[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY][1]

Organic Sulfur Derivatives. V.[2] Preparation and Properties of Some Long-Chain Mercapto Acids and Related Compounds[3]

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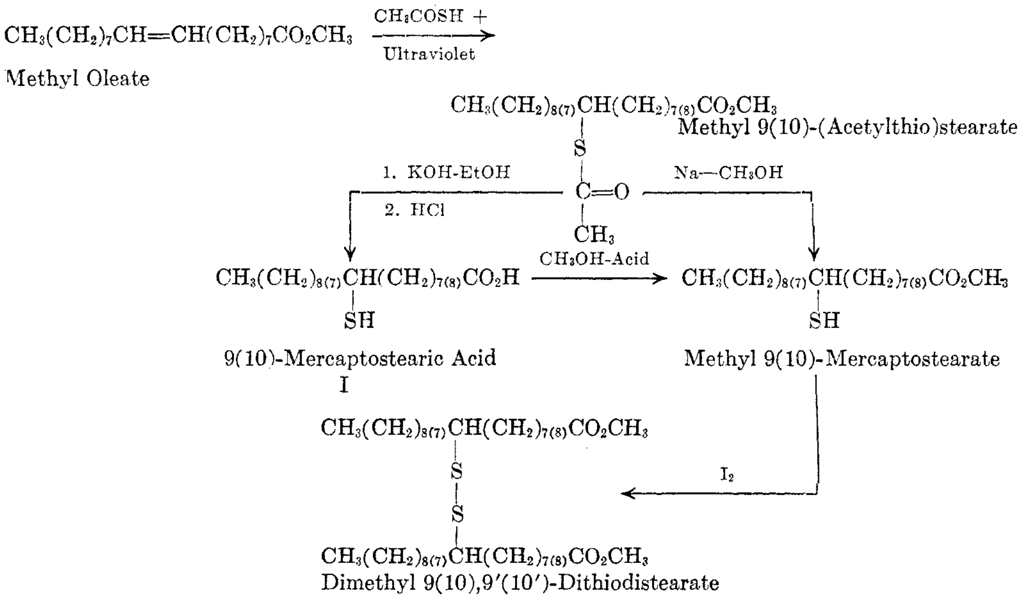
Fatty acids and their methyl esters have been prepared with a mercapto substituent in the center of the chain (I), alpha to the carboxyl or carbomethoxy group (II), and in the terminal position (III). The first and third types have been prepared by free-radical addition of thiolacetic acid to the appropriate olefinic acid followed by hydrolysis, whereas the second type has been prepared by reaction of the corresponding bromo acid with thiourea. Oxidation of the mercapto compounds with iodine yielded the corresponding disulfide derivatives. Chemical, physical, and spectral properties of the various sulfur derivatives have been determined. Infrared and ultraviolet spectra have also been obtained on several short-chain and hydroxy analogs. The mercapto group can be titrated with alcoholic sodium hydroxide when it is alpha to an ester group but not if it is alpha to a free carboxyl group. When the mercapto group is in the alpha position, the methyl ester absorption bands in the infrared region are shifted.

Addition of thiolacetic acid to monounsaturated long-chain compounds under free-radical conditions forms thiolacetates,[6] which can be hydrolyzed to mercaptans.[7] Mercapto acids can also be formed by the reaction of thiourea with bromo substituted fatty acids.[8] In the present investigation, the mercapto group has been substituted at different locations on the hydrocarbon chain of long-chain fatty acids or esters and the resulting effects on the physical, chemical, and spectral properties have been studied. Disulfides have also been prepared and studied. Short-chain analogs and related hydroxy compounds have been examined as well.

The compounds studied in this investigation were prepared by the following reactions:



Also prepared were the methyl esters of the last two compounds shown. Noteworthy is the conversion of methyl 9(10)-(acetylthio)stearate to the corresponding methyl mercaptostearate by alcoholysis with methanol containing small quantities of sodium. This procedure is much more convenient than hydrolysis and reesterification.

Of the sulfur-containing long-chain compounds just listed, 2-mercaptostearic acid and 11-mercaptoundecanoic acid are known substances.[8] The former has now been made by an improved procedure and the latter by a new route, the hydrolysis of 11-(acetylthio)undecanoic acid as shown. 9(10)-Mercaptostearic acid had been previously prepared

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[3] Presented in part at the 133rd meeting of the American Chemical Society, April 13–18, 1958, San Francisco, Calif.

