Hydrogen Sulfide Adducts of Methyl Oleate and Linoleate

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ABSTRACT

Sulfur compounds derived from photochemical addition of hydrogen sulfide to methyl oleate and linoleate were separated by preparative gas chromatography. The major compounds were investigated by NMR, mass and IR spectroscopy and by elemental analysis. The primary product of the methyl oleate reaction was methyl 9(10)-mercaptostearate. Gas chromatograms of the product from methyl linoleate showed four principal peaks. From mass spectra and NMR data, we identified methyl 9-(2-pentyl-1-thiolan-5-yl)nonanoate, methyl 8-(2-hexyl-1-thiolan-5-yl)octanoate and methyl 9-(3-hexyl-1,2-dithiolan-5-yl)nonanoate. Evidence for the formation of methyl mercapto-octadecenoates and methyl dimercaptostearates was also obtained.

INTRODUCTION

High molecular weight mercaptans have industrial applications as anticorrosive agents for lubricating oils (1), in making synthetic rubber (2) and as starting materials in manufacturing chemicals (3). A previous publication (4) described the free radical addition of hydrogen sulfide to conjugated and nonconjugated methyl esters and to vegetable oils. The products are largely mercapto-esters and mercapto-oils. Some components from the reaction of hydrogen sulfide with methyl oleate and linoleate have now been identified and are reported here. These components were separated by preparative GLC and examined by NMR, mass and IR spectroscopy and by elemental analysis.

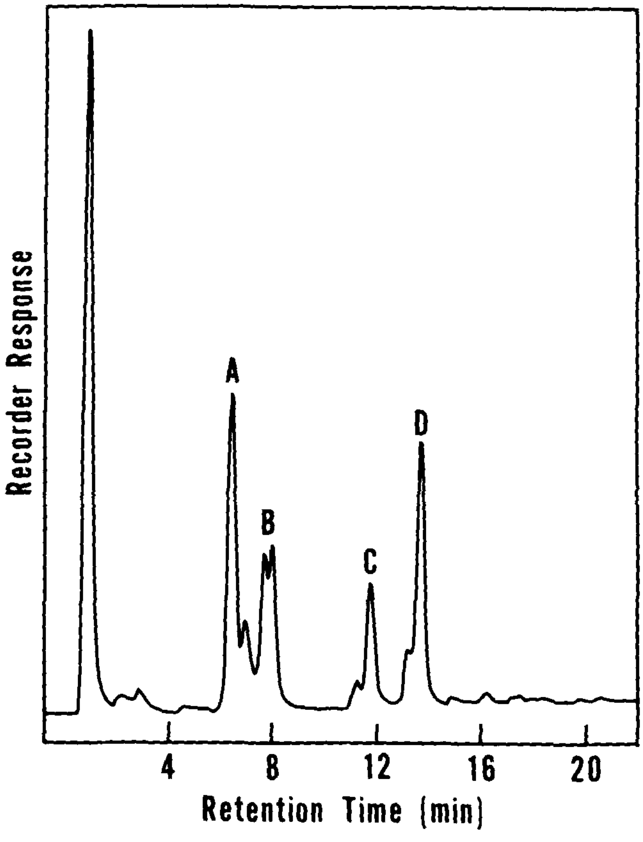

FIG. 1. Gas chromatogram of hydrogen sulfide-methyl linoleate adduct. Gas liquid chromatographic conditions given in Experimental Procedures.

EXPERIMENTAL PROCEDURES

Sample Collection and Analytical Procedures

Samples separated by gas liquid chromatography (GLC) were collected in 2 in., no. 14 Teflon tubes inserted at the exit port of an F&M Model 5750 research chromatograph. Programed runs were conducted on a 6 ft x 1/4 in. 3% JXR column at 180-300 C with a heating rate of 4 C/min and a helium carrier gas flow rate of 30 cc/min. This instrument was fitted with a microsplitter-collector that provided a 1:9 split ratio (1 part to the flame ionization detector and 9 parts to the collector tubes). Samples were rechromatographed to increase purity.

Mass spectra were measured on a Nuclide 12-90 G mass spectrometer equipped with an all-glass inlet; inlet temperature, 190 C; source temperature, 200 C; and electron energy, 70 V.

NMR analysis was carried out in $CDCl_3$ solution with a Varian HA-100 research model. Exchange experiments were made with deuterated sodium hydroxide.

IR analyses were performed on thin films or in carbon disulfide solution with a Beckman IR 8 spectrophotometer.

