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FATTY ACIDS, PART 42* THE PREPARATION AND PROPERTIES OF METHYL MONOMERCAPTOSTEARATES, SOME RELATED THIOLS, AND SOME METHYL EPITHIOSTEARATES

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Some saturated and unsaturated mercapto C_{18} esters have been obtained for the first time. Such compounds are prepared from hydroxy esters via their mesyloxy derivatives by reaction with sodium hydrogen sulphide or with potassium thioacetate (followed by deacetylation) or from alkene esters by radical addition of thioacetic acid. The mercapto esters are readily identified by infrared, nuclear magnetic resonance, and mass spectroscopic procedures, preferably after acetylation or trifluoroacetylation.

γ-Mesyloxy alkenes furnish tetrahydrothiophen rather than mercapto alkenes and methyl 9,12-epithiostearate was synthesised by an independent route from thiophen.

I. Introduction

The mono- and poly-hydroxy derivatives of long-chain acids have been extensively studied over many years but much less is known about the preparation and properties of related mercapto compounds [1]. In particular, recent studies have shown the importance of neighbouring group participation in the reactions of long-chain hydroxy compounds [2] and an attempt has now been made to see to what extent the corresponding mercapto compounds behave in a similar way.

A general synthetic route to thiols was first applied to the preparation of long-chain mercapto acids and esters by Swern et al. [3] who reported in 1958 that the only compounds of this type then known were derived from 11-mercaptohendecanoic acid, 2-mercapto-octadecanoic acid, and the mixed 9(10)-mercapto-octadecanoic acids. Since then the only method that has been successfully employed to prepare such compounds is the radical addition of thiols [4] and of hydrogen

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sulphide [5] to alkene acids and esters. With the exception of hendec-10-enoic acid most alkenoic acids furnish mixed products which, until recently, have not been well characterised.

In this and the following paper we report our recent studies of some long-chain mercapto compounds. When this work was completed Schwab et al. [6] published a paper on the products of the photochemical reaction between hydrogen sulphide and methyl oleate and methyl linoleate. Our structural indentifications confirm and extend their conclusions.

II. Preparation of methyl mercapto-alkanoates, methyl mercapto-alkenoates, and of some related long-chain sulphur compounds

We have had success with three preparative procedures. Two of these involve the conversion of a hydroxyl group to a mercapto group via the methanesulphonyl (mesyl) ester and the third proceeds via the more familiar radical addition of thioacetic acid to alkenes.

$$RCH(OH)R' \xrightarrow[\text{pyridine}]{CH_3SO_2Cl,} RCH(OMs)R' \xrightarrow[DMF]{NaHS} RCH(SH)R'$$

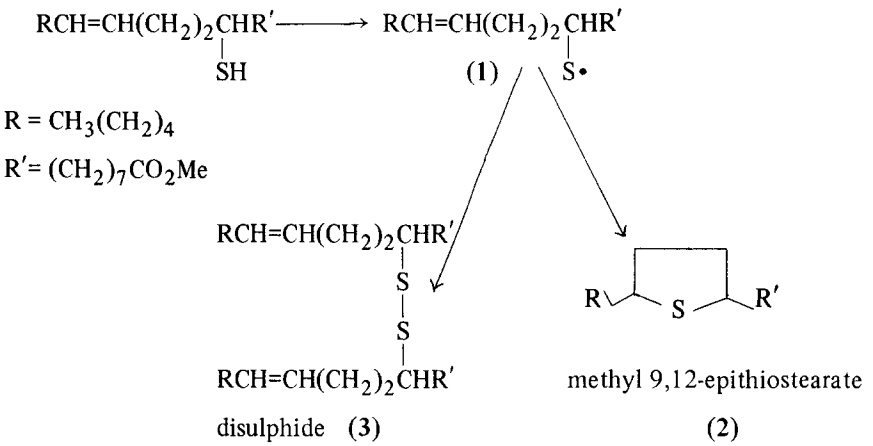
$$RCH(OH)R' \xrightarrow[\text{pyridine}]{CH_3SO_2Cl,} RCH(OMs)R' \xrightarrow[DMF]{KSAc} RCH(SAc)R' \xrightarrow[\text{or NaOMe, MeOH}]{MeOH,\ H_2SO_4} RCH(SH)R'$$

$$RCH{=}CHR' \xrightarrow[(Bu^tO)_2]{CH_3COSH} RCH\underset{SAc}{\overset{H}{\diagup}}CHR' \xrightarrow[\text{or NaOMe, MeOH}]{MeOH,\ H_2SO_4} RCH\underset{SH}{\overset{H}{\diagup}}CHR'$$

(i) The first procedure gave the best results when mesyloxy esters reacted with sodium hydrogen sulphide in dimethylformamide solution at room temperature for about 24 hr. The required thiol was then obtained in ~ 60% yield and the remainder of the product was usually alkene (~ 5%, resulting possibly from an elimination reaction), unchanged mesylate (~ 5%), and disulphide (~ 20%). The last product probably results from oxidation of the thiol and this undesirable reaction might have been reduced by taking greater care to exclude air from the reaction. By this method we prepared methyl 12-mercaptostearate, methyl 9-mercaptostearate, methyl 12-mercapto-oleate, and methyl 12-mercapto-elaidate from the corresponding mesyloxy esters which were themselves obtained from the appropriate and readily-accessible hydroxy esters.

Attempts to isolate the pure mercapto ester by preparative TLC gave a product contaminated with a little alkenoate and this mixture was separated by TLC only after acetylation of the mercapto ester.

In contrast to the reactions with methyl 12-mesyloxyoleate and methyl 12-mesyloxyelaidate, themselves derivatives of β-hydroxy alkenes, a different type of reaction occurred with the mesyl esters of γ- and δ-hydroxy alkenes. When methyl 9-mesyloxyoctadec-12-enoate was treated with sodium hydrogen sulphide the major products were disulphide (15–20%) and the cyclic sulphide, methyl 9,12-epithiostearate (2, 70–75%). We believe that the 9-mercapto ester is first formed and then is readily oxidised to the disulphide (3) or rearranged to the cyclic sulphide (2) via the radical (1). In support of this view we observed some thiol on



immediate examination of the reaction product but this had disappeared after two days. Immediate acetylation of the reaction product gave some methyl 9-acetylmercapto-octadec-12-enoate (55%). Deacetylation ($MeOH, H_2SO_4$) at room temperature gave unchanged ester (60%) and cyclic sulphide (40%) and reaction at reflux temperature gave the cyclic sulphide only.

