Technical

Synthesis of Thioethers from Hydroxy Olefinic Fatty Acids

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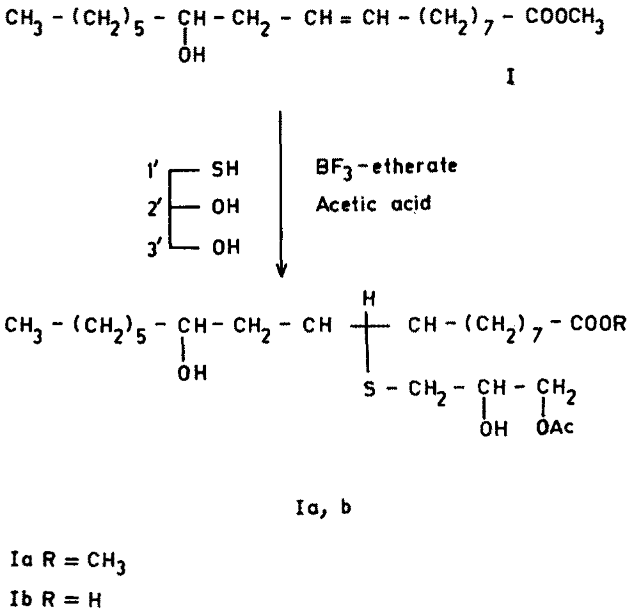
Reaction of 3-mercaptopropan-1, 2-diol with methyl ricinoleate (I) and methyl isoricinoleate (II) afforded their respective thioethers. The structure of the products was characterized by combustion and spectral (IR, NMR and MS) data.

Fatty materials containing bivalent sulphur find valuable application in the lubricant and polymer fields. Higher molecular weight mercaptans obtained by the addition of sulphur and/or sulphurated reagents to unsaturated oils have industrial applications. They have been described as useful lubricant additives, coatings, rubber substituents (1,2) and intermediates for the preparation of wetting agents and detergents (3). Some thioethers also have been synthesized and tested for anti-inflammatory, neurotropic, bactericidal, fungicidal, anticholesteremic and antimicrobial activities (4-8). A few thioethers also have been reported as tranquilizers (8) and road marking paint (10).

As a continuation of our synthesis of thioethers from unsaturated fatty esters (11), we have synthesized more thioethers by the reaction of 3-mercaptopropan-1, 2-diol with methyl 12-hydroxyoctadec-*cis*-9-enoate (methyl ricinoleate) and methyl 9-hydroxyoctadec-*cis*-12-enoate (methyl isoricinoleate).



Scheme 1.

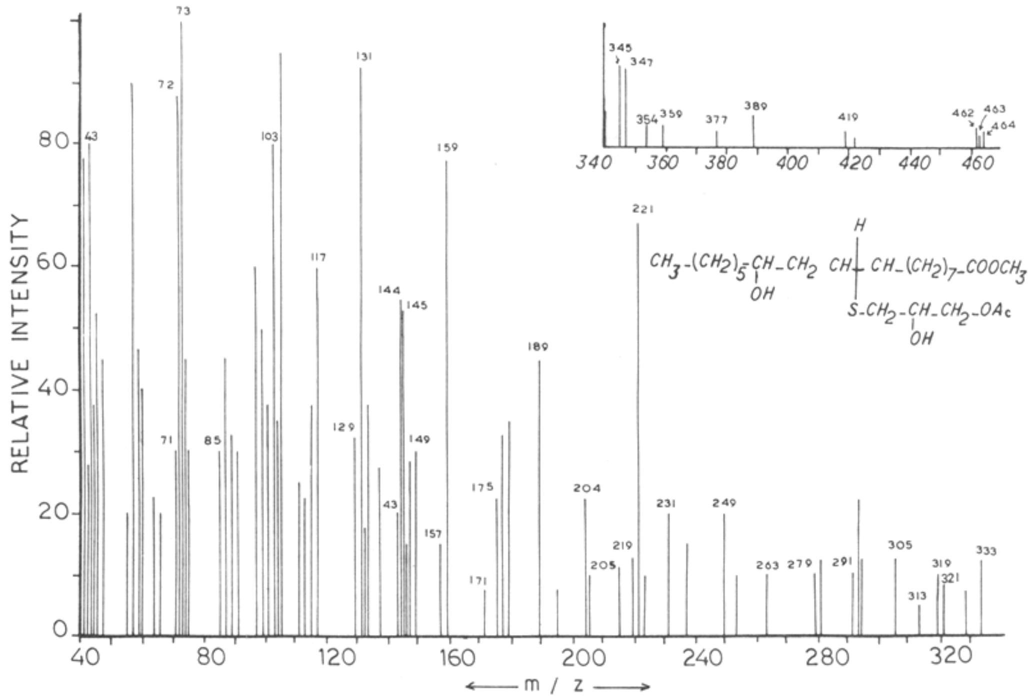


FIG. 1. Mass spectrum of Product Ia.