Starting Materials and Adduct Preparation

Methyl oleate was purchased from Applied Science Laboratories, Inc., and methyl linoleate from The Hormel Institute. These materials were 99% pure by GLC analyses. Hydrogen sulfide was Matheson CP grade.

The photochemical apparatus and procedure for preparing hydrogen sulfide adducts of methyl oleate and linoleate have been described previously (5).

RESULTS AND DISCUSSION

Methyl Oleate Adduct

A gas chromatogram of a sample from the methyl oleate-hydrogen sulfide reaction after irradiation for 26 hr showed two peaks, methyl oleate (I) and its hydrogen sulfide adduct (II). The identity of II was tentatively established by comparing the retention time of II on the GLC with an authentic sample of methyl 9(10)-mercaptostearate prepared from methyl oleate and thiolacetic acid (6). Additional evidence for the structure of II came from NMR and mass spectrometry. Both II and the authentic methyl 9(10)-mercaptostearate sample had identical mass spectra patterns. Figures in parentheses after the mass number indicate the intensity of that peak relative to the strongest peak in the spectrum. The parent peak was 330 (13%); loss of mercapto gave a peak at 297 (16%) and the further loss of methoxy gave a peak at 264 (53%). The spectra can also be characterized by the absence of significant peaks indicating cleavage of the carbon chain below 264. Both II and authentic methyl 9(10)-mercaptostearate were also examined by NMR. Again, spectra for the two were identical and the significant peaks were S-methine, 2.75, and a shoulder on the methylene proton peak at 1.4 for the thiol proton. No olefinic proton peaks were observed. Analysis–calculated for $C_{19}H_{36}O_2S$: C, 69.0; H, 11.58; S, 9.7. Found: C, 68.2; H, 11.78; S, 9.8.

Methyl Linoleate Adduct

The methyl linoleate reaction with hydrogen sulfide is

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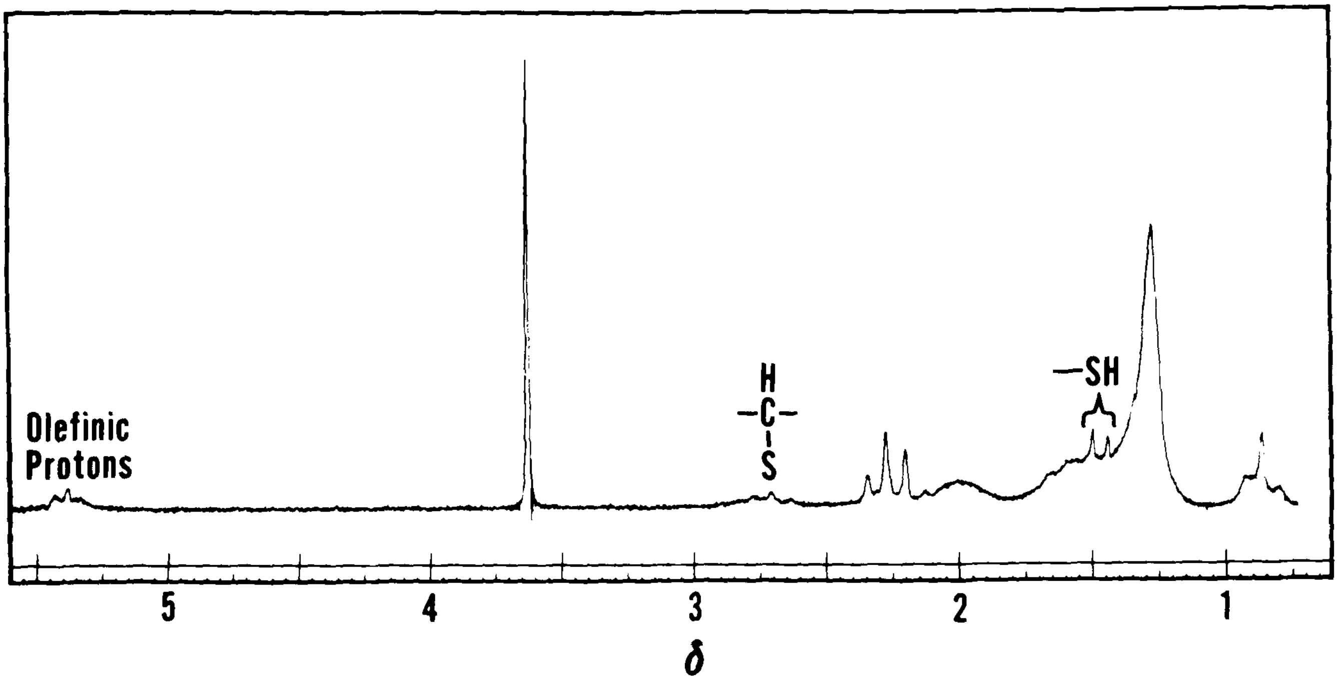


FIG. 2. NMR spectrum of product A (Fig. 1) from hydrogen sulfide-methyl linoleate reaction.