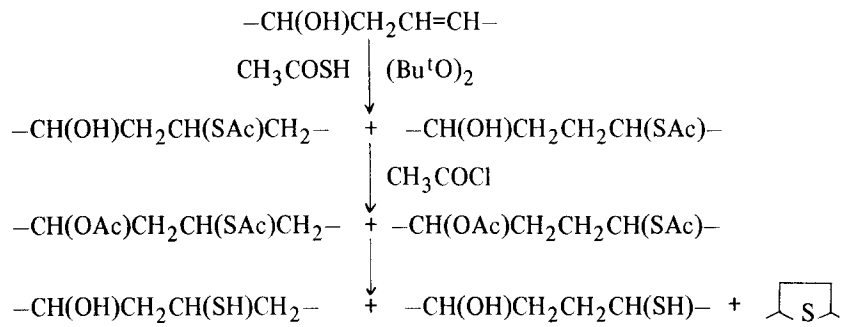
In similar reactions with 1-mesyloxyoctadec-4- and -5-ene the γ-mesyloxy alkene (Δ4) gave disulphide (46%), alkene thiol (14%) and cyclic sulphide (32%, 2-tetradecyltetrahydrothiophen) but the δ-mesyloxy alkene (Δ5) gave disulphide (60%), alkene thiol (30%), and little or no cyclic sulphide.

These results are in contrast to those observed with the analogous oxygen radicals. We have previously shown [7] that the O-radical derived from methyl ricinoleate undergoes cleavage and those derived from γ-hydroxy alkenes produce five and six membered oxygen heterocycles in similar proportions (~ 30% each).

(ii) Reaction of mesyloxy esters with potassium thioacetate in dimethylformamide solution at 100°C for 2–3 hr gave acetylmercapto esters in good yield (50–80%) and mercapto esters were then formed by deacetylation with methanolic sulphuric acid. The mercaptans were accompanied by a little disulphide but this could probably be reduced by employing the reducing conditions developed for preparing the dithiols (see following paper). Methyl 12-mesyloxystearate, methyl 12-mesyloxyoleate, methyl 12-mesyloxyelaidate, methyl 9-mesyloxyoctadec-12-enoate,

1-mesyloxyoctadec-4-ene, and 1-mesyloxyoctadec-5-ene readily furnished the corresponding acetylmercapto derivatives. These were deacetylated to thiols except insofar as cyclic sulphides were formed. Methyl 12-acetylmercapto-elaidate gave thiol along with a little methyl 9,12-epithiostearate (~ 5%). This cyclic sulphide was not observed with the oleate derivative whereas methyl 9-acetylmercapto-octadec-12-enoate gave the cyclic sulphide (2) as the only product. 1-Acetylmercapto-octadec-4-ene (also a γ-acetylmercapto alkene) gave thiol (57%) with some 2-tetradecyltetrahydrothiophen (20%). The Δ5 isomer (a δ-acetylmercapto alkene) gave only thiol and disulphide but the former was rearranged to 2-tridecyltetrahydrothiopyran on treatment with iodine.

(iii) We also examined the peroxide-catalysed addition of thioacetic acid to oleic acid, methyl oleate, methyl ricinoleate, and methyl 9-hydroxyoctadec-12-enoate. The first two gave the 9(10)-acetylmercapto derivatives and thence the 9(10)-thiols as previously reported. Methyl ricinoleate furnished the 9(10)-acetylmercapto-12-hydroxystearates (55%) which were acetylated to the O,S-bisacetyl esters and deacetylated to a mixture of the methyl 12-hydroxy-9(10)-mercaptostearates (~50%) and methyl 9,12-epithiostearate (~ 20%). There was no evidence of any 9,12-epoxystearate.



Methyl 9-hydroxyoctadec-12-enoate reacted in a similar way and furnished methyl 9-hydroxy-12(13)-mercaptostearates(~ 50%) and methyl 9,12-epithiostearates (~ 20%) after deacetylation of the intermediate acetylmercapto hydroxy esters (59%).

Of these three methods we prefer the reaction of mesyloxy esters with potassium thioacetate in dimethylformamide solution followed by deacetylation by alkali in a reducing medium (see following paper).

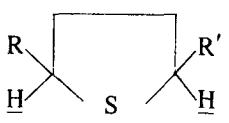
III. Structural indentification of mercapto and epithio esters

A. Infrared spectra

The weak S–H stretching band at 2560 cm^{-1} [3] shown by thiols was not particularly useful for the recognition of monomercapto compounds. More useful information came from the infrared spectra of their acetyl and trifluoroacetyl derivatives and the following C=O stretching frequencies proved to be of great diagnostic value: $SCOCH_3$ 1685, $SCOCF_3$ 1700, $COOCH_3$ 1730, $OCOCH_3$ 1740, and $OCOCF_3$ 1780 cm^{-1}.

B. NMR spectra [6]

The acetyl and trifluoroacetyl derivatives of the mercaptans also provided more informative NMR spectra. Frequent reference is made to the following signals in the experimental section: 6.38 ($C\underline{H}SCOCF_3$), 6.35–6.45 ($C\underline{H}SCOCH_3$), and a singlet at 7.72–7.76τ ($SCOC\underline{H}_3$). The relative areas of the singlets for $COOC\underline{H}_3$ and $SCOC\underline{H}_3$ were useful for checking the number of $SCOCH_3$ groups present. Some characteristic signals were also observed in the spectra of the epithio compounds:



6.45–6.95τ
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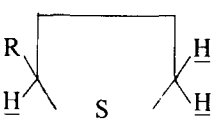
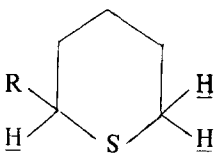


6.68–6.82τ
7.28τ



7.37–7.60τ methine H
8.18τ methylene H

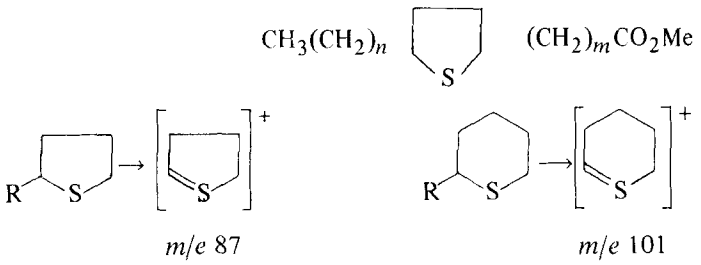
C. Mass spectra [6]

Details of the mass spectra of several mercapto and acetylmercapto esters are given in the appendix. In addition to the loss of 31 (OCH_3) and 32 (CH_3OH) mass units from the ester function the mercapto esters lose 33 (HS) and 34 (H_2S) mass units and the acetylmercapto esters lose 42 (CH_2CO), 43 (CH_3CO), 74 (CH_2COS), 75 (CH_3COS), and 76 (CH_3COSH) mass units.

