oxygen compounds, thiols, monosulfides, thiophenes, disulfides, trisulfides, and tetrasulfides.

**Oxygen Compounds.** In contrast to the report by Brodnitz *et al.* (1969) several carbonyl compounds were found in steam-distilled onion oil, namely, propanal, 2-methylpentanal, and 2-methylpent-2-enal. These compounds were identified in the oil by comparing their retention times and mass spectral pattern with those of authentic samples. The presence of these aliphatic aldehydes in onion oil is not surprising. Propanal is one of the most important flavor compounds in raw onions. Figure 7 shows its probable biogenesis, as suggested by Virtanen (1967). The important flavor precursor *S*-propenylcysteine-*S*-oxide forms the unstable lachrymatory factor thiopropanal-*S*-oxide (Brodnitz and Pascale, 1970b). This compound rearranges spontaneously to form propanal and sulfur. 2-Methylpent-2-enal can be formed by aldol condensation and subsequent dehydration of two molecules of

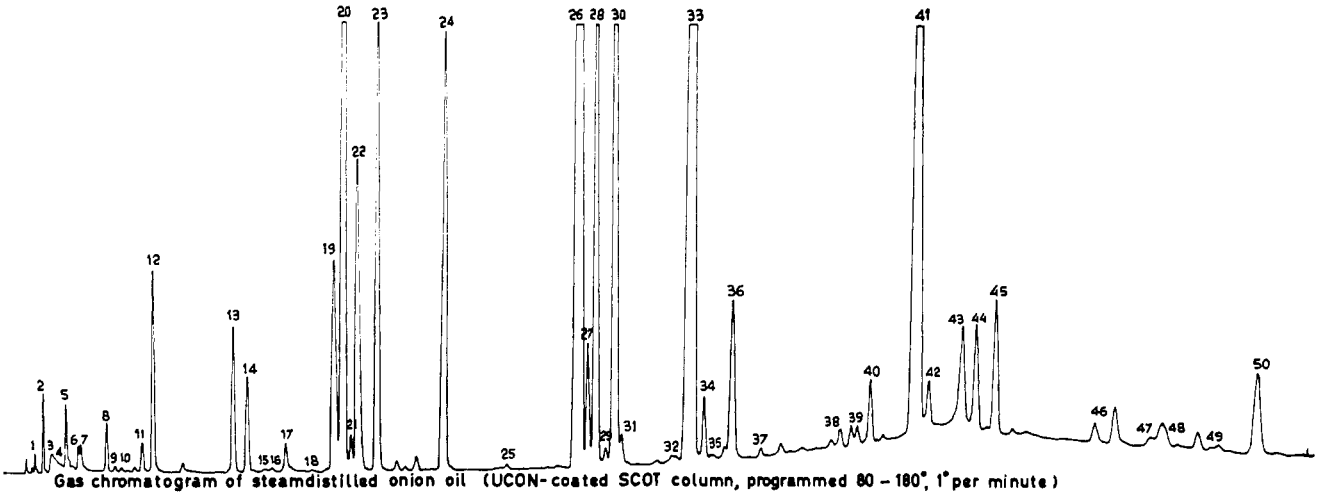



Figure 6. Gas chromatogram of steam-distilled onion oil. (For identification see Table III.)

**Table III. Compounds Identified in Steam-Distilled Onion Oil**

| Oxygen compounds | Peak no. |
|---|---|
| Propanal | 5 |
| Dimethylfuran[a] | 9 |
| 2-Methylpentanal[a] | 11 |
| 2-Methyl-pent-2-enal | 13 |
| Tridecan-2-one[a] | 47 |
| 5-Methyl-2-*n*-hexyl-2,3-dihydrofuran-3-one[a] | 50 |
| **Disulfides** | |
| Dimethyl disulfide | 12 |
| Methyl propyl disulfide | 20 |
| Allyl methyl disulfide | 21 |
| Methyl *cis*-propenyl disulfide | 22 |
| Methyl *trans*-propenyl disulfide | 23 |
| Isopropyl propyl disulfide[a] | 25 |
| Dipropyl disulfide | 26 |
| Allyl propyl disulfide | 27 |
| *cis*-Propenyl propyl disulfide | 28 |
| *trans*-Propenyl propyl disulfide | 30 |
| Diallyl disulfide | 29 |
| Allyl propenyl disulfide (2 isomers) tentative[a] | 31 |
| Dipropenyl disulfide (3 isomers) tentative[a] | 32 |

