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Thiol Esters of Long-Chain Acids and Long-Chain Alkanethiols[1]

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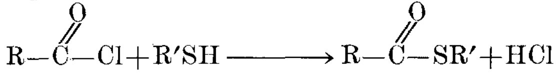
THIOL ESTERS of long-chain acids were believed to be unstable until Ralston and co-workers (5) demonstrated that methyl thiol esters through *n*-butyl thiol esters of lauric, myristic, palmitic, and stearic acids can be prepared in good yield by the action of an acyl halide on the appropriate mercaptan. The stability of the thiol esters was demonstrated by the fact that they can be purified by distillation under diminished pressure without decomposition.

This investigation continues the systematic study of the preparation, properties, and the reactions of thiol esters of long-chain acids. In our first paper (6) it was shown that aromatic as well as branched-chain thiol esters can be prepared by Ralston's procedure. In another paper (7) it was demonstrated that thiol esters of C_{12} to C_{18} saturated acids undergo ester interchange reactions with alkanethiols, arylthiols as well as with alcohols and phenol. Preliminary evaluations of thiol esters of long-chain acids as lube-oil additives indicate that some of these compounds show promise of having anti-wear and extreme pressure properties. They appear to be more promising in mineral oils than in synthetic oils.

In this investigation we extend the reactions of chlorides of long-chain acids to long-chain alkanethiols, forming some thiol esters having molecular weights of more than 500. *n*-Nonyl through *n*-octadecyl thiol esters of lauric, myristic, palmitic, and stearic acids were formed by treating the acyl halide with the appropriate mercaptan.



$$R-\overset{O}{\overset{/\!/}{C}}-Cl + R'SH \longrightarrow R-\overset{O}{\overset{/\!/}{C}}-SR' + HCl$$

The results are summarized in Table I.

Most of the alkanethiols were prepared by treating the appropriate alkyl bromide with thiourea (8). *n*-Pentadecanethiol and *n*-heptadecanethiol are believed to be new compounds. Heptadecyl, pentadecyl, and tridecyl bromides were prepared from the silver salts of stearic, palmitic, and myristic acids, respectively, by the silver salt reaction (2, 3).

Experimental

Materials. Undecyl bromide and nonanethiol were obtained from Matheson, Colman, and Bell. *n*-Decanethiol and *n*-dodecanethiol were obtained from the Aldrich Chemical Company. The tetradecyl, hexadecyl, and octadecyl bromides and myristic and palmitic acids as well as the lauroyl, myristoyl, and palmitoyl chlorides were obtained from Eastman. The HumKo Chemical Company supplied S-97, commercial stearic acid. This material was crystallized once from methanol and once from acetone and melted at 69°+. The properties, yields, and analyses of the thiol esters are summarized in Table I. All melting points are corrected.

Silver Myristate, Silver Palmitate, and Silver Stearate. These compounds were prepared from the appropriate ammonium salt dissolved in aqueous alcohol by the addition of silver nitrate (1).

Tridecyl, Pentadecyl, and Heptadecyl Bromide. Tridecyl and pentadecyl bromides (2) and heptadecyl bromide (3) were prepared by treating the anhydrous silver salts of myristic, palmitic, and stearic acids

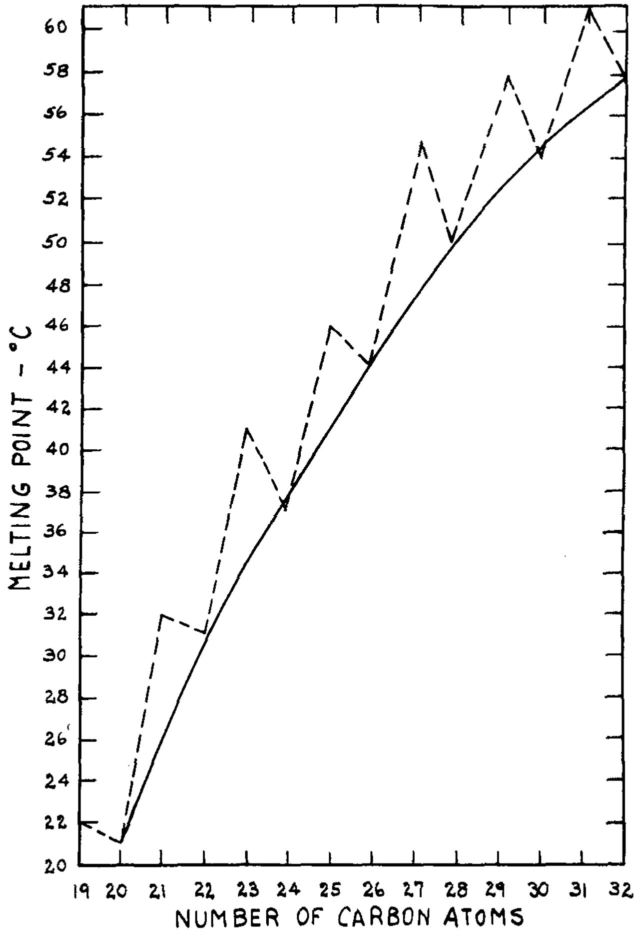


FIG. 1. Melting points of thiomyristates.