More usefully, mercapto and acetylmercapto esters give fragments arising from α-cleavage – possibly with additional loss of the fragments noted above – which indicate the position of the sulphur-containing substituent.

$$CH_3(CH_2)_n\underset{\underset{SR}{|}}{\overline{CH}}(CH_2)_mCO_2Me \qquad R = H \text{ or } Ac$$

The cyclic sulphides also undergo α-cleavage to give fragments such as those indicated below. Intense peaks at *m/e* 87 and 101 were indicative of five and six membered rings respectively.



m/e 87 *m/e* 101

D. Gas liquid chromatography

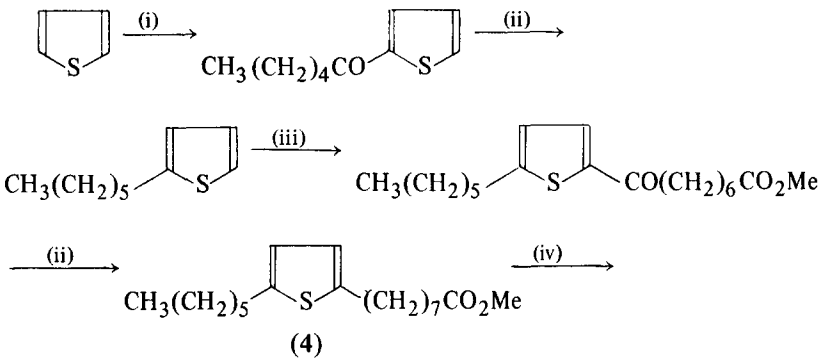
Gas liquid chromatography provides a useful indication of gross structure once a few compounds have been identified by other procedures. Some useful data are collated in table 1.

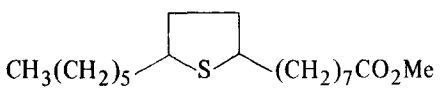
E. Alternative synthesis

The structure of the first cyclic sulphide obtained in this study – methyl 9,12-epithiostearate – was confirmed by an independent synthesis based on the standard thiophen route to saturated fatty acids [8]. The 2,5-disubstituted thiophen (4) is hydrogenated and the tetrahydrothiophen derivative was identical with the product obtained in several of our reactions.

Table 1
ECL of long-chain sulphur-containing compounds.

(i) Monomercapto compounds and their acyl derivatives	SH	$SCOCH_3$	$SCOCF_3$
Methyl 12-mercaptostearate	23.2	25.4	21.5
Methyl 9-mercaptostearate	23.2	25.5	21.7
Methyl 12-mercapto-oleate	23.7	26.0	–
Methyl 12-mercapto-elaidate	23.9	26.1	–
Methyl 9-mercapto-octadec-*cis*-12-enoate	23.6	26.1	–
1-Mercapto-octadec-4-ene	17.8	21.2	–
1-Mercapto-octadec-5-ene	17.8	21.2	–
(ii) Cyclic sulphur derivatives			
Methyl 9,12-epithiostearate		24.2	
2-Tetradecyltetrahydrothiophen		18.6	
2-Tridecyltetrahydrothiopyran		18.1	





methyl 9,12-epithiostearate

(i) $CH_3(CH_2)_4COCl, SnCl_4$; (ii) $N_2H_4, KOH, (HOCH_2CH_2)_2O$;

(iii) $ClCO(CH_2)_6CO_2Me, SnCl_4$; (iv) $H_2, Pd/C$.

IV. Experimental

A. Chromatography and spectroscopy

Thin layer chromatography was effected on thin layers of silica gel G (0.25 mm for analytical purposes and 1.00 mm for preparative purposes). Ether–petroleum mixtures were normally used as developing solvents and abbreviations such as PE20 indicate a mixture of ether (20%) and petroleum (80%) (b.p. 40–60°C) by volume. To observe separation, plates were sprayed with phosphomolybdic acid (10% solution in ethanol) and then heated to 120°C or with 2′,7′-dichlorofluorescein (0.2% solution in methanol). Separated products were eluted from the silica with mixtures of ether and methanol.

A Pye 104 model chromatograph (with FID) was used for gas liquid chromatography. This was fitted with columns of DEGS (20%) packed on HMDS Chromosorb W. Equivalent chain lengths, quoted by comparison with methyl alkanoates [9], are listed in table 1.

Spectra were obtained using a Unicam SP800 (methanol or ethanol solutions), a PE257 grating spectrometer (liquid films or 1% solutions in carbon disulphide or carbon tetrachloride), a Varian HA-100 NMR spectrometer (carbon tetrachloride solutions with tetramethylsilane as internal standard), and an AEI MS902 mass

spectrometer (at 70 eV unless stated otherwise). Mass spectra are reported in the appendix.

B. General chemical procedures and starting materials

Methyl esters were prepared from acids by reaction with methanolic boron trifluoride [10] or with methanolic sulphuric acid (0.25 *M*) or from glycerides by methanolysis with methanolic sodium methoxide (0.1 *M*).

Thiols (1–5 mg) were converted to their trifluoroacetyl derivatives by refluxing for 20–30 min with freshly distilled trifluoroacetic anhydride (0.5 ml). Removal of the excess of anhydride leaves a residue suitable for chromatographic and spectroscopic analysis.

Acetylation occurred when the thiol (50 mg) was refluxed with acetyl chloride (0.5 ml) for 2–3 hr. The product was extracted with ether and purified, when necessary, by prep TLC (PE25). Alternatively the excess of acetyl chloride was removed by evaporation.

Catalytic hydrogenation was effected with 10% palladium on charcoal in methanol solution. Hydrogeneloysis [1] occurred when thiols, sulphides, or disulphides (20 mg) were refluxed with a suspension of freshly prepared Raney nickel (250 mg) in water and ethanol (1 : 3, 4 ml) for 4–5 hr. The product (14 mg) was recovered by extraction with ether. Acids, esters, and glycerides (~ 100 mg) were reduced by lithium aluminium hydride (20 mg) in ether suspension.

Methyl ricinoleate was isolated from castor oil and converted as required to methyl 12-hydroxystearate and methyl 12-hydroxyelaidate [12]. Methyl 9-hydroxyoctadec-12-enoate was isolated from *Strophanthus sarmentosus* seed oil and reduced to methyl 9-hydroxystearate [7]. Oleic acid was obtained from the mixed acids of olive oil by urea fractionation and octadec-4 and 5-enols were prepared from the appropriate synthetic esters by lithium aluminium hydride reduction.

To prepare mesyloxy esters a solution of hydroxy ester (1 g) in pyridine was cooled in ice during the slow addition of methanesulphonyl chloride (0.7 g, 100% excess). The temperature was not allowed to rise above 20°C during this addition nor during a further four hours whilst the solution was stirred. The solution was kept cool during the addition of ice and hydrochloric acid (50 ml, 2*M*). The mesyloxy ester was finally recovered by ether extraction. Its NMR spectrum showed strong singlets at 6.4 ($COOC\underline{H}_3$) and 7.0τ ($OSO_2C\underline{H}_3$).

C. General procedures for making thiols and related compounds

(i) Sodium hydrogen sulphide (500 mg) [13] was swirled in dimethylformamide (5 ml) until the solution developed an intense green colour. Methyl 12-mesyloxystearate (1 g) was then added and the solution kept at room temperature for 24–30 hr during which time the colour faded. After addition of water the reaction mixture was extracted with ether (2 × 30 ml, the solution was usually acidified before the second extraction). The product (870 mg) was separated by preparative

TLC (PE25) into (a) a mixture of methyl alkenoate (~ 5%) and methyl mercaptostearate (~ 60%), (b) disulphide (~ 20%), (c) unreacted mesylate (~ 5%), and (d) an unidentified polar product (~ 10%). The mixture in (a) was separated by preparative TLC only after acetylation.