| Monosulfides | Peak no. |
|---|---|
| Dimethyl sulfide[a] | 1 |
| Allyl methyl sulfide[a] | 8 |
| Methyl propenyl sulfide[a] (2 isomers) | 10 |
| | 10 |
| Allyl propyl sulfide[a] | 14 |
| Propenyl propyl sulfide[a] (2 isomers) | 16 |
| Dipropenyl sulfide[a] (3 isomers) | 18 |
| **Trisulfides** | |
| Dimethyl trisulfide | 24 |
| Methylpropyl trisulfide | 33 |
| Allyl methyl trisulfide | 34 |
| Methyl *cis*-propenyl trisulfide | 35 |
| Methyl *trans*-propenyl trisulfide | 36 |
| Diisopropyl trisulfide[a] | 37 |
| Isopropyl propyl trisulfide[a] | 38 |
| Dipropyl trisulfide | 41 |
| Allyl propyl trisulfide[a] | 42 |
| Diallyl trisulfide[a] | 43 |
| *cis*-Propenyl propyl trisulfide | 44 |
| *trans*-Propenyl propyl trisulfide | 45 |

| Thiophene derivatives | Peak no. |
|---|---|
| 2,5-Dimethylthiophene[a] | 15 |
| 2,4-Dimethylthiophene[a] | 17 |
| 3,4-Dimethylthiophene | 19 |
| 3,4-Dimethyl-2,5-dihydrothiophen-2-one[a] | 49 |
| **Thiols** | |
| Hydrogen sulfide | 3 |
| Methanethiol[a] | 4 |
| Propanethiol | 6 |
| Allylthiol[a] | 7 |
| *m/e* 154 $C_4H_9S_2SH$[a] | 40 |
| *m/e* 180 $C_6H_{11}S_2SH$[a] | 46 |
| *m/e* 182 $C_6H_{13}S_2SH$[a] | 48 |
| **Tetrasulfide** | |
| Dimethyl tetrasulfide[a] | 39 |
| **Hydrocarbon** | |
| Propene[a] | 2 |
| **Additional compounds identified in an onion extract** | |
| Methyl methanethiosulfonate[a] | |
| Propyl methanethiosulfonate[a] | |
| Propyl propanethiosulfonate[a] | |

[a] Not reported earlier as a constituent of onion (*Allium cepa*).

propanal. 2,5-Dimethylfuran was not isolated but was identified by its mass spectral pattern and glc retention time. It is a known degradation product of sugars.

Tridecan-2-one (methyl undecyl ketone) was isolated by spinning-band distillation of onion oil and preparative scale gas chromatographic separation. Mass spectrum and retention time agreed with those of an authentic sample. Tridecanone is a well known degradation product of myristic acid (Jasperson and Jones, 1947). 2-*n*-Hexyl-5-methyl-2,3-dihydrofuran-3-one was isolated in the same way as tridecanone. The structure of this new compound is evident from its spectral properties, which are shown in Table IV. This compound may also have been formed from a fatty acid precursor *via* the $C_{11}$-hydroxy diketone.

**Thiols.** The gas chromatogram in Figure 6 shows, at the far left side, the peaks from methanethiol, 1-propanethiol, and 2-propanethiol. The tailing peak is from hydrogen sulfide.