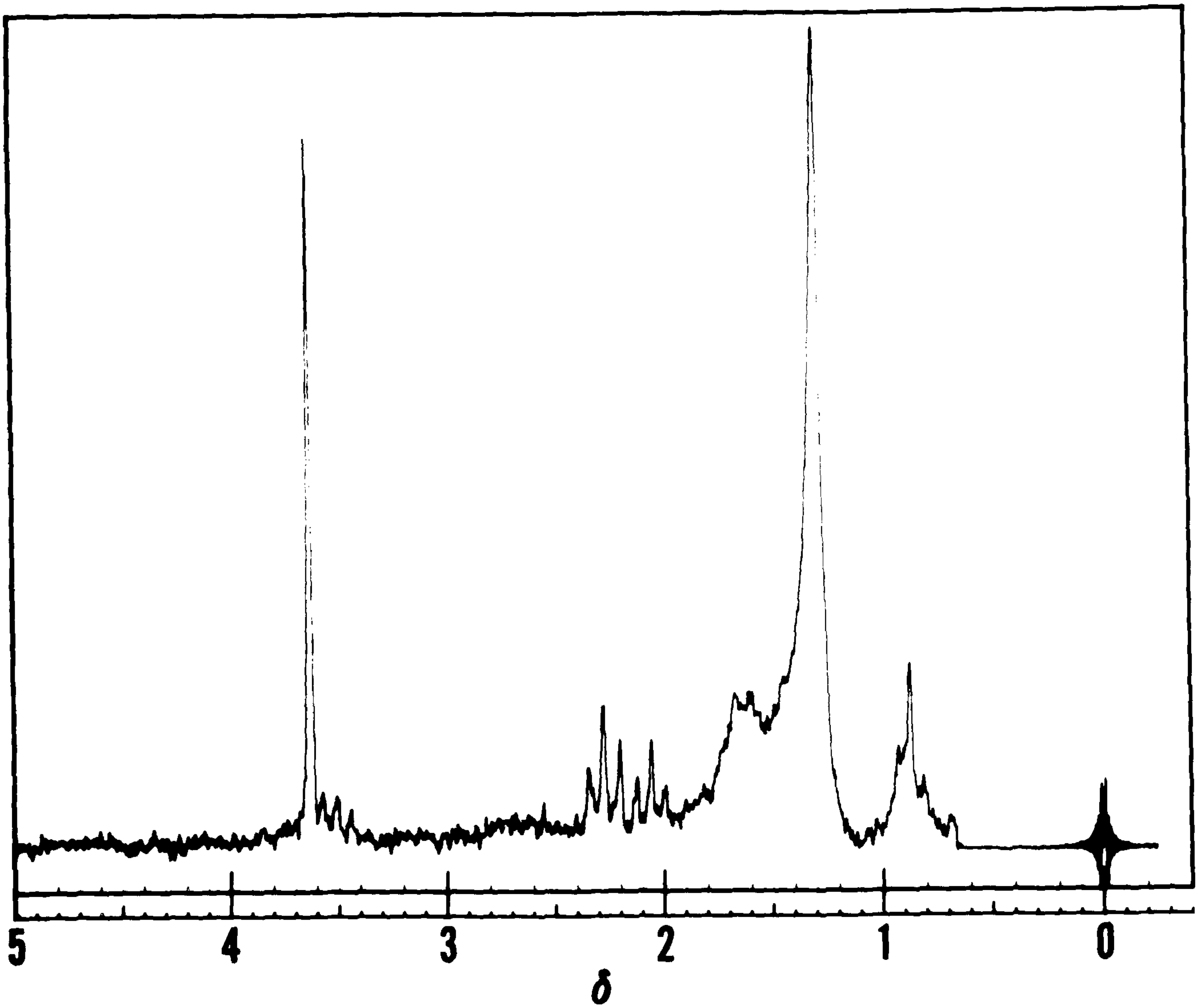
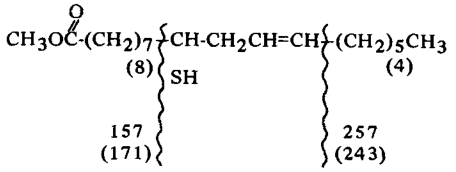


FIG. 3. NMR spectrum of product D (Fig. 1) from hydrogen sulfide-methyl linoleate reaction.