(ii) Methyl 12-mesyloxyoleate (170 mg) was heated to 100°C with potassium thioacetate (228 mg) [14] in dimethylformamide for 2 hr. After removal of the solvent and extraction with ether (2 × 20 ml) the product (162 mg) was purified by preparative TLC (PE25) to give methyl 12-acetylmercapto-oleate (112 mg, 69%). This was deacetylated by refluxing with methanolic sulphuric acid (1 *M*) for 2 hr to give the mercapto ester accompanied by a little disulphide.

(iii) Oleic acid (2.08 g), thioacetic acid (1.14 g), and di-t-butyl peroxide (150 mg) were heated under nitrogen for two periods of 8 hr and for a further 8 hr after addition of more peroxide (150 mg). The product was extracted with ether and the extract washed successively with water, aq. sodium hydroxide, aq. sodium sulphite, and water. The crude product (2.3 g) was hydrolysed with methanolic potassium hydroxide, esterified with methanolic boron trifluoride, and purified by preparative TLC (PE15) to give methyl 9(10)-mercaptostearate (28%) and a second product (11%) which is probably disulphide. (This procedure is based on directions given by Swern et al. [3].)

D. Methyl 12-mercaptostearate

Treated with sodium hydrogen sulphide, methyl 12-mesyloxystearate (1 g) gave methyl octadecenoate (5%), methyl 12-mercaptostearate (~ 60%), disulphide (~ 20%), unreacted mesylate (5%), and unidentified polar material (10%).

Methyl 12-mesyloxystearate (130 mg) reacted with potassium thioacetate (250 mg) to give methyl 12-acetylmercaptostearate (66%) which was deacetylated to furnish methyl 12-mercaptostearate.

The mercaptostearate displayed an NMR signal at 7.20–7.55τ (–C<u>H</u>(SH)–) and gave methyl stearate on hydrogenolysis.

Methyl 12-acetylmercaptostearate also gave methyl stearate on hydrogenolysis. It showed a C=O stretching band at 1685 cm^{-1} ($SCOCH_3$) and NMR signals at 6.4 (–C<u>H</u>(SAc)–) and 7.72 τ (s, –SCOC<u>H</u>$_3$).

Methyl 12-trifluoroacetylmercaptostearate had a C=O stretching band at 1700 cm^{-1} ($SCOCF_3$).

When reduced by lithium aluminium hydride both the disulphide and methyl 12-mercaptostearate gave 12-mercapto-octadecanol. Its bistrifluoroacetyl derivative showed infrared absorption at 1780 ($OCOCF_3$) and 1700 cm^{-1} ($SCOCF_3$) and NMR signals at 5.75 (–C<u>H</u>$_2$OCOCF$_3$) and 6.38 τ (–C<u>H</u>(SCOCF$_3$)–). The disulphide gave methyl stearate on hydrogenolysis. On reaction with iodine methyl mercaptostearate was oxidised to the disulphide.

E. Methyl 9-mercaptostearate

After reaction with sodium hydrogen sulphide (100 mg), methyl 9-mesyloxystearate (100 mg) furnished a product (80 mg) which contained methyl 9-mercaptostearate (~ 47%) and its disulphide (~ 23%). Both of these gave methyl stearate when submitted to hydrogenolysis.

The mercapto ester was converted to its S-acetyl and S-trifluoroacetyl derivatives. These showed infrared absorption at 1685 ($SCOCH_3$) and 1700 cm^{-1} ($SCOCF_3$) respectively and the former had NMR signals at 6.40–6.44 (–C<u>H</u>(SAc)–) and 7.72τ (–SCOC<u>H</u>$_3$).

F. Methyl 12-mercapto-oleate

Methyl 12-mesyloxyoleate (500 mg) and sodium hydrogen sulphide (300 mg) gave a product (425 mg) containing methyl 12-mercapto-oleate (50–55%) and its disulphide (25–30%).

The mesyloxyoleate (170 mg) and potassium thioacetate (228 mg) reacted to give a product (162 mg) which was mainly methyl 12-acetylmercapto-oleate (112 mg). This was hydrolysed to the mercapto ester.

The mercapto ester gave methyl stearate on hydrogenolysis, nonanedioic acid as the only dibasic acid after von Rudloff oxidation [15], and showed an NMR signal at 7.1–7.4τ (–C<u>H</u>(SH)–).

Its S-acetyl derivative had NMR signals at 6.45–6.80 (–C<u>H</u>(SAc)–) and 7.72τ (–SCOC<u>H</u>$_3$) and infrared absorption at 1685 cm^{-1} ($SCOCH_3$) but not at 970 cm^{-1} (no *trans* unsaturation).

The disulphide, which gave methyl stearate on hydrogenolysis, could be produced from the mercapto ester by oxidation with iodine. Both the mercapto ester and its disulphide were reduced by lithium aluminium hydride to 12-mercapto-octadec-*cis*-9-enol which formed a bistrifluoroacetyl derivative (ECL 20.3) having NMR signals at 5.70 (–C<u>H</u>$_2$OCOCF_3), 6.35 (–C<u>H</u>(SCOCF_3)–), 7.62 (–CH(SCOCF_3)C<u>H</u>$_2$ CH=CH–), and 8.00τ (–CH=CHC<u>H</u>$_2$–) and infrared absorption at 1780 ($OCOCF_3$) and 1700 cm^{-1} ($SCOCF_3$).

G. Methyl 12-mercapto-elaidate

Methyl 12-mesyloxyelaidate (90 mg) and sodium hydrogen sulphide (50 mg) gave methyl 12-mercapto-elaidate isolated as its acetyl derivative (72 mg).

With potassium thioacetate (114 mg), the mesyloxyester (100 mg) gave methyl acetylmercapto-elaidate (112 mg), which was purified by preparative TLC. Deacetylation with methanolic sulphuric acid (1 *M*) furnished the mercapto ester and its disulphide.

The S-acetyl ester showed infrared peaks at 1685 ($SCOCH_3$), 1735 ($COOCH_3$), and 970 cm^{-1} (*trans* –CH=CH–). Prolonged acid hydrolysis (2 hr) gave disulphide,

mercapto ester, methyl octadecadienoate, and an additional component (~ 5%) which, on the basis of its GLC behaviour, may have been methyl 9,12-epithiostearate (There was no sign of this component when methyl 12-acetylmercapto-oleate was treated in a similar way.)

H. Methyl 9,12-epithiostearate

When methyl 9-mesyloxyoctadec-12-enoate (500 mg) reacted with sodium hydrogen sulphide (300 mg) the major product (70–75%) was methyl 9, 12-epithiostearate on the basis of the following evidence.