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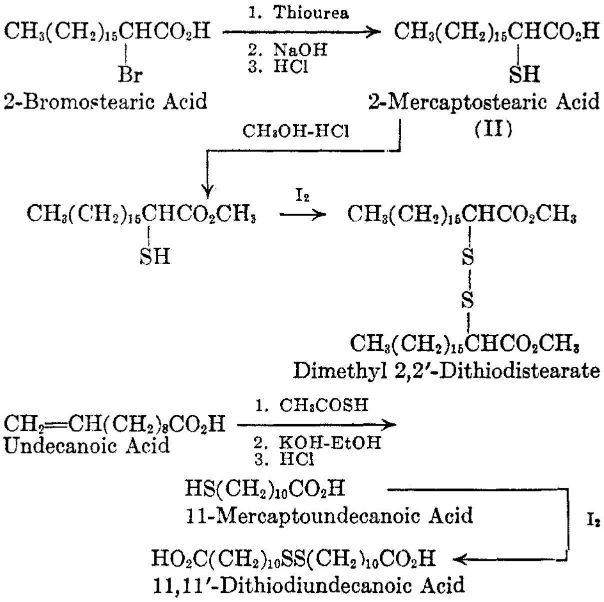
[6] N. H. Koenig and D. Swern, *J. Am. Chem. Soc.*, **79**, 4235 (1957).

[7] F. G. Bordwell and W. A. Hewett, *J. Am. Chem. Soc.*, **79**, 3493 (1957).



$$\underset{\text{2-Bromostearic Acid}}{CH_3(CH_2)_{15}\underset{\substack{|\\ Br}}{C}HCO_2H} \xrightarrow[\text{2. NaOH}\ \text{3. HCl}]{\text{1. Thiourea}} \underset{\text{2-Mercaptostearic Acid (II)}}{CH_3(CH_2)_{15}\underset{\substack{|\\ SH}}{C}HCO_2H}$$

$$\xrightarrow{CH_3OH\text{-}HCl} CH_3(CH_2)_{15}\underset{\substack{|\\ SH}}{C}HCO_2CH_3 \xrightarrow{I_2} \underset{\text{Dimethyl 2,2'-Dithiodistearate}}{\begin{matrix} CH_3(CH_2)_{15}CHCO_2CH_3 \\ | \\ S \\ | \\ S \\ | \\ CH_3(CH_2)_{15}CHCO_2CH_3 \end{matrix}}$$

$$\underset{\text{Undecanoic Acid}}{CH_2{=}CH(CH_2)_8CO_2H} \xrightarrow[\text{2. KOH-EtOH}\ \text{3. HCl}]{\text{1. CH}_3\text{COSH}} \underset{\text{11-Mercaptoundecanoic Acid}}{HS(CH_2)_{10}CO_2H} \xrightarrow{I_2} \underset{\text{11,11'-Dithiodiundecanoic Acid}}{HO_2C(CH_2)_{10}SS(CH_2)_{10}CO_2H}$$

by a method different from ours but had not been well characterized.[9]

Infrared spectra. The effect of the position of the mercapto group on the infrared absorption is probably most clearly shown in the spectra of the methyl esters. Unlike the acids, all of the mercapto esters are liquids, and can thus be compared readily in the same physical state. Moreover, the weak SH stretching band is covered by carboxyl group absorptions in the case of the mercapto acids. The methyl esters have the further advantage of normally showing a triplet absorption at about 1250, 1195, and 1170 cm.$^{-1}$ Some or all of these bands are probably associated with C—O stretching vibrations of the carbomethoxy group.[10] This region is included in the spectra from 1500–650 cm.$^{-1}$ of some methyl esters (Fig. 1). The normal methyl ester triplet is seen in methyl 9(10)-mercaptostearate (Fig. 1A), and shows the usual stepwise increase in band intensity with decrease in frequency. The position and pattern of this triplet is very regular for unsubstituted long-chain methyl esters,[11] and for certain sulfur derivatives of fatty acids.[12] This pattern also occurs in terminally substituted methyl 11-mercaptoundecanoate.