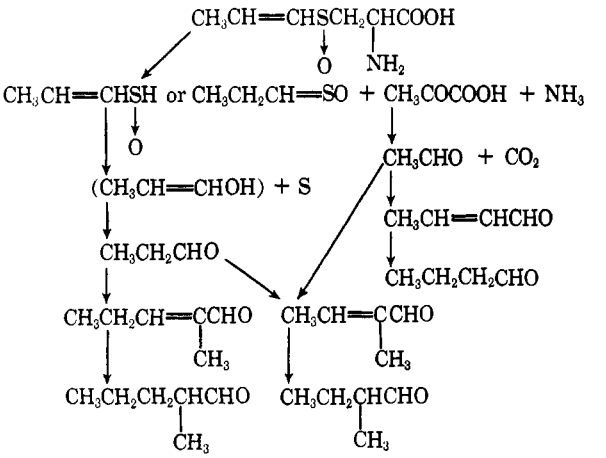



Figure 7. Formation of carbonyl compounds in onion

Table IV. Spectral Data of Constituents of Onion Oil and Onion Extracts

| | | |
|---|---|---|
| **Oxygen compounds** | | |
| 2-Methylpentanal | Mass | 100 (2), 71 (11), 58 (77), 57 (14), 55 (9), **43 (100)** |
| | nmr | δ 0.94 (3 H, t), 1.07 (3 H, d), 1.1–1.9 (4 H, m), 2.23 (1 H m), 9.55 (1 H, d) |
| | ir | 3.55, 3.67, 5.78, 7.18, 7.27, 10.75, 13.55 |
| Tridecan-2-one | Mass | 198 (21), 140 (22), 96 (29), 85 (44), 82 (29), 71 (53), **58 (100)**, 43 (78) |
| | nmr | δ 0.90 (3 H, t), 1.1–1.8 (18 H, m), 2.11 (3 H, s), 2.41 (2 H, t) |
| | ir | 5.81, 7.10, 7.38, 8.61, 13.87 |
| 2-*n*-Hexyl-5-methyl-2,3-dihydrofuran-3 one | Mass | 182 (9), 111 (51), **98 (100)**, 85 (9), 68 (13), 55 (10), 43 (20), 41 (14) |
| | nmr | δ 0.90 (3 H, t), 1.1–2.1 (10 H, m), 2.20 (3 H, s), 4.25 (1 H, t), 5.28 (1 H, s) |
| | ir | 5.85, 6.21, 7.23, 7.43, 8.72, 10.54, 12.78, 13.72–13.83 |
| **Thiophene derivatives** | | |
| 2,4-Dimethylthiophene | Mass | 112 (76), **111 (100)**, 97 (50), 77 (14), 71 (10), 69 (8), 67 (9), 45 (24), 39 (20) |
| | nmr | δ 2.17 (3 H, s), 2.42 (3 H, s), 6.51 (2 H, m) |
| | ir | 3.24, 3.28, 6.39, 7.25, 8.24, 8.58, 8.92, 11.73 12.12, 13.80 |
| 2,5-Dimethylthiophene | Mass | The same as the 2,4 isomer |
| | nmr | δ 2.37 (6 H, s), 6.40 (2 H, s) |
| | ir | 3.27, 6.41, 6.70, 8.15, 8.40, 8.70, 9.58, 12.65 |
| 3,4-Dimethylthiophene | Mass | The same as the 2,4 isomer |
| | nmr | δ 2.13 (6 H, s), 6.77 (2 H, s) |
| 3,4-Dimethyl-2,5-dihydrothiophen-2-one | Mass | **128 (100)**, 100 (15), 99 (22), 85 (55), 67 (37), 65 (12), 59 (16), 55 (28), 45 (28), 41 (27), 39 (35) |
| | nmr | δ 1.76 (3 H, m), 2.12 (3 H, s), 3.80 (2 H, m) |
| | ir | 5.92, 6.00, 7.10, 7.28, 7.75, 8.17, 10.14, 10.74, 12.14, 13.03, 14.88 |
| **Polysulfides** | | |
| Diisopropyl trisulfide | Mass | 182 (34), 140 (4), 117 (3), 98 (5), 75 (60), 47 (16), 45 (17), **43 (100)**, 41 (55), 39 (22) |
| Dimethyl tetrasulfide | Mass | 160 (10), 158 (47), 126 (9), 111 (9), 94 (32), 79 (90), 64 (47), 61 (17), 48 (26), 47 (80), 46 (42), **45 (100)** |
| **Thiosulfonates** | | |
| Methyl methanethiosulfonate | Mass | 126 (44), 81 (73), 79 (46), 64 (34), 63 (60), **47 (100)**, 45 (65) |
| | nmr | δ 2.69 (3 H, s), 3.25 (3 H, s) |
| | ir | 7.54, 7.60, 7.70, 8.85, 10.45, 13.39 |
| Propyl methanethiosulfonate | Mass | 154 (20), 125 (7), 113 (9), 112 (7), 81 (18), 79 (29), 75 (38), 74 (84), 63 (20), 47 (47), 45 (27), 4 (60), **41 (100)** |
| | nmr | δ 1.07 (3 H, t) 1.75 (2 H, h), 3.13 (2 H, t), 3.27 (3, H, s) |
| | ir | 7.64, 8.85, 10.48, 13.41 |
| Propyl propanethiosulfonate | Mass | 182 (3), 140 (1), 118 (6), 89 (4), 76 (46), 47 (19), 45 (11), **43 (100)**, 42 (50), 41 (55) |
| | nmr | $\delta_{DMSO}$ 0.97 (3 H, t), 1.02 (3 H, t), 1.80 (4 H, m), 3.15 (2 H, t), 3.50 (2 H, t) |
| | ir | 7.60, 7.74, 8.88, 13.10, 13.50–14.58 |
| **Unknown compounds** | | |
| **Peak no.** / **Suggested formula** | | |
| 40 $C_4H_9S_2SH$ | Mass | 154 (6), 126 (4), 89 (87), 73 (20), 61 (21), 47 (34), 45 (50), **41 (100)** |
| 46 $C_6H_{11}S_2SH$ | Mass | 180 (5), 115 (60), 81 (28), 73 (51), 47 (42), 45 (81), 43 (62), **41 (100)** |
| 48 $C_6H_{13}S_2SH$ | Mass | 182 (11), 154 (9), 117 (46), 75 (59), 47 (44), 45 (47), 43 (92), **41 (100)** |