(i) Hydrogenolysis gave methyl stearate. (ii) There was chromatographic and spectroscopic evidence that the product was unchanged after treatment with acetyl chloride or trifluoroacetic anhydride. (iii) Unlike 1,2-epithio compounds the compound was not desulphurised on reaction with methyl iodide and dry acetone [16]. (iv) Combustion analysis: Found C, 69.35; H, 10.96%; Calc. for $C_{19}H_{36}O_2S$: C, 69.47; H, 11.05%. (v) The NMR spectrum contained signals at 6.45–6.95τ (–C<u>H</u>CH$_2$CH$_2$C<u>H</u>(S)–). (vi) MS results: see the appendix. (vii) Comparison with an authentic sample prepared by an alternative route (see below).

When the preparation was repeated in the presence of antioxidant (BHT) and the reaction product immediately subjected to acetylation, GLC indicated the presence of both methyl epithiostearate (36%) and methyl 9-acetylmercapto-octadec-12-enoate (18%).

J. Methyl 9-acetylmercapto-octadec-12-enoate

This compound (147 mg), formed by heating potassium thioacetate (300 mg) and methyl 9-mesyloxyoctadec-12-enoate (270 mg), had a strong infrared absorption band at 1685 cm^{-1} and NMR signals at 6.4–6.6 (–C<u>H</u>(SAc)–) and 7.74τ (–SCOC<u>H</u>$_3$).

The acetylmercapto ester (109 mg) was refluxed with methanolic sodium methoxide (0.25 *M*, 5 ml) in the presence of Zn/Hg for 2 hr and diluted with degassed water before acidification and extraction. The resulting methyl 9-mercapto-octadec-12-enoate gave a single spot on TLC (71 mg) but two peaks on GLC of ECL 23.6 (20%, mercapto ester) and 24.2 (76%, epithiostearate). Its NMR spectrum contained signals at 4.72 (–C<u>H</u>=C<u>H</u>–) and 7.32τ (–C<u>H</u>(SH)–).

After reaction with methanolic sulphuric acid (1 *M*) at room temperature for 16 hr the acetylmercapto ester was partly converted to methyl 9,12-epithiostearate. This change was complete when the reaction was conducted at reflux temperature for 3 hr.

K. Methyl 9(10)-mercaptostearate

Oleic acid (2.08 g), thioacetic acid (1.14 g) and di-t-butyl-peroxide (two lots of

150 mg), reacted as described under the general procedures (Section IVC (iii)), gave a crude acetylmercaptostearic acid (2 g). After deacetylation and esterification, the product (1.13 g) contained methyl 9(10)-mercaptostearate (28%) and disulphide (11%) which were separated by preparative TLC (PE15).

Methyl oleate (960 mg) and thioacetic acid (530 mg), similarly treated in the presence of di-t-butyl-peroxide (100 + 200 mg), gave a product (970 mg) which furnished methyl 9(10)-acetylmercaptostearate (36%) when purified by preparative TLC (PE20).

After hydrolysis (aqueous methanolic potassium hydroxide) and re-esterification (methanolic boron trifluoride) the acetylmercapto ester was converted to methyl 9(10)-mercaptostearate (45%) and some disulphide (15%). Both products gave methyl stearate on hydrogenolysis.

The mixed acetylmercapto esters showed infrared absorption at 1685 ($SCOCH_3$) and 1735 cm^{-1} ($COOCH_3$) and an NMR signal at 7.72τ ($-SCOCH_3$). In the mercapto esters there was an NMR signal at 7.25–7.65τ (–C<u>H</u>(SH)–).

L. Methyl 12-hydroxy-9(10)-mercaptostearate

Methyl ricinoleate (2 g), thioacetic acid (1 g), and di-t-butyl peroxide 150 and 200 mg) heated to 60°C for 5 hr gave a product (2.26 g) from which methyl 9(10)-acetylmercapto-12-hydroxystearate (55%) was isolated by preparative TLC (PE25). This showed infrared absorption at 1685 ($SCOCH_3$), 1735 ($COOCH_3$) and 3500 cm^{-1} (OH) and NMR signals at 6.35 (–C<u>H</u>(SAc)– and –C<u>H</u>(OH)–), 7.73 (–SCOC<u>H</u>$_3$), and 8.25τ [–CH(OH)C<u>H</u>$_2$CH(SAc)–].

With methanolic sodium methoxide this (60 mg) gave the hydroxy mercapto ester mixture (52 mg) which was examined as a bistrifluoroacetyl derivative.

With boiling methanolic sulphuric acid the acetylmercapto hydroxy ester (113 mg) gave a mixture (93 mg) containing methyl 9,12-epithiostearate (~ 20%) and methyl 12-hydroxy-9(10)-mercaptostearate (~ 50%). The latter formed a bistrifluoroacetyl derivative.

The bistrifluoroacetyl compound showed three peaks on GLC (ECL 22.7, 23.0, and 23.5) and had infrared absorption bands at 1700 ($SCOCF_3$) 1735 ($COOCH_3$) and 1770 cm^{-1} ($OCOCF_3$).

The bisacetyl esters showed infrared absorption bands at 1685 ($SCOCH_3$) and 1735 cm^{-1} ($COOCH_3$ and $OCOCH_3$) and NMR signals at 6.4–6.8 (–C<u>H</u>(SAc)– and –C<u>H</u>(OAc)–), 7.72 (–SCOC<u>H</u>$_3$), 8.04 (–OCOC<u>H</u>$_3$), and 8.28τ (–CH(OAc)C<u>H</u>$_2$CH(SAc)–).

M. Methyl 9-hydroxy-12(13)-mercaptostearate

Methyl 9-hydroxyoctadec-12-enoate (635 mg), thioacetic acid (500 mg), and di-t-butyl peroxide (200 mg), reacted in the usual manner, gave a product (750 mg) which was mainly methyl 12(13)-acetylmercapto-9-hydroxystearate (464 mg, 59%)

This was deacetylated (methanolic sodium methoxide) to the hydroxy mercapto esters which were examined as their bisacetyl and bistrifluoroacetyl derivatives.

Refluxed with methanolic sulphuric acid (2.5 *M*, 12 ml) for 2 hr the acetylmercapto hydroxy esters (137 mg) gave a product (102 mg) containing both methyl 9,12-epithiostearate (~ 20%) and methyl 9-hydroxy-12(13)-mercaptostearate (~ 50%). The latter mixture was converted to its bisacetyl and bistrifluoroacetyl derivatives.

The methyl 12(13)-acetylmercapto-9-hydroxystearates had carbonyl stretching bands at 1685 ($SCOCH_3$) and 1735 cm^{-1} ($COOCH_3$) and O–H stretching absorption at 3500 cm^{-1} in the infrared spectrum and NMR signals at 6.4–6.8 (–C<u>H</u>(SAc)– and –C<u>H</u>(OH)–) and 7.72τ (–SCOC<u>H</u>$_3$).

The bisacetyl esters had infrared absorption bands at 1685 ($SCOCH_3$) and 1735 cm^{-1} ($COOCH_3$ and $OCOCH_3$) and NMR signals at 6.4–6.8 (–C<u>H</u>(SAc)– and –C<u>H</u>(OAc)–), 7.72 (–SCOC<u>H</u>$_3$) and 8.05τ (–OCOC<u>H</u>$_3$).