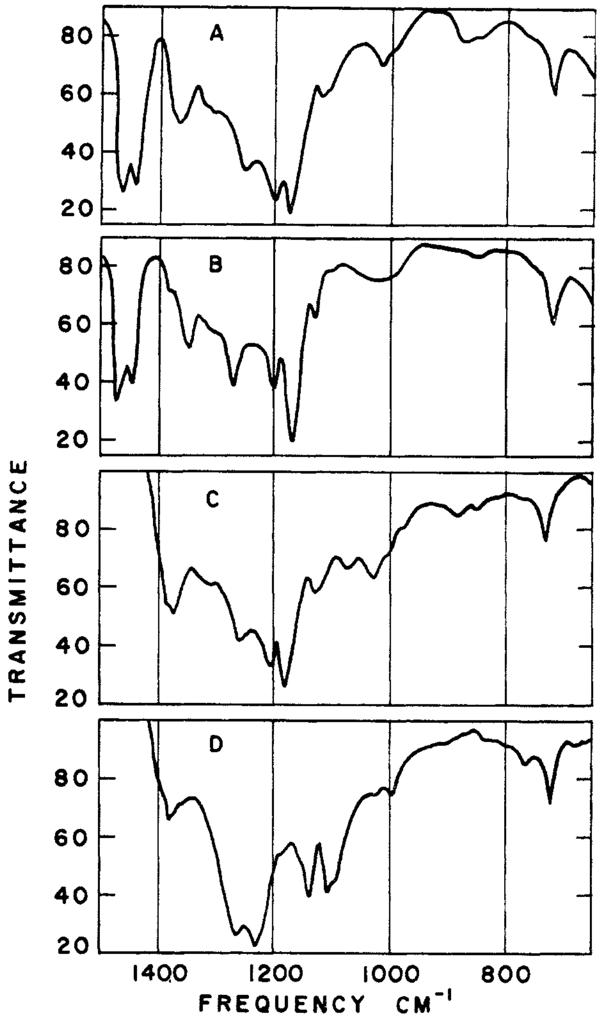


Fig. 1. Infrared spectra of methyl esters. A: Methyl 9(10)-mercaptostearate (liquid). B: Methyl 2-mercaptostearate (liquid). C: Methyl 12-hydroxystearate (CS_2 solution). D: Methyl 2-hydroxystearate (CS_2 solution)

When the mercapto group is in the alpha position, the characteristic pattern of the methyl ester triplet is distinctly modified. Thus, in methyl 2-mercaptostearate (Fig. 1B) the bands are at 1267, 1193, and 1160 cm.$^{-1}$ and the relative intensities of the bands, especially the middle one, are changed. Another change is the shift of the methyl group absorptions, arising both from the terminal aliphatic methyl group and from the methyl group attached to the carbonyl of the carbomethoxy group. These methyl group vibrations normally occur at 1380–1378 cm.$^{-1}$ in linear aliphatic hydrocarbons and at 1362–1360 cm.$^{-1}$ in carbomethoxy esters, respectively.[13] In methyl 9(10)-mercaptostearate (Fig. 1A), the chain methyl band is unresolved from the more intense carbomethoxy methyl band, resulting in a single broad band with maximum intensity at 1360 cm.$^{-1}$ In methyl 2-mercaptostearate, on the other hand, the aliphatic methyl band at about 1378 cm.$^{-1}$ is just discernible because the ester methyl band, now sharper, has been shifted to 1342 cm.$^{-1}$ The shifts in absorption of the carbomethoxy group alpha to a mercapto

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(8) (a) B. H. Nicolet and L. F. Bate, *J. Am. Chem. Soc.*, 49, 2064 (1927). (b) L. Rapoport, A. Smith, and M. S. Newman, *J. Am. Chem. Soc.*, 69, 693 (1947).

(9) G. Collin, T. P. Hilditch, P. Marsh, and A. F. McLeod, *J. Soc. Chem. Ind.*, 52, 272T (1933).

(10) R. G. Sinclair, A. F. McKay, and R. N. Jones, *J. Am. Chem. Soc.*, 74, 2570 (1952).

(11) O. D. Shreve, M. R. Heether, H. B. Knight, and D. Swern, *Anal. Chem.*, 22, 1498 (1950).

(12) H. Susi, N. H. Koenig, W. E. Parker, and D. Swern, *Anal. Chem.*, 30, 443 (1958).

(13) R. N. Jones and C. Sandorfy in *Technique of Organic Chemistry*, Vol. 9, Interscience Publishers, N. Y., 1956, p. 571.

group are not only analytically useful in distinguishing closely related compounds but reflect molecular interactions of general importance, as illustrated later by the neutralization behavior of alpha mercapto esters.

Conversion of methyl 2- or 9(10)-mercaptostearate to the corresponding disulfide leaves the infrared spectrum essentially unchanged except for the disappearance of the small 2560 cm.$^{-1}$ SH band. Since the irregular methyl ester bands are noted for an α-disulfide, dimethyl 2,2′-dithiodistearate, as well as in the parent mercapto ester, the shifts are not based merely on interaction with the SH group. This conclusion is supported by the fact that the SH frequency is the same within our experimental precision in methyl 2-mercaptostearate as in the 9(10)-compound.