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EXPERIMENTAL PROCEDURES

Except where specified, the experimental conditions and procedures used are as described in our previous paper (11).

Pure ricinoleic and isoricinoleic acids were isolated from *Ricinus communis* and *Wrightia tinctoria* seed oils, respectively, by Gunstone's partition method (12). Their methyl esters were prepared by a traditional methylation method (H^+/CH_3OH) (I and II).

Reaction of 3-mercaptopropan-1,2-diol with methyl ricinoleate (I). Methyl ricinoleate, I (5 mmol) in glacial acetic acid (20 ml) was treated with 3-mercaptopropan-1,2-diol (5 mmol) in the presence of a few drops of BF_3-etherate at 120 C. The reaction was completed in about 30 min as evidenced by thin layer chromatography (TLC). The reaction mixture was worked up by adding water and then extracting with ether. The ether layer was washed first with 5% sodium bicarbonate solution, then with water, and finally dried over anhydrous sodium sulfate. Evaporation of ether yielded viscous oil showing two distinct spots on TLC (light petroleum ether-ether-acetic acid, 80:20:1, v/v/v). The reaction mixture chromatographed on a silica gel (45 g) column using petroleum ether-ether as moving phase, and each 15-ml fraction was collected. Elution with petroleum ether-ether (82:18, v/v) yielded methyl 12-hydroxy-9(10)-(3′mercaptopropan-1′-acetoxy-2′-ol)octadecanoate (Ia) as viscous liquid (50%, Rf 0.78). It resisted all attempts of crystallization. Analysis, found; C, 62.30, H, 9.82 calcd. for $C_{24}H_{46}O_6S$: C, 62.34; H, 9.96%.

The subsequent second fraction eluted by petroleum ether-ether (77:23, v/v) was the hydrolyzed product, 12-hydroxy-9(10)(3′-mercaptopropan-1′-acetoxy-2′-ol)-octadecanoic acid (Ib), a viscous liquid (35%, Rf 0.72). Analysis found: C, 61-51; H, 9.74. Calcd. for $C_{23}H_{44}O_6S$: C, 61.61; H, 9.82%.

Reaction of 3-mercaptopropan-1,2-diol with methyl isoricinoleate (II). Similarly, the reaction of methyl isoricinoleate, II (5 mmol) with 3-mercaptopropan-1,2-diol (5 mmol) in acetic acid (20 ml) at 120 C was completed in 30 min. The final reaction mixture showed two distinct spots on TLC (petroleum ether-ether-acetic acid, 80:20:1, v/v/v). The reaction mixture was chromatographed on silica gel column (45 g) using petroleum ether-ether as the eluent. The elution with petroleum ether-ether (80:20, v/v) yielded methyl 9-hydroxy-12(13)(3′-mercaptopropan-1′-acetoxy-2′-ol)-octadecanoate, IIa (66.7%, Rf 0.77). Analysis, found: C, 62.25; H, 9.84, calcd. for $C_{24}H_{46}O_6S$: C, 62.34; H, 9.96%.

The second hydrolyzed product (23.3%, Rf 0.70), 9-hydroxy-12(13)-(3′-mercaptopropan-1′-acetoxy′-2′-ol)-octadecanoic acid (IIb) was collected by elution with petroleum ether-ether (74:26, v/v) as a viscous oil. Analysis, found: C, 61.54; H, 9.71, Calcd. for $C_{23}H_{44}O_6S$: C, 61.61; H, 9.82%.

RESULTS AND DISCUSSION

The addition of 3-mercaptopropan-1,2-diol with methyl ricinoleate (I) (Scheme 1) afforded two products (Ia and Ib).

