2,4,5-Trithiahexane from Photolysis of Dimethyl Disulfide

Irradiation of dimethyl disulfide with ultraviolet (UV) (2537 Å) light at room temperature for 16 h gave a 15% yield of 2,4,5-trithiahexane, a known component of cabbage.

Dimethyl disulfide occurs in a number of foods (cf. Schutte, 1974). The authors (Buttery et al., 1976) recently studied the volatile flavor components of cabbage, broccoli, and cauliflower confirming the previously found dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide but also characterizing for the first time the related unusual compound 2,4,5-trithiahexane ($CH_3SCH_2SSCH_3$). It seemed reasonable that the 2,4,5-trithiahexane could be formed from a free-radical reaction involving $CH_3S\cdot$ and CH_3SSCH_3 in the cabbage. The action of ultraviolet (UV) light on dimethyl disulfide is known to give the free radical $CH_3S\cdot$. However, in the several studies reported on the photolysis of dimethyl disulfide (e.g., Parker and Kharasch, 1959; Sayamol and Knight, 1968; Carlson and Knight, 1973; Inaba and Ogoro, 1969) the formation of 2,4,5-trithiahexane has not been reported. The authors undertook to reinvestigate the photolysis of dimethyl disulfide to specifically look for 2,4,5-trithiahexane.

EXPERIMENTAL SECTION

Dimethyl disulfide (1 ml, Eastman Organic Chemicals No. 1825) was placed in a Vicor tube under a nitrogen atmosphere and irradiated with quartz mercury arc UV lamps (2537 Å, total of 35 W) for 16 h. The product was analyzed directly by gas–liquid chromatography (GLC) using a 1 m × 0.63 cm o.d. aluminum column packed with 80–100 mesh Chromosorb P coated with 10% Tween 20, collecting the samples in 150 × 3 mm Pyrex glass tubes. The GLC conditions were column temperature 150 °C and flow rate 40 ml/min helium.

Mass Spectra. Samples collected from the GLC column were analyzed using batch introduction with a modified Consolidated 21-620 mass spectrometer. Ionization voltage was 70 V.

Authentic 2,4,5-Trithiahexane. This was synthesized by the reaction of CH_3SNa with $ClCH_2SCl$ using the method of Brintzinger and Schmahl (1954) as described previously by the authors (Buttery et al., 1976).

RESULTS AND DISCUSSION

Analysis of the products of the irradiation of dimethyl disulfide for 16 h by GLC separated mostly unchanged dimethyl disulfide together with a 15% yield of 2,4,5-trithiahexane whose mass spectrum (molecular ion 140, other important ions at 61, 45, 125, 108, and 94; cf. Buttery et al., 1976) and GLC retention time were consistent with that of the authentic sample.

There is not much dimethyl disulfide in raw cabbage and it is doubtful whether 2,4,5-trithiahexane could be formed by the action of sunlight on cabbage during the growing period. Dimethyl disulfide is chiefly produced when cabbage is cooked. The formation of 2,4,5-trithiahexane probably also occurs during the cooking. Schutte (1974) has outlined a likely mechanism for the formation of dimethyl disulfide in foods from the breakdown of the amino acid methionine to CH_3SH which is oxidized by atmospheric oxygen to CH_3SSCH_3. The formation of $CH_3S\cdot$ is probably part of this process and could react with dimethyl disulfide already formed to give the 2,4,5-trithiahexane present in cabbage.

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Patulin Content of Juice and Wine Produced from Moldy Grapes

Patulin is a mycotoxin produced by a number of fungal spoilage organisms, some of which may be present on moldy grapes. Juices and wines produced from Rauschling and Gamay grapes (moldy at harvest) and from Concord and V.53263 grapes (moldy after extended storage) were analyzed for patulin. Patulin was present in the juices but was not detected in a partially fermented juice (Gamay) and the wines. *Penicillium* spp. were the predominant microflora of samples of the Rauschling grapes, from which were isolated strains of *P. expansum* that produced patulin and citrinin.

The mycotoxin patulin (4-hydroxy-4*H*-furo[3,2-*c*]-pyran-2(6*H*)-one) is a metabolite of several *Aspergillus* and *Penicillium* spp. (Scott, 1974) and of *Byssochlamys fulva* and *nivea* (Escoula, 1975). Patulin occurs widely in commercial apple juice in North America (Stoloff, 1975) and this problem deserves attention as there is some in-