As a further illustration of the interaction of the carbomethoxy groups with alpha substituents, a comparison was made between two hydroxy analogs of the mercapto esters. The spectra of these compounds were measured in carbon disulfide solution because they are solids. Also, the solution spectra avoid complications in the interpretation of intermolecular hydrogen bonding.[11]

The spectrum of methyl 12-hydroxystearate (Fig. 1C) where the hydroxyl group is remote from the carbomethoxy group, is entirely regular in the 1400–1150 cm.$^{-1}$ region containing the aliphatic methyl and the methyl ester absorptions. It is very similar in this region to methyl 9(10)-mercaptostearate (Fig. 1A) or to methyl stearate.[11] Published spectra of somewhat lower resolution show that the spectrum of methyl 12-hydroxystearate is also similar to that of methyl 10-hydroxystearate, an even closer analog to methyl 9(10)-mercaptostearate.[14]

With methyl 2-hydroxystearate (Fig. 1D), however, there is a very striking change in the pattern of absorption in the 1400–1150 cm.$^{-1}$ region. It is found, moreover, that the hydroxyl group absorptions differ in the two compounds. The OH stretch is a sharp band at about 3650 cm.$^{-1}$ in the methyl 12-hydroxystearate, indicating a free hydroxyl group. In the α-hydroxy compound however, the band is at approximately 3560 cm.$^{-1}$ and of greater intensity but still sharp, suggesting intramolecular hydrogen bonding. Weak bonding between the α-hydroxyl group and the carbonyl oxygen atom seems reasonable since it involves a five membered ring.[14a] Pronounced changes are also observed in the 1150–1000 cm.$^{-1}$ region. These changes probably include a shift in position and intensity of the C—OH stretching vibration in the case of methyl 2-hydroxystearate. The changes in hydroxyl group absorptions, in contrast to the negligible change in the mercapto group absorptions, support other data showing that hydroxyl groups form hydrogen bonds much more readily than mercapto groups do.[15]

Acidity. Evidence for group interactions has also been obtained from titration data on the mercapto compounds. In a chain substituted methyl ester the mercapto group is acidic only when it is in the α-position. When the mercapto group is separated from the ester group, as in methyl 9(10)-mercaptostearate or methyl 11-mercaptoundecanoate, there is no significant uptake of aqueous sodium hydroxide when an alcoholic solution of the ester is titrated to the phenolphthalein end point at room temperature (the usual procedure for determining neutralization equivalents of long-chain carboxylic acids). Methyl 2-mercaptostearate, on the other hand, titrates more like a weak acid. Neutralization to the phenolphthalein end point requires almost an equimolar amount of sodium hydroxide.

A variety of data support the interpretation that the uptake of sodium hydroxide by methyl 2-mercaptostearate involves neutralization of an acidic mercapto group. The interpretation explains the very gradual indicator color change since the mercapto group should act as a weak acid and thus buffer the solution at the end point. Infrared evidence eliminates the possibility that the acidity may result from facile hydrolysis of the methyl ester group α to a mercapto group, because neutralization of methyl 2-mercaptostearate followed by acidification gives a compound with the same spectrum as the starting material. This experiment also shows that the mercaptide salt is reconverted to the mercaptan by acid. Finally, it has been shown that methyl mercaptoacetate,[15a] which also has an α-mercapto group, likewise neutralizes a nearly equimolar amount of sodium hydroxide under the foregoing titration conditions.

Although the methyl esters are acidic when they have an α-mercapto group, the mercapto group does not titrate as an acid when it is α- to a carboxyl group. Although 2-mercaptostearic acid is titrated to the phenolphthalein end point by an equimolar amount of sodium hydroxide, the product is sodium 2-mercaptostearate rather than the sodium mercaptide. This is shown by the infrared spectrum of the sodium salt, which has the carboxylate ion bands and no carboxyl group bands.

The difference in neutralization behavior between α-mercapto esters and α-mercapto acids may be explained as follows. The positive dipole on the carbonyl group of the methyl ester exerts sufficient electron pull (or proton repulsion) making the mercapto group more acidic. The mercapto

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(14) R. T. O'Connor, C. H. Mack, E. F. DuPré, and W. G. Bickford, *J. Org. Chem.*, **18**, 693 (1951).

(14a) L. Pauling, *The Nature of the Chemical Bond*, 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 329.

(15) D. Plant, D. S. Tarbell, and C. Whiteman, *J. Am. Chem. Soc.*, **77**, 1572 (1955).

(15a) pK_a = 7.8 in 0.15N NaCl, 25°, reported by M. Calvin in *Glutathione*, Academic Press, N. Y., 1954, p. 9.

group in the α-mercapto acids is, however, less acidic than the carboxyl group. Formation of a carboxylate ion makes the mercapto group less acidic because the negative charge of this ion decreases the positive dipole which tends to dissociate the mercapto group proton in the ester. Furthermore, the product from the neutralization of both the mercapto and carboxyl groups would be a dianion whose formation would be minimized because of the coulombic repulsion of the neighboring negative groups.

