cyclo-Octasulfur in Swine Manure

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Synopsis. Pale-yellowish white needles were isolated from a rotten mixture of swine urine and feces by vacuum distillation and identified to be *cyclo*-octasulfur by means of mass spectrometry and other methods. This is the first time that this compound has been detected in swine manure.

cyclo-Octasulfur is the most stable form having a crown structure[1] and a main component in monoclinic and rhombic sulfurs.[2] Khare and Sagan[3] detected large amounts of *cyclo*-octasulfur in photoreaction products of hydrogen sulfide and other gaseous compounds. This compound was also isolated from a culture filtrate when a marine fungus was cultivated in a sulfite-pulp waste-liquor medium and was characterized by mass spectrometry.[4] White and Lee[5] found *cyclo*-octasulfur in a coal extract by gas chromatography-mass spectrometry using a capillary column and flame photometric detection. *cyclo*-Octasulfur has hardly been detected in other environmental samples. This article describes an identification of *cyclo*-octasulfur in swine manure.

Experimental

Isolation of cyclo-*Octasulfur.* A rotten mixture of swine urine (700 mL) and feces (400 g) was frozen at *ca.* −80 °C and vacuum-distilled in a frozen state at a pressure of *ca.* 10^{-4} Torr (1 Torr=133.322 Pa): The trap for volatile substances was cooled at −80 to −100 °C. The sample flask was kept at room temperature for 1 d, heated at 40 °C for 2 d, and finally heated at 100 °C for 4 d. The distillation residue (35 g) was mixed with diethyl ether (1 L) for 1 d. The filtrate was concentrated to *ca.* 50 mL and then vacuum-distilled in order to separate volatile from nonvolatile matters. The volatile matters were combined with the volatile in the trap as described below.

The ice (960 mL) containing the volatile compounds in the trap was melted and the volatile substances were extracted with diethyl ether (200 mL) by a liquid-liquid continuous extractor for 2 d. The extracted solution was combined with the volatile matters from the residue and then concentrated at atmospheric pressure with a Kuderna–Danish concentrator. When most of the diethyl ether was removed, white needle crystals were precipitated from the solution. The isolated crystals (3.35 mg), mp 112—119 °C, were characterized by mass spectrometry and other methods.

Gas Chromatography–Mass Spectrometry. The gas chromatographic conditions used were as follows: apparatus, HEWLETT PACKARD HP5710A gas chromatograph; column, glass column (3 m×3 mm i.d.) packed with 5% Thermon-3000 on 80—100 mesh Chromosorb W (AM-DMCS); column temperature, 50 °C initially for 2 min, increased to 250 °C at a rate of 4 °C/min; injection temperature, 250 °C; helium flow rate, 20 mL/min. The mass spectrometric conditions used were as follows: apparatus, JEOL JMS-DX 300 mass spectrometer and JEOL JMA 3500 mass data analysis system; ionizing current, 300 μA; electron energy, 70 eV; accelerating voltage, 3 kV; scan range, *m/e* 10—400; scan speed, 1.6 s/scan; repetition time, 2.5 s; ionization chamber pressure, $1—2\times10^{-6}$ Torr; ionization chamber temperature, 180—210 °C.

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Results and Discussion

The needle crystals isolated from rotten swine manure were pale-yellowish white and smelled of sulfur, which we usually experience near volcanos. They were easily soluble in benzene and chloroform, slightly soluble in diethyl ether and tetrahydrofuran, and insoluble in acetone. Their mass spectra were measured both by the direct inlet method and by the GC/MS method. The mass spectra, shown in Fig. 1, were identical with each other and only one peak was observed in a total ion monitoring by GC/MS, as shown in Fig. 2. Therefore, these crystals are not a mixture but a single compound. The mass spectrum measured in this study is the same as that of *cyclo*-octasulfur, though the relative intensities of the peaks at *m/e* 128, 160, 192, and 256 are somewhat different from those already reported.[4,6,7] With the direct inlet method, all mass spectra are essentially identical irrespective of sample temperature. No signals were observed in a measurement of ^{1}H NMR spectra, indicating that there is no hydrogen atom in the molecule. The electronic spectrum of this compound in

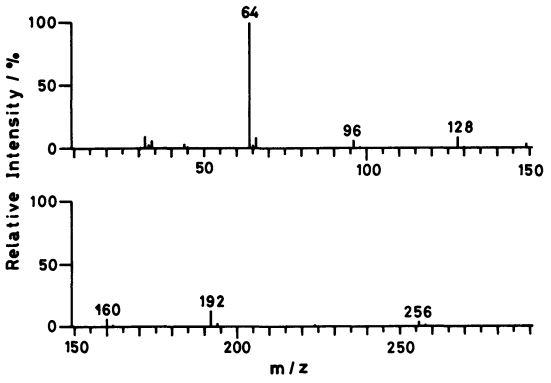

Fig. 1. Mass spectrum of *cyclo*-octasulfur.