These compounds were identified by comparing their retention times and mass spectra with those of authentic samples.

**Thiophene Derivatives.** The thiophene derivatives listed in Table III were isolated from the onion oil by a sequence of spinning-band distillation and preparative scale gas chromatographic separations. Their structures are evident from their spectral properties, which are shown in Table IV.

**Monosulfides.** So far, only a few monosulfides have been reported to occur in onion oil. As mentioned before, the disproportionation of unsaturated disulfides *in vitro* gives rise to the formation of three different propenyl monosulfides and these compounds are indeed found in onion oil. More surprising is the presence of appreciable quantities of allyl methyl and allyl propyl monosulfide. As a possible explanation, the direct coupling of allyl cations with alkylthiolate anions can be suggested. The structures of these monosulfides were confirmed by comparison with those of authentic products.

**Disulfides.** The presence of disulfides in onion oil and their biosynthesis from *S*-alkylcysteine-*S*-oxides has been thoroughly discussed by Carson (1967), Virtanen (1967), Brodnitz *et al.* (1969) and their collaborators. Not counting cis–trans isomers, nine disulfides were definitely identified and two more were tentatively identified. Except for allyl propenyl disulfide, all the structures are proven by comparison of their spectral data with those of the synthetic products.

**Trisulfides.** The seven trisulfides reported in literature were easily identified by their spectral properties and comparison with authentic samples. New in onion are the allyl- and isopropyl-containing trisulfides: allyl methyl, allyl propyl, diallyl, isopropyl propyl, and diisopropyl trisulfide.

**Tetrasulfides.** The first tetrasulfide was identified in onion oil, namely dimethyl tetrasulfide. The presence of higher polysulfides has been suggested in literature (Semmler, 1892) but never confirmed. Upon distillation of onion oil an appreciable quantity of semisolid material that is soluble in polar solvents, like acetone, dioxane, and diglyme, is left behind. This residue may well contain polysulfides such as dipropyl tetrasulfide.

**Components of Molecular Weights 180 and 182.** There remained a group of at least four unidentified peaks in the gas chromatogram (Figure 6) of onion oil between peaks 45 and 50.