Ultraviolet spectra. Further evidence of interaction of the carbomethoxy group with sulfur in the α-position is given by the ultraviolet absorption spectra of the disulfide dimethyl esters. Dimethyl 9(10),9′(10′)-dithiodistearate has an absorption maximum at 247 mμ and log $\epsilon = 2.62$ (Fig. 2A), and is thus similar to alkyl disulfides.[16] In dimethyl 2,2′-dithiodistearate the sulfur atoms are in the α-position to the ester groups. The effect of this proximity is a continuous absorption increasing toward the short wave length region (Fig. 2B). The generality of this phenomenon is shown by spectra on two other compounds. Dimethyl 11,11′-dithiodiundecanoate, in which the disulfide group is far removed from the ester groups, has an absorption curve similar to that of dimethyl 9(10),-9′(10′)-dithiodistearate and a maximum at 250 mμ. On the other hand, dimethyl 2,2′-dithiodiacetate, in which the disulfide and ester groups are separated by only one carbon atom, has a continuous absorption curve nearly identical to that of dimethyl 2,2′-dithiodistearate. It has been reported recently[17] that similar effects are shown by some disulfide dicarboxylic acids and their sodium salts.

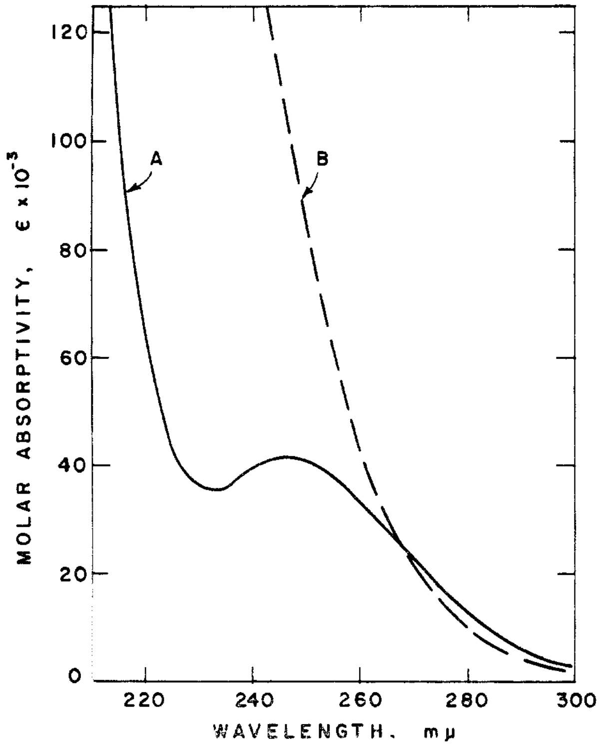

Fig. 2. Ultraviolet absorption spectra of disulfides: (A) Dimethyl 9(10),9′(10′)-dithiodistearate and (B) Dimethyl 2,2′-dithiodistearate

EXPERIMENTAL

Starting materials and reference compounds. Thiolacetic acid was purified by fractional distillation of the best commercial grade. Methyl 2-hydroxystearate, m.p. 63–65°, was prepared from 2-hydroxystearic acid.[18] Methyl 12-hydroxystearate, m.p. 56–58°, was prepared by methanolysis of fully hydrogenated castor oil followed by three crystallizations from acetone at 15°. Methyl oleate was prepared from methyl esters of olive oil by multiple fractional distillation and low temperature crystallization.[19] Dimethyl 2,2′-dithiodiacetate, n_D^{26} 1.5090, was prepared from methyl mercaptoacetate by oxidation with iodine in ethanol solution, followed by extraction with ether. Methyl mercaptoacetate was Eastman White Label Grade.

Methyl 9(10)-(acetylthio)stearate. A mixture of methyl oleate (115 g., 0.39 mole) and freshly-distilled thiolacetic acid (59 g., 0.77 mole) was irradiated in a quartz flask by a high pressure quartz mercury arc for 24 hr. at 70°. The reaction mixture was distilled under diminished pressure; yield, 115 g. (70%), n_D^{30} 1.4666, b.p. 191° at 0.8 mm.

Anal. Calcd. for $C_{21}H_{40}O_3S$: C, 67.7; H, 10.8; S, 8.61. Found: C, 67.7; H, 10.8; S, 8.56.

In accordance with its branched structure, this compound does not form a complex with urea. The urea complexing technique has been used to remove unreacted linear methyl oleate in crude reaction products.

The infrared spectrum of a liquid film shows clearly resolved ester carbonyl (1740 cm.$^{-1}$) and thiocarbonyl (1690 cm.$^{-1}$) bands of equal intensity. Characteristic bands of long-chain methyl esters are present. Strong bands are also present at 1115 and 950 cm.$^{-1}$ These latter bands are also found in 11-(acetylthio)undecanoic acid and other thiolacetates.[6,20]

Additional confirmation of the thiolacetate structure is provided by the ultraviolet absorption spectrum, which has a maximum in methanol of 232 mμ and a molar extinction coefficient of 4.4×10^3.[20b]

9(10)-Mercaptostearic acid. This compound has been mentioned in the literature,[9] but it has not been well characterized. The procedure described below is an improvement over the literature method.