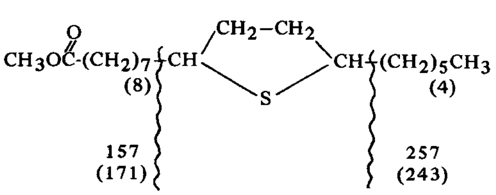
more complex than the methyl oleate reaction. Figure 1 is a gas chromatogram of hydrogen sulfide-treated methyl linoleate after 62 hr irradiation. Of the four major peaks, B is a doublet and A, C and D are accompanied by minor peaks. Addition of an internal standard (lauryl mercaptan) to the 62 hr irradiated reaction product showed that 95% of the material placed on the GLC emerged from the column.

Mass spectra data on products obtained by preparative GLC from peaks A and B were similar, but the spectrum of A showed that a small amount of an impurity was present. The product from peak B was of good purity according to its mass spectrum and showed a parent peak at 328 (50%) with strong peaks at 157 (100%), 171 (94%), 211 (38%), 225 (38%), 243 (34%) and 257 (32%). These spectra are consistent with compounds whose structures are illustrated by:



$$CH_3O\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_7\text{-}\underset{SH}{CH}\text{-}CH_2CH{=}CH\text{-}(CH_2)_5CH_3$$

[A]



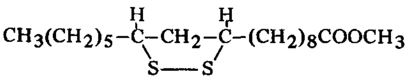
[B]

NMR data on A (Fig. 2) reveal proton peaks expected for terminal methyl, 0.88 δ; chain methylene, 1.27 δ; carbonyl methylene, 2.30 δ; and a methyl ester singlet at 3.66 δ. A peak for olefinic protons found at 5.41 δ lends support for structure A. Proton peaks were also evident for S-methine, 2.73 δ, a sharp doublet for the thiol proton at 1.47 δ with a coupling constant of 5.6 Hz and a broad complex peak of 2.01 δ. The NMR spectra from peak B had peaks expected for terminal methyl, 0.88 δ; chain methylene groups, 1.30 δ; α-carbonyl triplet, 2.30 δ; and the methyl ester singlet, 3.66 δ. Significantly, the little or no evidence for olefinic protons supported structure B. Other peaks occurred in two broad, poorly defined, multiplets. One multiplet ranged from the α-carbonyl peak at 2.30 δ into the β carbonyl region, ~1.5 δ. An S-methine multiplet was centered ~3.3 δ.

The products shown by structures A and B would be expected from a multistep radical chain mechanism generally accepted for the photochemical addition of hydrogen sulfide to olefins (7). The initial reaction product, a methyl mercapto-octadecenoate A, undergoes an intermolecular addition to give B. Naylor (8) reports similar results in his studies on intermolecular addition of hydrogen sulfide to dienes, such as dihydromyrscene.

The parent peak of 362 for product C is evidence of a methyl dimercaptostearate. This product is expected from the addition of 2 mol hydrogen sulfide to methyl linoleate with no accompanying intermolecular additions. The NMR spectrum of peak C indicates no olefinic protons, in accordance with the diaddition product. This spectrum has a terminal methyl triplet at 0.88 δ, a broad chain methylene peak at 1.30 δ, an α-carbonyl triplet at 2.30 δ and a methyl ester singlet at 3.65 δ. An -SH doublet appears at 1.38 δ. A broad S-methine peak occurs at ~2.75 δ. The β-functional group region at 1.55 δ is more prominent in this spectrum than in the spectra of the other components.

Product D is a surprisingly stable compound, as evidenced by a high intensity parent mass of 360 (60%) in its mass spectrum. Other prominent bands show loss of -SH (327, 20%), loss of methanol (295, 6%) and loss of a second sulfur atom (263, 16%). The 263 fragment contains no sulfur, since there is no evidence for S_{34} at mass 265. NMR data of product D (Fig. 3) are consistent for a dithiolan structure, such as:



[D]

Fatty ester peaks occur at 0.87 δ, methyl triplet; 1.28 δ, chain methylenes; 2.29, α-carbonyl methylene triplet; and 3.64 δ, methyl ester singlet. Characteristic peaks for this type of compound are a triplet at 2.07 δ (9) and a broad multiplet at ~3.55 δ. Decoupling experiments reveal that the triplet at 2.07 δ is coupled only to the multiplet at 3.55 δ.

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