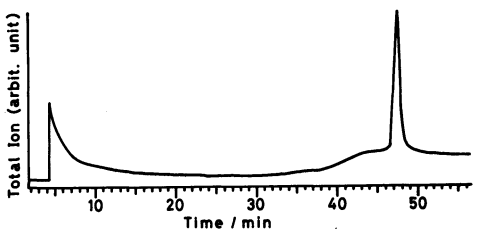

Fig. 2. Total ion monitoring of *cyclo*-octasulfur in GC/MS.

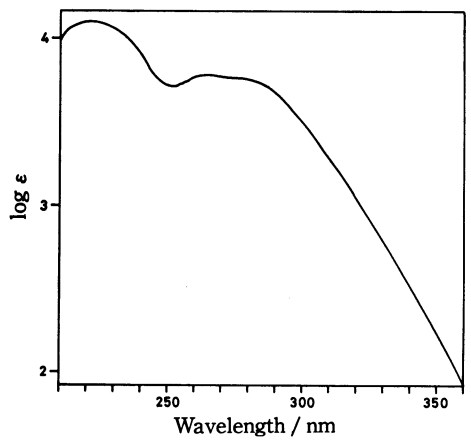

Fig. 3. Electronic spectrum of *cyclo*-octasulfur. Solvent, THF.

tetrahydrofuran solution, shown in Fig. 3, is slightly different from the one in the literature.[8] The IR spectrum of *cyclo*-octasulfur has already been reported by a few investigators,[3,9] although it is not clear-cut because of too small a sample amount. From these results, this compound has been decided to be *cyclo*-octasulfur.

cyclo-Octasulfur was detected only in rotten mixtures of swine urine and feces (two samples) and not in rotten swine urine (two samples). A semiquantitative result gave an amount of 3.35 mg of *cyclo*-octasulfur with a rotten mixture of 700 mL urine and 400 g feces. This compound has not always been detected in swine manure, since the formation of *cyclo*-octasulfur as a single substance of elemental sulfur might require some specific conditions which can seldom been realized in natural environment. According to Yurovskii's theory,[10] *cyclo*-octasulfur might be produced *via*

$$2FeSO_4+5H_2S\longrightarrow 2FeS_2+2S+H_2SO_4+4H_2O,$$

where the hydrogen sulfide is anaerobically formed from sulfate by bacteria. It has been known that a large amount of hydrogen sulfide is produced from liquid swine manure by anaerobic digestion.[11] Furthermore, dimethyl disulfide is found in swine manure.[12] It is reasonable to consider that *cyclo*-octasulfur results from the hydrogen sulfide evolved in swine manure. Since the offensive hydrogen sulfide raises environmental odor problems, the conversion of hydrogen sulfide to *cyclo*-octasulfur is very desirable. Also, it is interesting to examine whether or not *cyclo*-octasulfur is to be detected in other environments where hydrogen sulfide is evolved.

cyclo-Octasulfur can be detected by means of GC/MS or GC with a flame photometric detector, since GC with a flame ionization detector cannot have any responses. The ionization efficiency of *cyclo*-octasulfur in mass spectrometry was roughly investigated. Dimethylsulfone was used as a reference material, because it is often contained in swine manure and it gives a weak peak at mass number 64 (SO_2^+) in its mass spectrum. In the mass spectrum of *cyclo*-octasulfur, a base peak (S_2^+) locates at mass number 64. The molar ratio in peak intensity of *cyclo*-octasulfur to dimethylsulfone at *m/e* 64 is 0.200. As the relative intensity of the peak at *m/e* 64 to the base peak at *m/e* 79 ($CH_3SO_2^+$) in dimethylsulfone is 0.021, the molar ratio in base peak intensity of *cyclo*-octasulfur to dimethylsulfone is 0.0041. Namely, the ionization efficiency of *cyclo*-octasulfur is very low compared with dimethylsulfone which is detectable at usual sensitivities. The detection limit is around 100 ng. Therefore, the determination of a trace amount of *cyclo*-octasulfur by mass spectrometry is very difficult.

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