Methyl 9(10)-(acetylthio)stearate (11 g., 0.030 mole) was hydrolyzed by refluxing for 2 hr. in a solution of 10 g. (0.18 mole) of potassium hydroxide in 100 ml. of 50% aqueous ethanol. The solution was acidified with hydrochloric acid and extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulfate, and evaporated to give 7.7 g. (91%) of 9(10)-mercaptostearic acid as a pale yellow liquid, n_D^{27} 1.4724.

Anal. Calcd. for $C_{18}H_{36}O_2S$. C, 68.3; H, 11.5; S, 10.1; neut. equiv., 317. Found: C, 68.3; H, 11.5; S, 10.2; neut. equiv., 313.

Fractional crystallization from petroleum ether at −30°

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(16) Q. W. Decker and H. W. Post, *J. Org. Chem.*, **22**, 145 (1957).

(17) L. Schotte, *Arkiv för Kemi*, **9**, 441 (1956).

(18) P. A. Levene and P. S. Young, *J. Biol. Chem.*, **102**, 557 (1933).

(19) H. B. Knight, E. F. Jordan, Jr., E. T. Roe, and D. Swern, *Biochemical Preparations*, **2**, 100 (1952).

(20) (a) C. Knuth, A. Bavley, and W. A. Lazier, *J. Org. Chem.*, **19**, 845 (1954). (b) L. H. Noda, S. A. Kuby, and H. A. Lardy, *J. Am. Chem. Soc.*, **75**, 913 (1953).

gave approximately equal precipitate and filtrate fractions with the same refractive index. These fractions were solid slightly below room temperature, but had no sharp melting point.

The infrared spectrum in carbon disulfide is very similar to that of stearic acid.[11]

Sodium 9(10)-mercaptostearate. The sodium salt, m.p. approximately 250°, was recovered by evaporating the solution from the neutralization equivalent determination of 9(10)-mercaptostearic acid.

Anal. Calcd. for $C_{18}H_{35}O_2SNa$: S, 9.47; Na, 6.79. Found. S, 9.40; Na, 7.19.

9(10),9′(10′)-Dithiodistearic acid. 9(10)-Mercaptostearic acid (3.46 g., 0.011 mole) was treated with a slight excess (101 ml.) of 0.1*N* iodine in ethanol, with the addition of 35 ml. of water to speed the reaction near the end point. The solution was diluted with a large amount of water and extracted with ether. The extract was dried over anhydrous sodium sulfate and evaporated to give 3.3 g. of a reddish viscous oil, n_D^{24} 1.4870.

Anal. Calcd. for $C_{36}H_{70}O_4S_2$: C, 68.6; H, 11.2; S, 10.1; neut. equiv., 316. Found. C, 69.0; H, 11.3; S, 9.21; neut. equiv., 316.

The infrared spectrum is very similar to that of 9(10)-mercaptostearic acid.

Methyl 9(10)-mercaptostearate. (*a*) *By esterification of 9(10)-mercaptostearic acid.* 9(10)-Mercaptostearic acid (1.24 g., 0.004 mole), 2% by weight (25 mg.) of naphthalene-2-sulfonic acid catalyst, and 10 ml. (0.25 mole) of methanol were refluxed for 6 hr. The solution was diluted with water and extracted with ether. The ether extract was washed with water, dried with anhydrous sodium sulfate and evaporated. The residual liquid, methyl 9(10)-mercaptostearate, weighed 1.01 g., n_D^{25} 1.4648.

Anal. Calcd. for $C_{19}H_{38}O_2S$: C, 69.0; H, 11.6; S, 9.70. Found: C, 69.1; H, 11.6; S, 9.62.

(*b*) *By alcoholysis of methyl 9(10)-(acetylthio)stearate.* Base-catalyzed alcoholysis[21] of methyl 9(10)-(acetylthio)-stearate gave the desired mercapto ester directly. Sodium (0.1 g.) was dissolved in 60 ml. (1.5 moles) of methanol. Methyl 9(10)-(acetylthio)stearate (11 g., 0.030 mole) was added, and the solution was refluxed for 4 hr. The solution was evaporated to a gel-like solid, acidified with dilute hydrochloric acid, and extracted with ether. The ether extract, after washing and drying, was evaporated to give 8.5 g. of crude product. The analytical sample, n_D^{27} 1.4638, was obtained by high-vacuum distillation in a short path still. Its infrared spectrum was the same as that of the product obtained by esterification of 9(10)-mercaptostearic acid.

Anal. Calcd. for $C_{19}H_{38}O_2S$: C, 69.0; H, 11.6; S, 9.70. Found: C, 69.0; H, 12.3; S, 9.70.