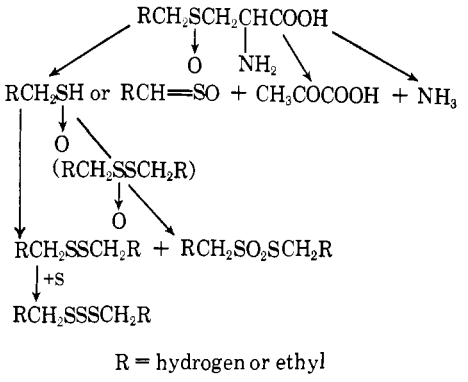



Figure 8. Formation of sulfur compounds in onion

Table V. Threshold Values of Onion Compounds

| | μg/l. of Water |
|---|---|
| Onion oil | 0.8 (0.1–2.7) |
| Dipropyl disulfide | 3.2 (2.2–4.0) |
| Methyl propenyl disulfide | 6.3 (2.7–8.1) |
| Propyl propenyl disulfide | 2.2 (0.3–2.7) |
| 3,4-Dimethylthiophene | 1.3 (0.2–2.7) |
| Propyl methanethiosulfonate | 1.7 (0.3–2.7) |
| Propyl propanethiosulfonate | 1.5 (0.3–2.7) |

These compounds had a molecular weight of 180 and 182 corresponding to $C_6H_{18}S_3$ and $C_6H_{14}S_3$ or $C_6H_{12}S_2O_2$ and $C_6H_{14}S_2O_2$. This led us to the synthesis of thiosulfonates R–S–$SO_2$–R, with R = propyl, propenyl, and allyl as reference materials. It turned out that no thiosulfonates were present in the steam-distilled onion oil above the detection level, which can be estimated at less than 10 parts per million. This corresponds to 1 part per billion in weight of steam-distilled onions.

An attempt to concentrate the fraction of onion oil that contains these four unknown components failed because of their thermolability. It was not possible to obtain the nmr and ir spectra and, as a consequence, the identification of these compounds could not be completed. We would like to suggest as a possible structure the products with formulae $C_6H_{11}S_2SH$ and $C_6H_{13}S_2H$ which can be formed by the addition of hydrogen sulfide to the double bond of unsaturated disulfides.

**Isolation and Identification of Alkyl Alkane Thiosulfonates from Freshly Cut Onions.** Several authors have suggested the formation of thiosulfonates as a secondary reaction in the enzymatic cleavage of *S*-alkylcysteine derivatives. A scheme depicting the biosynthesis of sulfur compounds in onion is proposed in Figure 8. The abundant disulfides are supposedly formed by disproportionation of the unstable thiosulfinates. This reaction was studied *in vitro* by Backer and Kloosterziel (1954). Brodnitz and Pascale (1970a) very recently found that thiosulfinates undergo dehydration and disproportionation reactions leading to the formation of saturated and unsaturated polysulfides. Ostermayer and Tarbell (1960) studied the hydrolysis of *S*-methyl-L-cysteine sulfoxide and showed that most of the material was converted to pyruvic acid, ammonia, dimethyl disulfide, and methyl methanethiosulfonate. We repeated this reaction with the propyl derivative and found a nearly quantitative yield of dipropyl disulfide and propyl propanethiosulfonate. The propenyl derivative gave neither disulfide nor thiosulfonate.

Thiosulfonates have never been found in Allium species. If the scheme in Figure 8 is indeed the only pathway leading to the formation of disulfides, an equimolar amount of thiosulfonate should be formed. Thiosulfonates however are absent in onion oil. This may well be caused by the low vapor pressure and fairly good water solubility of these compounds. Consequently they may not have been transferred during the steam-distillation or else they may have remained in the water layer.

Therefore the extracts of chopped raw onions were analyzed for the presence of thiosulfonates. The gas chromatograms were scanned for compounds that would give the desired molecular ion peak as well as the known fragmentation pattern in the mass spectrometer (see Experimental). The presence of methyl methane, propyl methane, and propyl propane thiosulfonate in extracts of raw onions was unambiguously proven. The concentration of, for instance, propyl propane thiosulfonate in onion can be estimated at about 0.5 ppm. The quantities that are present in the extract are much smaller than those expected on mechanistic grounds. Either the thiosulfonates—known to be stable compounds—are rapidly reduced, which seems unlikely, or the extraction has been inefficient, which cannot be excluded, or else the main reaction path leading to the formation of disulfides in onion must be a different one, which concurs with the recent suggestion by Brodnitz and Pascale (1970a).