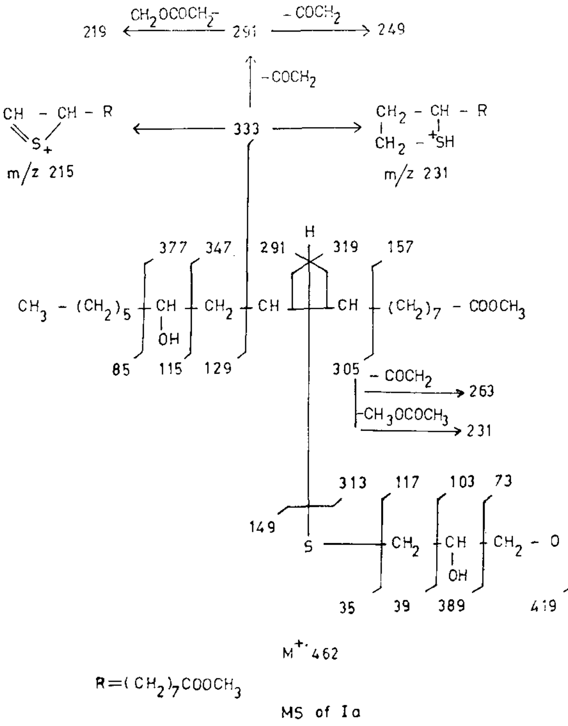
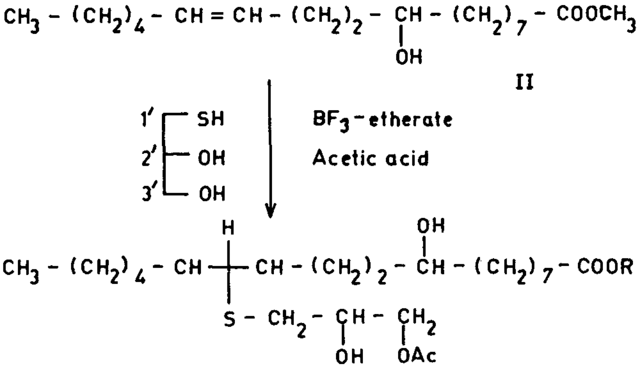


Chart 1. Mass fragmentation of Product Ia.



II a, b

IIa, R = CH_3

IIb R = H

Scheme 2.

Product Ia was analyzed for $C_{24}H_{46}O_6S$. Its IR spectrum showed bands at 3450 (2 × CH-OH). 2920 (CH_2-S, asymmetric stretch) 2840 (CH_2-S, symmetric stretch), 1745 ($OCOCH_3$), 1730 ($COOCH_3$), 1410 (CH_2-S deformation), 1240 (acetate), 1220 (CH_2-S wagging), 1100 and 1040 cm^{-1} (CO). Its NMR spectrum exhibited peaks at δ 0.88 t (terminal CH_3), 1.3 (br, s, chain CH_2), 2.1 (s, 3H, OCO-CH_3), 2.22 (m, 2H, CH_2-$COOH_3$, merged with acetate protons), 2.9 (m, 3H, CH-S-CH_2), 3.8 (m, 2H, 2 × CH-OH), 3.68 (s, 3H, $COOCH_3$), 4.0 (m, 2H, CH_2-OAc) and 6.7-6.3 (br s, 2H, 2 × CH-OH, disappeared on D_2O shake). Its mass spectrum (Fig. 1) showed a molecular ion peak at m/z 462. The other diagnostic peaks (Chart I) observed were at m/z 419, 389, 377, 359, 347, 345, 333, 319, 313, 305, 291, 157, 149, 129, 117, 115, 103, 73 and 43. On the