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[1] This paper was given the 1957 Fatty Acid Producers' Award, administered by the American Oil Chemists' Society.

TABLE I
Thiol Esters

Compound	M.P., °C.	Yield, %	Formula	Analyses, %			
				Carbon		Hydrogen	
				Calcd.	Found	Calcd.	Found
n-Nonyl thiolaurate	32.0–32.5	79.0	$C_{21}H_{42}OS$	73.7	73.7	12.3	12.4
n-Decyl thiolaurate	29.5–30.0	86.0	$C_{22}H_{44}OS$	74.1	73.8	12.4	12.5
n-Undecyl thiolaurate	43.0–43.5	95.0	$C_{23}H_{46}OS$	74.5	74.5	12.4	12.3
n-Dodecyl thiolaurate	37.5–38.0	93.0	$C_{24}H_{48}OS$	75.2	75.5	12.6	12.6
n-Tridecyl thiolaurate	47.0–47.5	83.0	$C_{25}H_{50}OS$	75.3	75.2	12.6	12.5
n-Tetradecyl thiolaurate	45.0–45.5	90.0	$C_{26}H_{52}OS$	75.8	75.6	12.7	12.5
n-Pentadecyl thiolaurate	51.5–52.0	83.0	$C_{27}H_{54}OS$	76.1	75.8	12.7	12.7
n-Hexadecyl thiolaurate	49.5–50.0	98.0	$C_{28}H_{56}OS$	76.3	76.1	12.8	12.6
n-Heptadecyl thiolaurate	55.0–55.5	85.0	$C_{29}H_{58}OS$	76.7	76.5	12.8	12.7
n-Octadecyl thiolaurate	54.0–54.5	85.0	$C_{30}H_{60}OS$	76.8	76.7	12.9	12.7
n-Nonyl thiomyristate	40.5–41.0	68.0	$C_{23}H_{46}OS$	74.7	74.9	12.5	12.5
n-Decyl thiomyristate	38.0–38.5	96.0	$C_{24}H_{48}OS$	74.9	74.6	12.5	12.4
n-Undecyl thiomyristate	45.5–46.0	88.0	$C_{25}H_{50}OS$	75.3	75.2	12.6	12.6
n-Dodecyl thiomyristate	43.5–44.0	91.0	$C_{26}H_{52}OS$	75.8	76.0	12.7	12.7
n-Tridecyl thiomyristate	54.0–54.5	73.5	$C_{27}H_{54}OS$	76.0	75.9	12.8	12.7
n-Tetradecyl thiomyristate	50.0–50.5	95.0	$C_{28}H_{56}OS$	76.0	75.8	12.8	12.6
n-Pentadecyl thiomyristate	57.0–58.0	88.0	$C_{29}H_{58}OS$	76.6	76.3	12.8	12.8
n-Hexadecyl thiomyristate	53.5–54.0	99.0	$C_{30}H_{60}OS$	77.0	76.9	12.9	12.7
n-Heptadecyl thiomyristate	61.0–61.5	84.0	$C_{31}H_{62}OS$	77.1	77.1	12.9	12.7
n-Octadecyl thiomyristate	57.5–58.0	98.0	$C_{32}H_{64}OS$	77.4	77.3	12.9	12.9
n-Nonyl thiopalmitate	44.5–45.0	94.0	$C_{25}H_{50}OS$	75.3	75.0	12.6	12.6
n-Decyl thiopalmitate	43.5–44.0	70.0	$C_{26}H_{52}OS$	75.6	75.2	12.6	12.6
n-Undecyl thiopalmitate	51.0–51.5	94.0	$C_{27}H_{54}OS$	76.1	76.2	12.7	12.8
n-Dodecyl thiopalmitate	48.5–49.0	83.0	$C_{28}H_{56}OS$	76.5	76.8	12.8	12.9
n-Tridecyl thiopalmitate	56.0–56.5	86.0	$C_{29}H_{58}OS$	76.6	76.4	12.8	12.8
n-Tetradecyl thiopalmitate	54.5–55.0	91.0	$C_{30}H_{60}OS$	77.0	77.0	12.9	12.7
n-Pentadecyl thiopalmitate	61.0–61.5	92.0	$C_{31}H_{62}OS$	77.4	77.2	12.9	13.0
n-Hexadecyl thiopalmitate	58.5–59.0	90.0	$C_{32}H_{64}OS$	77.4	77.5	13.0	13.0
n-Heptadecyl thiopalmitate	64.5–65.0	80.0	$C_{33}H_{66}OS$	77.7	77.5	13.0	13.1
n-Octadecyl thiopalmitate	62.5–63.0	96.0	$C_{34}H_{68}OS$	77.8	77.5	13.0	13.0
n-Nonyl thiostearate	50.5–51.0	65.0	$C_{27}H_{54}OS$	76.1	75.8	12.7	12.5
n-Decyl thiostearate	50.0–50.5	80.5	$C_{28}H_{56}OS$	76.3	76.3	12.8	12.7
n-Undecyl thiostearate	55.5–56.0	81.5	$C_{29}H_{58}OS$	76.4	76.4	12.9	12.9
n-Dodecyl thiostearate	54.5–55.0	85.5	$C_{30}H_{60}OS$	77.0	77.2	12.9	12.8
n-Tridecyl thiostearate	59.5–60.5	79.8	$C_{31}H_{62}OS$	77.1	76.8	12.9	12.9
n-Tetradecyl thiostearate	58.5–59.0	74.0	$S_{32}H_{64}OS$	77.3	77.3	13.0	13.0
n-Pentadecyl thiostearate	64.0–65.0	82.5	$C_{33}H_{66}OS$	77.7	77.5	13.0	12.9
n-Hexadecyl thiostearate	63.0–63.5	80.5	$C_{34}H_{68}OS$	77.8	77.3	13.0	12.8
n-Heptadecyl thiostearate	69.5–70.0	90.5	$C_{35}H_{70}OS$	77.9	77.6	13.1	13.0
n-Octadecyl thiostearate	65.5–66.0	81.0	$C_{36}H_{72}OS$	78.1	77.9	13.1	13.2