Dimethyl 9(10),9′(10′)-dithiodistearate. This disulfide was prepared by titrating methyl 9(10)-mercaptostearate with iodine in ethanol as described earlier. The solution was cooled to −20° and the resulting crystalline precipitate was separated, washed with cold acetone, and dried. The product (yield about 50%) was a pale liquid, n_D^{25} 1.4790.

Anal. Calcd. for $C_{38}H_{74}O_4S_2$: C, 69.2; H, 11.3; S, 9.71. Found: C, 69.0; H, 11.1; S, 9.83.

2-Bromostearic acid. 2-Bromostearic acid was prepared by a previously reported procedure.[22]

2-Mercaptostearic acid. This compound has been described previously,[8a] but the procedure given below is an improvement over earlier ones. 2-Bromostearic acid (181.5 g., 0.5 mole), 38 g. (0.5 mole) of thiourea, and 1000 ml. of ethanol were refluxed for 4 hr. A solution of 220 g. of sodium hydroxide in 1200 ml. of 80% aqueous ethanol was then added and the reaction mixture was refluxed for an additional 46 hr. The cooled reaction mixture was then added to 1500 ml. of 4*N* hydrochloric acid with stirring at such a rate that the temperature did not rise above 60°. After the acidification was completed, the reaction mixture was heated on a steam bath until the crude 2-mercaptostearic acid was molten and had collected on the surface of the aqueous layer. The mixture was cooled to room temperature, a hole was punched in the crude solidified 2-mercaptostearic acid, and the aqueous layer was poured off. The crude 2-mercaptostearic acid was washed free of salt and acid by melting and stirring it on a steam bath with several 500-ml. portions of water and intervening solidification as described. The crude product was air-dried and crystallized from 1300 ml. of ethanol (charcoal used); yield, 106 g., (67%) m.p. 75–78°; neut. equiv. calcd., 316.5; found, 320. Three recrystallizations of a small sample of the above product yielded analytically pure 2-mercaptostearic acid, m.p. 79–79.5° (lit. 80°); neut. equiv. 318.

The infrared spectrum of 2-mercaptostearic acid in carbon tetrachloride solution is quite similar to that of 9(10)-mercaptostearic acid except in two respects. The band at 1240 cm.$^{-1}$ is shifted to 1210 cm.$^{-1}$ This is the region where some of the alpha mercapto ester shifts occur. In addition 2-mercaptostearic acid has a weak band at about 690 cm.$^{-1}$

Methyl 2-mercaptostearate. Ten grams of 2-mercaptostearic acid was refluxed for 4 hr. in 1 l. of methanol containing 3% HCl. The methanol was evaporated and the residue was extracted with ether. The extract was washed with water, dried over anhydrous sodium sulfate, and evaporated to give 9.7 g. of amber liquid, n_D^{29} 1.4621. A purified product was obtained as a colorless liquid by high vacuum distillation, b.p. 130° at 0.3 mm., n_D^{27} 1.4607.

Anal. Calcd. for $C_{19}H_{38}O_2S$: S, 9.70. Found: S, 9.74.

Dimethyl 2,2′-dithiodistearate. Methyl 2-mercaptostearate (2 g.) was titrated with 0.1*N* iodine in 80% ethanol until a permanent yellow color was obtained. The oil that separated from the solution was dissolved in ether. The ether extract was washed with water, dried over anhydrous sodium sulfate, and evaporated, yielding 1.5 g. of a colorless liquid, n_D^{26} 1.4749.

Anal. Calcd. for $C_{38}H_{74}O_4S_2$: C, 69.2; H, 11.3; S, 9.71. Found: C, 69.6; H, 11.4; S, 9.20.

11-Mercaptoundecanoic acid. 11-(Acetylthio)undecanoic acid[6] (26 g., 0.10 mole) was refluxed for 3 hr. with a solution of 11.2 g. (0.20 mole) of potassium hydroxide in 100 ml. of 50% aqueous ethanol. Acidification with hydrochloric acid gave a solid, which was filtered, washed with water, and dried; yield, 20.1 g. (92%); m.p. 45°. An analytical sample, m.p. 49–51°,[8b] was obtained by low temperature crystallization from petroleum ether.

The infrared spectrum, run on a pressed potassium bromide disk, resembles that of a typical long-chain unsubstituted acid. The band progression region showed six bands, excluding the 1300 cm.$^{-1}$ carboxyl band, in accordance with studies of other terminally substituted sulfur-containing undecanoic acids.[12]

11,11′-Dithiodiundecanoic acid. 11-Mercaptoundecanoic acid was further characterized by oxidation with iodine to the known disulfide, m.p. 93° (lit.[23] 92°). The ultraviolet spectrum of the disulfide in methanol showed the expected maximum at 240 mμ, log ϵ = 2.61.