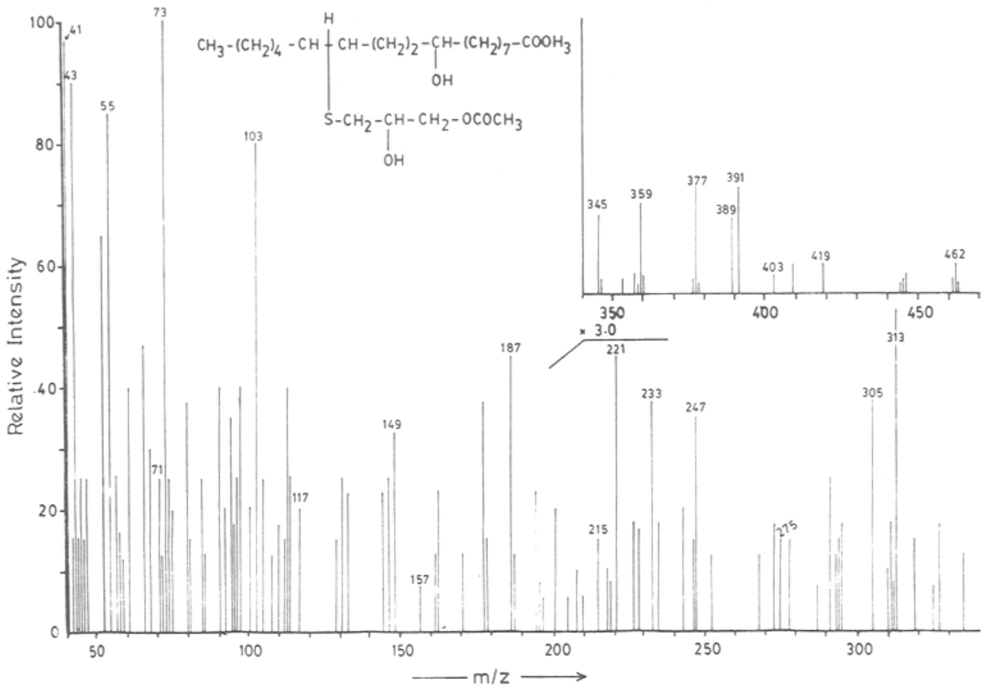


FIG. 2. Mass spectrum of Product IIa.

basis of these data the product Ia was identified as methyl 12-hydroxy-9(10)-(3′mercaptopropan-1′-acetoxy-2′-ol) octadecanoate.

The product Ib was analyzed for $C_{23}H_{44}O_6S$. Its IR and NMR spectral values were almost the same as product Ia except for the disappearance of the ester peaks at 1730 cm^{-1} and δ 3.68. In addition, it showed carboxylic peaks at 3450 and 1710 cm^{-1} in its IR spectrum and δ 9.45 in NMR spectrum. Hence the product Ib ws identified as the hydrolyzed product of Ia and characterized as 12-hydroxy-9(10)(3′mercaptopropan-1′-acetoxy-2′-ol) octadecanoic acid.

A similar treatment of methyl isoricinoleate (II) with 3-mercaptopropan-1,2-diol (Scheme 2) yielded an isomeric ester (IIa) and hydrolyzed products (IIb). The product IIa was analyzed for $C_{24}H_{46}O_6S$. Its IR spectrum revealed the same bands as that of product Ia. Its NMR spectrum also showed similar signals except for variations in the chemical shifts of the hydroxy peaks. The two protons of both hydroxy functions (2 × CH-O$\underline{H}$), appearing in the range of 2.7-2.48, disappeared on D_2O shake. The mass spectrum (Fig. 2) of IIa showed a molecular ion peak at m/z 462. The other diagnostic peaks (Chart 2) were at m/z 419, 391, 389, 377, 359, 345, 313, 305, 275, 247, 233, 215, 187, 157, 149, 117, 103, 73, 71 and 43. On the basis of the elemental and spectral data, the product (IIa) was characterized as methyl 9-hydroxy-12(13)(3′-mercaptopropan-1′-acetoxy-2′ol) octadecanoate.

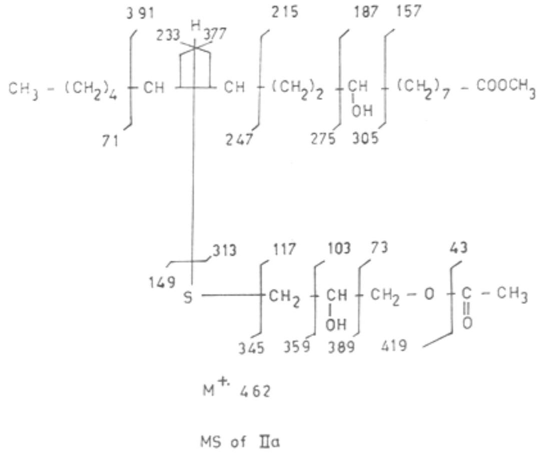


Chart 2. Mass fragmentation of Product IIa.

The product IIb was analyzed for $C_{23}H_{44}O_6S$. In comparison with the IR spectrum of IIa the only difference is the absence of the ester band at 1735 cm^{-1} and an additional band at 1710 cm^{-1} ascribed to the carboxylic group. The NMR spectrum has peaks similar to those of IIa except for the disappearance ester peak at δ 3.68. The carboxylic proton appears at δ 9.1. Thus, it is clear from the above data that the ester group of IIa was hydrolyzed to product IIb and was characterized as 9-hydroxy-12(13)-(3′mercaptopropan-1′-acetoxy-2′-ol) octadecanoic acid.

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