suspended in dry carbon tetrachloride with bromine.

n-Undecanethiol, n-Tridecanethiol, n-Pentadecanethiol, n-Hexadecanethiol, n-Heptadecanethiol, and n-Octadecanethiol. All of these thiols were prepared from the appropriate alkyl bromide and thiourea by a well-known reaction (8). A literature search disclosed that *n*-pentadecanethiol and *n*-heptadecanethiol apparently had not previously been reported. Data for these compounds are thus hereby submitted.

n-Pentadecanethiol. From 34 g. (0.117 mole) of pentadecyl bromide and 8.9 g. (0.117 mole) of thiourea there were obtained 17.3 g., or 60.5% of product boiling at 144–145° at 2 mm. Anal. Calcd. for $C_{15}H_{32}S$: S, 13.1%. Found: S, 12.9%.

n-Heptadecanethiol. From 46 g. (0.144 mole) of heptadecyl bromide and 10.9 g. (0.144 mole) of thiourea there were obtained 28.4 g., or 72.5% of *n*-heptadecanethiol boiling at 167–168° at 2 mm. This product was crystallized from alcohol until successive crystallizations showed no increase in melting point. The melting point was found to be 34°. Anal. Calcd. for $C_{17}H_{36}S$: S, 11.7%. Found: S, 11.5%.

Stearoyl Chloride. To 0.1 mole of molten stearic acid in a 125-ml. separatory funnel, protected by a calcium chloride drying tube, were added 5.5 g. of phosphorus trichloride. The mixture was heated with a steam cone for one hour and then was allowed to stand over-night. The acid chloride was separated from the phosphorous acid formed in the reaction and was used without further purification (6).

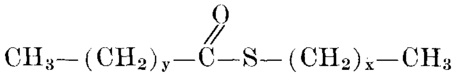
Preparation of Thiolesters (6). Method A. Thiolaurates. Thiomyristates and Thiopalmitates. To 0.05 mole of the acid chloride in a 200-ml., round-bottomed flask, fitted with a reflux condenser, was added 0.055 mole of the appropriate mercaptan, and the mixture was allowed to stand over-night. The mixture than was heated in a water-bath for 6 hrs. The solid which formed on cooling was crystallized from acetone-alcohol until successive crystallizations showed no increase in melting point. In all cases at least four crystallizations were necessary.

Method B. Thiostearates. To 0.05 mole of stearoyl chloride in a 200-ml., round-bottomed flask, fitted with a reflux condenser, was added 0.055 mole of the appropriate mercaptan, and the mixture was allowed to stand over-night. The mixture then was heated in a water-bath for 6 hrs. The resulting solid, which contained some free fatty acid, was dissolved in 100 ml. of acetone, and 6 N sodium hydroxide solution in a 5% excess over that necessary to neutralize the free fatty acid was added with stirring. The insoluble soap was separated by filtration and washed with 20 ml. of acetone (4). The solution then was cooled to 0°, and the resulting solid was separated by filtration. The product was crystallized from acetone until successive crystallizations showed no increase in melting point.