**Odor Evaluation and Threshold Determinations.** The organoleptic properties of the compounds listed in Table V were evaluated by 14 expert flavorists. They were asked to describe the odor and taste of the compound dissolved in water. The flavor of the finely crushed onions is much more fruity (apple-like) than that of the onions chopped by hand.

Thiosulfonates with four or more carbon atoms display a powerful and distinct odor of freshly cut onions.

The propyl- and propenyl-containing di- and trisulfides possess the flavor of cooked onions. This is in agreement with the findings of Brodnitz *et al.* (1969). The odor of steam-distilled onion oil is much closer to that of cooked than to that of freshly cut onions.

The flavor character of 2,4- and 3,4-dimethylthiophenes is distinctly that of fried onion.

Table V shows threshold values for the more important onion flavor components. These figures show that the threshold level of propyl propane thiosulfonate (1.5 ppb) is several hundred times lower than its concentration (0.5 ppm) and thus this compound may be expected to give a significant contribution to the overall flavor.

ACKNOWLEDGMENT

The authors thank Willem Brackmann, Piet C. Traas, and Anton Vlas for their technical assistance in isolating and synthesizing the compounds and Jac. Groot and Wim J. Hoffmann for assistance in obtaining the mass spectral and gas chromatographic data.

LITERATURE CITED

Backer, H. J., Kloosterziel, H., *Recl. Trav. Chim. Pays-Bas* **73,** 129 (1954).
Bandyopadhyay, C., Srirangarajan, A. N., Sreenivasan, A., *J. Chromatogr.* **47,** 400 (1970).

Bernhard, R. A., *Qual. Plant. Mater. Veg.* **18,** 72 (1969).
Boelens, H., Brandsma, L., submitted for publication, *Recl. Trav. Chim. Pays-Bas* (1971).
Boldyrev, B. G., Litkovets, A. K., Trofimova, T. A., *Zh. Obshch. Khim.* **26,** 3360 (1956).
Brodnitz, M. H., Pascale, J. V., Abstracts, 53, Division of Agricultural and Food Chemistry, 160th Meeting, ACS, Chicago, Ill., September 1970a.
Brodnitz, M. H., Pascale, J. V., Abstracts, 98, Division of Agricultural and Food Chemistry, 160th Meeting, ACS, Chicago, Ill., September 1970b.
Brodnitz, M. H., Pollock, C. L., *Food Technol.* **24,** 78 (1970).
Brodnitz, M. H., Pollock, C. L., Vallon, P. P., J. AGR. FOOD CHEM. **17,** 760 (1969).
Carson, J. F., in "Chemistry and Physiology of Flavors," Avi, Westport, Conn., 1967, p 390.
Carson, J. F., Wong, F. F., *J. Org. Chem.* **24,** 175 (1959).
Giusti, G., *Informazione Aromatica*, No. 5, Sept. (1968).
Henneberg, D., *Z. Anal. Chem.* **183,** 12 (1961).
Jasperson, H., Jones, R., *J. Soc. Chem. Ind.* **66,** 15 (1947).
Linstead, R. D., Noble, E. G., Wright, J. M., *J. Chem. Soc.* 911 (1937).
Ostermayer, F., Tarbell, D. S., *J. Amer. Chem. Soc.* **82,** 3752 (1960).
Price, C. C., Snyder, W. H., *J. Org. Chem.* **27,** 4639 (1962).
Semmler, F. W., *Arch. Pharmacol.* **230,** 443 (1892).
Sicé, J., *J. Org. Chem.* **19,** 70 (1954).
Virtanen, A. I., in "Nutritio et Dieta," Vol. 9, Karger, Basel/New York, N.Y., 1967, p 1.
Wijers, H. E., Boelens, H., van der Gen, A., Brandsma, L., *Recl. Trav. Chim. Pays-Bas* **88,** 519 (1969).

*Received for review December 24, 1970. Accepted March 11, 1971. Presented at the Division of Agricultural and Food Chemistry, 160th Meeting, ACS, Chicago, Illinois, September 1970.*