The bistrifluoroacetyl esters (ECL 22.7, 23.0, and 23.3) had infrared absorption at 1700 ($SCOCF_3$), 1735 ($COOCH_3$) and 1770 cm^{-1} ($OCOCF_3$).

N. 1-Mercapto-octadec-4-ene and 2-tetradecyltetrahydrothiophen

1-Mesyloxyoctadec-4-ene (168 mg), reacted with sodium hydrogen sulphide (100 mg) in the usual way, gave a product (148 mg) which contained 1-mercapto-octadec-4-ene (14%), the corresponding disulphide (46%), and 2-tetradecyltetrahydrothiophen (32%).

With potassium thioacetate (100 mg), 1-mesyloxyoctadec-4-ene (130 mg) furnished a product (128 mg) which was mainly 1-acetylmercapto-octadec-4-ene (112 mg). With refluxing methanolic sulphuric acid it gave the mercaptan (57%) and some cyclic sulphide (20%).

The mercaptan gives two peaks on GLC (17.8 and 18.6). Since there is only one peak after acetylation it is concluded that there is some formation of cyclic sulphide (18.6) during chromatography. The mercaptan displays NMR signals at 7.3–7.7 (–C<u>H</u>$_2$SH) and 8.30τ (=CHCH$_2$C<u>H</u>$_2$CH$_2$SH). On standing in ether at room temperature the thiol is slowly converted over 7 days to a mixture of disulphide and cyclic sulphide.

The disulphide is reduced by lithium aluminium hydride to the thiol which is accompanied by a little cyclic sulphide.

1-Acetylmercapto-octadec-4-ene has an absorption band at 1685 cm^{-1} ($SCOCH_3$) in its infrared spectrum and signals at 7.20 (–C<u>H</u>$_2$SCOCH$_3$), 7.74 (–SCOC<u>H</u>$_3$), and 8.41τ (=CHCH$_2$C<u>H</u>$_2$CH$_2$SCOCH$_3$) in its NMR spectrum.

2-Tetradecyltetrahydrothiophen shows NMR signals at 6.66–6.82 (C(2) proton), 7.28 (C(5) protons), and 8.04τ (C(3) and C(4) protons) but no signal for olefinic protons.

P. 1-Mercapto-octadec-5-ene and 2-tridecyltetrahydrothiopyran

(i) 1-Mesyloxyoctadec-5-ene (153 mg) and sodium hydrogen sulphide (90 mg) gave a product (138 mg) which contained 1-mercapto-octadec-5-ene (30%), its disulphide (60%, reduced by lithium aluminium hydride to the thiol), and only a little (3%) of what might be the cyclic sulphide.

(ii) With potassium thioacetate (110 mg) the mesyloxy alkene (140 mg) gave a product (128 mg) which was mainly 1-acetylmercapto-octadec-5-ene (115 mg). When refluxed with methanolic sulphuric acid this furnished the thiol which was converted by an ethanolic solution of iodine (0.05 *M*, 40 hr, room temperature) to a mixture of disulphide and 2-tridecyltetrahydrothiopyran. On standing in ether solution at room temperature the thiol was slowly converted over 7 days to a mixture of disulphide and cyclic sulphide.

The thiol showed NMR signals at 7.3–7.7 ($-C\underline{H}_2SH$) and 8.4–8.5 τ ($=CHCH_2C\underline{H}_2C\underline{H}_2CH_2SH$). The S-acetyl derivative had infrared absorption at 1685 cm^{-1} ($SCOCH_3$) and an NMR signal at 7.76 τ ($-SCOC\underline{H}_3$).

The cyclic sulphide showed NMR signals at 7.4–7.6 (C(2) proton) and at 8.18 τ (C(6) protons).

Q. Synthesis of methyl 9,12-epithiostearate from thiophen

A mixture of hexanoyl chloride (20 g), thiophen (14 g), and benzene (170 ml) was kept at 0–5°C during the addition of freshly distilled stannic chloride (44 g) over 30 min. The cooling bath was removed, the mixture stirred for 1 hr, and then cooled again during acidification with hydrochloric acid (1 *M*, 110 ml). The benzene extract furnished 2-hexanoylthiophen (22 g, 82%, b.p. 116–118°C/2 mm, lit. 117–119/1 mm [17]; Found: C, 66.08; H, 8.03; Calc. for $C_{10}H_{14}OS$: C, 65.92; H, 7.74%), which showed an infrared absorption band at 1660 cm^{-1} and NMR signals at 2.35–2.55 (C(3) and C(5) protons), 2.96 (C(4) proton), 7.20 ($-C\underline{H}_2CO-$), and 8.30 τ ($-C\underline{H}_2CH_2CO-$).

The ketone (15 g) was reduced by stirring at 120°C for 30 min with hydrazine hydrate (17 g) in diethylene glycol (200 ml) and then at 150–155°C for 1 hr after addition of potassium hydroxide (15 g) in hot diethylene glycol (100 ml). Volatile material was distilled, the internal temperature rose to 190°C, and stirring was continued at this temperature for 3 hr. The reaction mixture was then poured on to ice, acidified with hydrochloric acid (2 *M*), and the product recovered by extraction with chloroform to give 2-hexylthiophen (12.6 g, 90%, b.p. 58–59°C/0.5 mm, lit. 79–82/1 mm [15]; Found: C, 71.29; H, 9.54; Calc. for $C_{10}H_{16}S$: C, 71.36; H, 9.59%) which shows NMR signals at 3.03 (C(5) proton), 3.21 (C(4) proton), 3.34 (C(3) proton), 7.20 ($C\underline{H}_2C(S)=$), and 8.40 τ ($-C\underline{H}_2CH_2C(S)=$).

Hexylthiophen (1.2 g) was reacted with 7-carbomethoxyheptanoyl chloride (4 g) in benzene (15 ml) in the presence of stannic chloride as already described. The product (5.5 g) after purification by chromatography gave methyl

8-(2′-5′-hexylthienyl)-8-oxo-octanoate (1.6 g) with infrared absorption at 1660 cm^{-1} and NMR signals at 2.58 (C(3′) proton), 3.30 (C(4′) proton), 7.20 ($-COC\underline{H}_2-$), 7.26 ($-C\underline{H}_2C(S)=$) and 8.38 τ ($-COCH_2C\underline{H}_2-$).

The oxo ester (550 mg) was reduced with hydrazine hydrate (2 g) in diethylene glycol (7 ml) as described above and the product (530 mg) was purified by preparative TLC to furnish methyl 8-(2′-5′hexylthienyl) octanoate (360 mg, ECL 23.5), with NMR signals at 3.58 (C(3′) and C(4′) protons), 7.30 ($-C\underline{H}_2C(S)=$), and 8.44 τ ($-C\underline{H}_2CH_2C(S)=$).