Discussion

Thiol esters of lauric, myristic, palmitic, and stearic acids prepared from C_9–C_{18} alkanethiols are white solids. The lower members are sparingly soluble in alcohol and very soluble in acetone. Their solubility decreases in the above-mentioned solvents with increasing molecular weight. The lower members have a distinct mercaptan-like odor while the higher members are odorless.

Each of the four series of thiol esters shows an alternation of melting points. Figure 1 represents the plot of melting points of thiomyristates against the number of carbon atoms in the ester. Similar curves were obtained for thiolaurates, thiopalmitates, and thiostearates. The melting point data for *n*-amyl, *n*-hexyl, *n*-heptyl, and *n*-octyl thiol esters were taken from two previous papers (6, 7). The odd members in all of the series melt at a higher temperature than the even members. The melting points of the even members fall on single ascending curves while the melting points of the odd members fall on two distinct and separate ascending curves. The melting points of thiol esters, prepared from alkanethiols containing fewer carbons than alkyl radical belonging to the acid, fall on ascending curves, which are lower than the melting points of thiol esters prepared from alkanethiols containing an equal or greater number of carbon atoms than the alkyl radical belonging to the acid. The compounds



$$CH_3{-}(CH_2)_y{-}\overset{\overset{O}{/\!/}}{C}{-}S{-}(CH_2)_x{-}CH_3$$

form a lower melting series if the value of x is smaller than the value of y, and they form a higher melting series if the value of x is equal to or higher than the value of y. The higher melting series begins with undecyl thiolaurate, tridecyl thiomyristate, pentadecyl thiopalmitate, and heptadecyl thiostearate in lauric, myristic, palmitic, and stearic thiol esters, respectively. To our knowledge two similar series of melting points have not been previously observed with other homologous series.

Infrared Spectra of Thiopalmitates. The infrared spectra of *n*-nonyl, *n*-tridecyl, and *n*-heptadecyl thiopalmitates, as pressed potassium bromide disks, were measured from 4,000–650 cm.$^{-1}$ Methylene bands occurred at about 2,910, 2,840, 1,475, 730, and 720 cm.$^{-1}$ The thiolester stretching bands were also observed at about 1,070, 965, and 780 cm.$^{-1}$

Summary

n-Nonyl through *n*-octadecyl thiol esters of lauric, myristic, palmitic, and stearic acids are being reported for the first time. The four series of thiol esters show an alternation of melting points. The melting points of the even members fall on a single ascending curve. The melting points of the odd members fall on two separate ascending curves.

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Cocoa Butter-Like Fats from Domestic Oils[1,2]

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COCOA BUTTER is a premium candy fat primarily because of its unique physical characteristics. At room temperatures below about 26°C. it is hard and brittle, yet when eaten it melts completely in the mouth with a pleasing, cooling sensation. The solids content of a sample of cocoa butter has been estimated to be 71% at 25°C., 51% at 30°C., and only 5% at 35°C. (1, 8). The plastic range is very short when compared with that of most other fats.

The fatty acid composition of cocoa butter is not unique. According to Meara (11), the component fatty acids and their mole percentages in a sample of cocoa butter he examined were found to be as follows: oleic, 37.3; stearic, 34.4; palmitic, 26.2; and linoleic, 2.1. Others have obtained similar data. The percentages and types of fatty acids cited are similar to those occurring in the glycerides of mutton tallow.

The distinctive physical properties of cocoa butter are a reflection of an unusual glyceride composition. Unlike most fats and oils, the types of glycerides occurring in cocoa butter are small in number, and two or three of these comprise 80–85% of the total weight. Meara (11) calculated the composition for one apparently representative sample of cocoa butter to be as follows:

	Mole percentage
Fully saturated triglycerides	2.6
Oleodipalmitin	3.7
Oleopalmitostearin	57.0
Oleodistearin	22.2
Palmitodiolein	7.4
Stearodiolein	5.8
Triolein	1.1

The development of a good cocoa butter-like fat from domestic oils is desirable in a number of respects. Also a cocoa butter-like fat could have properties even more desirable than those of cocoa butter itself. The latter has a softening point which is slightly too low for products intended for consumption in the summer-time.

The armed forces have need for a confectionery fat similar to cocoa butter but with an appreciably higher melting point. Such a product would most logically be based on a fat mixture resembling cocoa butter but having a slightly higher melting point; that is, the main ingredient would be a fat closely resembling cocoa butter.

Any cocoa butter replacement, whether it be for general use or for the armed forces, would in most instances be used in combination with cocoa or chocolate liquor. This imposes the further restriction that the solid forms of the replacement fat and the fat in cocoa or chocolate liquor be mutually compatible; that is, one must not change the softening or melting characteristics of the other. A fat like palm kernel stearin would not be a satisfactory replacement. Re-

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[3] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.