Methyl 11-mercaptoundecanoate. 11-Mercaptoundecanoic acid was esterified with methanol by the procedure used in preparing methyl 9(10)-mercaptostearate. The ester was purified by crystallization at −20° from methanol, followed by vacuum distillation. It was a colorless liquid, n_D^{24} 1.4641, that froze at or above 2°.

Anal. Calcd. for $C_{12}H_{24}O_2S$: C, 62.0; H, 10.4; S, 13.8. Found: C, 62.2; H, 10.4; S, 13.1.

The infrared spectrum had the normal long-chain methyl ester triplet. It was similar to that of methyl 9(10)-mercaptostearate except that its lower molecular weight resulted in

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[21] G. S. Sasin, P. R. Schaeffer, and R. Sasin, *J. Org. Chem.*, **22**, 1183 (1957).

[22] R. S. Sweet and F. L. Estes, *J. Org. Chem.*, **21**, 1426 (1956).

[23] A. Cohen, *J. Chem. Soc.*, 593 (1932).

somewhat stronger bands at 2560 cm.$^{-1}$ (mercapto group) and 1440 cm.$^{-1}$ (carbomethoxy group).

Dimethyl 11,11'-dithiodiundecanoate. When the ethanol solution from the iodine titration of methyl 11-mercaptoundecanoate was cooled to 0°, a crystalline precipitate formed. This solid crystallized from petroleum ether as transparent plates, m.p. 56°.

Anal. Calcd. for $C_{24}H_{46}O_4S_2$: C, 62.3; H, 10.0; S, 13.9. Found: C, 62.7; H, 10.1; S, 13.7.

Analytical and physical data. The mercapto compounds described in this paper were analyzed by titration with 0.1*N* iodine in ethanol. Water was added during the titration in case of slow decolorization as the end point was approached.

With mercapto acids, the sample was first titrated in ethanol with 0.1*N* aqueous sodium hydroxide to the phenolphthalein end point. Following this determination of the carboxyl group, the pink color was just discharged with a few drops of 0.1*N* hydrochloric acid and the solution was then titrated with 0.1*N* iodine in ethanol to a faint permanent yellow color. The solution was titrated once again with 0.1*N* sodium hydroxide solution until the yellow color began to turn pink. The latter titration measured hydriodic acid liberated by the reaction of iodine with the mercapto group, and checked on possible impurities that merely absorbed iodine. With pure mercapto acids analysis showed equivalent amounts of carboxyl and mercapto groups and liberated hydriodic acid.

Infrared absorption spectra were obtained on thin liquid films or on carbon disulfide solutions with a Perkin-Elmer Model 21 spectrophotometer, using sodium chloride optics. In a few instances, solid compounds were examined as pressed potassium bromide disks or as nujol mulls. Ultraviolet absorption spectra were recorded on methanol solutions with a Carey Model 11 recording spectrophotometer.

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Some α-Carbalkoxyalkoxysilanes

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Several α-carbalkoxyalkoxysilanes were prepared by the reaction of ethyl lactate or methyl α-hydroxyisobutyrate with a methyl- or phenylchlorosilane in the presence of a tertiary amine, or by interchange with the corresponding ethoxysilane. When these substances react with glycols, either the ester bond or the silicon-oxygen bond may be attacked. This competition was studied, particularly as affected by the structure of the reactants.

Alkoxysilanes derived from alcohols containing a second functional group are of interest because they offer an opportunity to carry out subsequent reactions with relative ease and thereby to arrive at new organo-silicon compounds. Among representatives of these classes of compounds, only the β-halogenoalkoxysilanes[1] and the β-alkoxyalkoxysilanes[2] are as yet reasonably well known. Recently Henglein and coworkers[3] described trimethylsiloxy derivatives of lactic and tartaric acids and their ethyl esters.

α-Carbalkoxyalkoxysilanes can be prepared readily from the appropriate chlorosilane and an α-hydroxy ester in the presence of a tertiary amine; or they can be prepared from the corresponding methoxy- or ethoxysilane in the presence of an ester interchange catalyst. The former method, due to Martin[4] was discussed at some length by the present author and L. S. Nelson.[5] α-Carbalkoxyalkoxysilanes based on ethyl lactate or methyl α-hydroxyisobutyrate as the alkoxy component and methyl- or phenylchlorosilanes as the organosilicon component were prepared and their subsequent reaction with a diol or a dibasic acid were studied.

The α-carbalkoxyalkoxysilanes prepared are di- and triesters, and should be convertible to polymeric esters by normal reesterification procedures. However, a competing reaction is always possible—a reaction that is formally the reverse of that by which the ester was prepared. A diol can attack such a molecule either at the terminal ester function or at the interior silicon-oxygen bond. The first mode of attack produces a poly(siloxy ester); the second liberates the hydroxy ester and produces a poly(alkylenesilane) instead. These relations are shown, for the case of a difunctional reactant, in the following scheme.

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