Palladium charcoal (10%, 500 mg), previously saturated with hydrogen at atmospheric pressure, the thiophen (180 mg), and methanol containing a trace of conc. sulphuric acid were shaken for 24 hr. GLC showed the presence of a new compound (5%, ECL, 24.2). Additional catalyst was added at daily intervals and the reduction continued for four days. The product was then separated by preparative TLC (PE25) into methyl stearate (30%) and methyl 9,12-epithiostearate (50%) with NMR signals at 6.45–6.95 τ ($-C\underline{H}SC\underline{H}-$).

Acknowledgements

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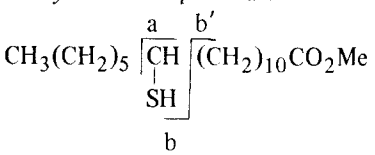
Appendix. Mass spectra of some mercapto C_{18} esters and related compounds

In the following data major peaks (m/e) are reported along with peak intensity relative to the base peak (100) and, where possible, a tentative explanation of the origin of the peak. Fragments from the series $(CH_2)_nCO_2Me$, C_nH_{2n+1}, and C_nH_{2n-1} are also generally present. The more commonly eliminated fragments are:

−18 loss of H_2O
−31 loss of CH_3O
−32 loss of CH_3OH
−33 loss of HS
−34 loss of H_2S
−42 loss of CH_2CO
−43 loss of CH_3CO
−50 loss of H_2O and CH_3OH
−52 loss of H_2O and H_2S
−60 loss of H_2O and CH_2CO
−61 loss of H_2O and CH_3CO
−64 loss of CH_3. and HS

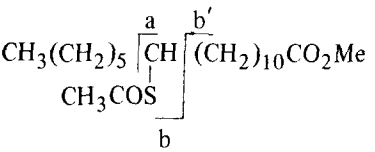
−65 loss of CH_3O and H_2S or CH_3OH and HS
−66 loss of CH_3OH and H_2S
−73 loss of CH_3O and CH_2CO
−74 loss of CH_2COS (or $C_3H_6O_2$)
−75 loss of CH_3COS
−76 loss of CH_3COSH
−92 loss of H_2O, CH_3O, and CH_3CO
−106 loss of CH_3O and CH_3COS or CH_3OH and CH_2COS
−107 loss of CH_3O and CH_3COSH or CH_3OH and CH_3COS
−108 loss of CH_3OH and CH_3COSH or H_2S and $C_3H_6O_2$
−150 loss of $C_3H_6O_2$ and CH_3COSH

1. Methyl 12-mercaptostearate



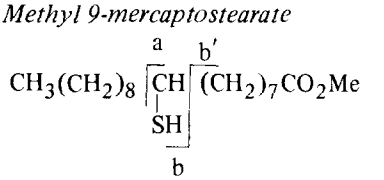
Peaks at: 330 (M, 12), 299 (M−31, 6), 298 (M−32, 6), 297 (M−33, 12), 296 (M−34, 6), 265 (M−65, 21), 264 (M−66, 36), 222 (M−108, 9), 213 (a−32, 12), 200 (b′+1, 4), 199 (b′, 4), 131 (b, 5), and 74 ($C_3H_6O_2$, 64), base peak at 55.

2. Methyl 12-acetylmercaptostearate



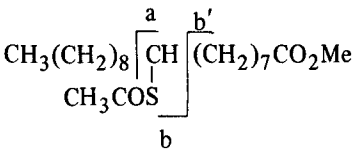
Peaks at: 372 (M, 3), 330 (329 + 1, 22), 329 (M−43, 100), 299 (M−73, 30), 298 (M−74, 20), 297 (M−75, 100), 296 (M−76, 13), 264 (M−107, 30), 264 (M−108, 50), 222, (M−150, 11), 213 (a−74, 19), 200 (b′+1, 3), 199 (b′, 5), and 131 (b−42, 15).

3. Methyl 9-mercaptostearate



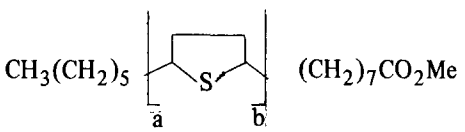
Peaks at: 330 (M, 9), 299 (M−31, 7), 298 (M−32, 6), 297 (M−33, 20), 296 (M−34, 6), 266 (M−64, 9), 265 (M−65, 16), 264 (M−66, 40), 222 (M−108, 10), 173 (b, 6), 171 (a−32, 12), 158 (b′+1, 4), 157 (b, 4), 141 (b−32, 5), 74 ($C_3H_6O_2$, 72), base peak at 55.

4. Methyl 9-acetylmercaptostearate



Peaks at: 372 (M, 1), 330 (329+1, 8), 329 (M–43, 39), 299 (M–73, 13), 298 (M–74, 9), 297 (M–75, 35), 296 (M–76, 13), 264 (M–107, 13), 264 (M–108, 17), 222 (M–150, 7), 173 (b–42, 7), 171 (a–74, 13), 158 (b′+1, 2), 157 (b′, 4), base peak at 57.

5. Methyl 9,12-epithiostearate

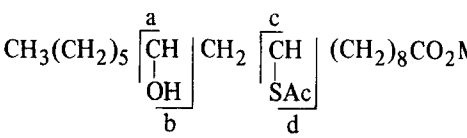


The four figures for peak intensity were derived from four different preparations of this epithio ester. These were: product of reaction of methyl 9-mesyloxyoctadec-12-enoate and sodium hydrogen sulphide, acidic methanolysis of methyl 9-acetylmercapto-12-hydroxystearate, acidic methanolysis of methyl 12-acetylmercapto-9-hydroxystearate, synthetic sample from thiophen.

Peaks at: 328 (M, 40, 28, 28, 27), 297 (M–31; 27, 17, 16, 16), 243 (a; 57, 40, 38, 38), 211 (a–32; 68, 50, 30, 50), 173 (b+2; 11, 7, 8, 15), 172 (b+1; 25, 14, 13, 17), 171 (b; 100, 100, 100, 100), and 87 (c; 96, 70, 50, 97).

Fragment c(m/e = 87) is probably the ion C_4H_7S resulting after α-cleavage a and b with addition of hydrogen.

6. Methyl 9(10)-acetylmercapto-12-hydroxystearate



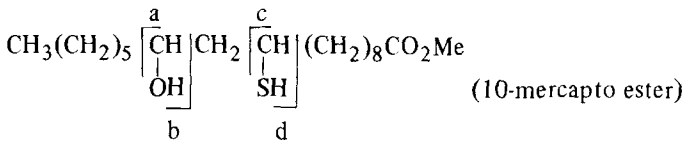
(10-acetylmercapto ester)

Peaks at: 389 (M+1, 25), 371 (389–18, 47), 329 (389–60, 19), 328 (389–61 or M–60, 9), 327 (M–61, 42), 312 (M–76, 9), 311 (?, 38), 297 (371–74, 9), 295 (371–76, 10), 243 (a–60, 25), 115 (b, 7), 97 (b–18, 25), base peak at 55.

185 (c–74, 4), 153 (c–106, 5), 143 (d–74, 13) from the 10-acetylmercapto isomer.

171 (c–74 and/or d–60, 15), 139 (c–106, 3) from the 9-acetylmercapto isomer.

7. Methyl 12-hydroxy-9(10)-mercaptostearate



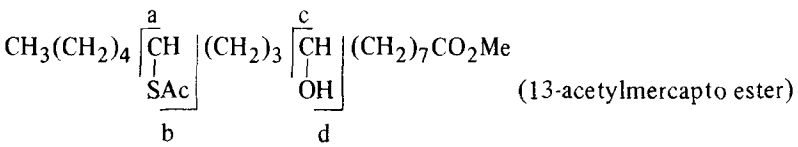
(10-mercapto ester)

Peaks at: 328 (M−18, 7), 297 (328−31, 5), 243 (a−18, 13), 211 (a−50, 11), 143 (?, 30), 115 (b, 8), 97 (b−18, 15) along with peaks of the series $(CH_2)_nCO_2Me$, C_nH_{2n-1}, and C_nH_{2n-3}, base peak at 55.

183 (c−34, 5), 157 (d−18, 1), 151 (c−66, 6), 123 (d−52, 4) from the 10-mercapto ester.

171 (c−32 and/or d−18, 42), 169 (c−34, 3), 137 (c−66 and/or d−52, 5) from the 9-mercapto ester.

8. Methyl 12(13)-acetylmercapto-9-hydroxystearate



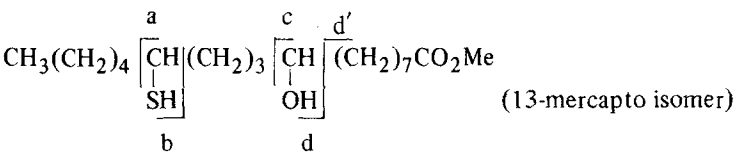
(13-acetylmercapto ester)

Peaks at: 389 (M+1, 11), 371 (389−18, 30), 329 (389−60, 24), 328 (389−61 and/or M−60, 20), 327 (M−61, 52), 312 (M−76, 10), 311 (?, 44), 297 (371−74, 22), 295 (371−76, 18), 213 (d−18, 8), 200 (?, 18), 187 (c, 12), 185 (?, 4), 171 (d−60, 80), 155 (c−32, 30), 143 (?, 22), 137 (c−50, 8), base peak at 55.

257 (a−60, 5), 243 (a−74, 6), 225 (a−92, 5), 159 (b, 6), 117 (b−42, 8), from the 13-acetylmercapto ester.

243 (a−60, 6), 229 (a−74, 1). 211 (a−92, 1), 173 (b, 8), 131 (b−42, 14), from the 12-acetylmercapto ester.

9. Methyl 9-hydroxy-12(13)-mercaptostearate



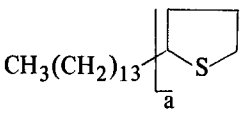
(13-mercapto isomer)

Peaks at: 328 (M−18, 21), 297 (328−31, 15), 295 (328−33, 15), 263 (297−34 and/or 295−32, 12), 213 (?, 12), 189 (d, 5), 187 (c, 9), 185 (?, 15), 171 (d−18, 57), 169 (c−18, 5), 157 (d′, 33), 155 (c−32 and/or d−34, 51), 153 (?, 18), 143 (?, 15) 138(?, 15) 137 (c−50 and/or d−52, 15), 135 (?, 11), base peak at 55.

257 (a−18, 18), 243 (a−32, 15), 225 (a−50, 39), 117 (b, 9), 83 (b−34, 75) from the 13-mercapto isomer.

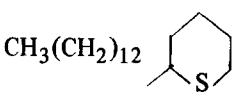
243 (a–18, 15), 211 (a–50, 15), 131 (b, 9), 97 (b–34, 57) from the 12-mercapto isomer.

10. 2-Tetradecyltetrahydrothiophen



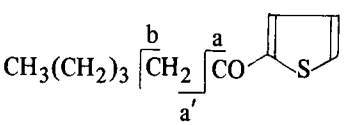
Peaks at: 284 (M, 22) and 87 (a, 100) along with peaks of the series C_nH_{2n+1} and C_nH_{2n-1}.

11. 2-Tridecyltetrahydrothiopyran



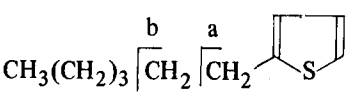
Peaks at: 284 (M, 15) and 101 (a, 100) along with peaks of the series C_nH_{2n+1} and C_nH_{2n-1}.

12. 2-Hexanoylthiophen



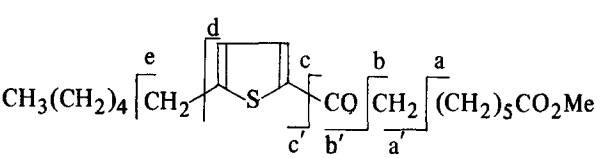
Peaks at: 182 (M, 6), 126 (b+1, 10), 111 (a, 12), 71 (a′, 90), base peak at 57.

13. 2-Hexylthiophen



Peaks at: 168 (M, 27), 153 (?, 7), 111 (b, 7), 99 (a+2, 11), 98 (a+1, 50), and 97 (a, 100).

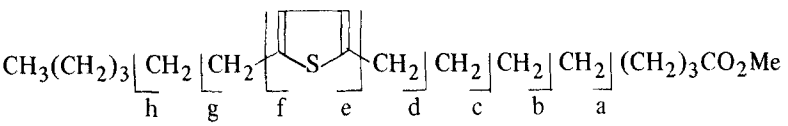
14. Methyl 8-(2′, 5′-hexylthienyl)-8-oxo-octanoate



Peaks at: 338 (M, 28), 306 (M–32, 20), 267 (e, 4), 253 (d, 20), 223 (?, 24), 211 (a′+2, 48), 210 (a′+1, 100), 198 (?, 18), 197 (b′+2, 32), 196 (b′+1, 95), 157 (c′, 6), 140 (f + 2, 18), 139(c–32 and/or f+1, 94), 138(f, 28), 126 (g+2, 6), 125 (g+1, 14), 124 (g, 15), 111 (b–32, 30), 97 (a–32, 42), 96 (?, 22).

[f is the central unit remaining after β-cleavages a and e, g is the central unit remaining after two α-cleavages d and a or e and b.]

15. Methyl 8-(2′,5′-hexylthienyl) octanoate



Peaks at: 325 (M+1, 80), 324 (M, 94), 294 (325–31, 22), 293 (M–31, 96), 267 (h, 20), 264 (?, 18), 255 (g+2, 20), 254 (g+1, 58), 253 (g, 96), 239 (f, 28), 223 (a, 20), 221 (g–32, 20), 209 (b, 20), 207 (f–32, 28), 197 (c+2, 18), 196 (c+1, 14), 195 (c, 76), 183 (d+2, 52), 182 (d+1, 96), 181 (d, 100), 169 (e+2, 24), 168 (e+1, 26), 167 (e, 96), and many peaks below 150.

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