extract of a plasticized poly (vinyl chloride) bottle cap liner. The di(2-ethylhexyl)-o-phthalate (DOP) plasticizer is a major feature of the chromatogram. Even though the DOP is about 30% of the sample, all of the amides except palmitamide can be found and measured. Table 3 summarizes the analytical data obtained from both polymer extracts.

TABLE 3

Qualitative and Quantitative Results from Extracts of Plastic Parts

Species	Percent found	
	Polypropylene extract	PVC extract
Myristamide	<0.01	<0.01
Palmitamide	<0.01	*
Palmitelaidamide	<0.01	0.02
Palmitoleamide	<0.01	0.02
Stearamide	<0.01	0.05
Elaidamide	<0.01	0.11
Oleamide	0.01	0.30
Linoleamide	0.04	0.05
Linolenamide	0.02	0.03
Erucamide	1.1	0.40
Total	1.2	1.0

*Interference by DOP.

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W. Greive prepared and purified the amides used in this work.

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Derivatization of Keto Fatty Acids, Part IX. Synthesis and Characterization of Oxathiolanes

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Oxathiolanes are prepared from the condensation of the oxo fatty acids with β-mercaptoethanol using BF_3-etherate as catalyst. 10-Oxoundecanoic acid (I) reacts with the reagent promptly and gives 10-(ethylene oxathiolane) undecanoic acid (V). A similar reaction of 9-oxooctadecanoic acid (II) yields 9-(ethylene oxathiolane) octadecanoic acid (VII). Hemimercaptals (VI, VIII) are also isolated as minor products in the above reactions. Methyl 9,10-dioxooctadecanoate (III) is also found to react readily and affords methyl 9(10)-(ethylene oxathiolane)-10(9)-oxooctadecanoate (IX) as the sole product. There is no reaction with 2-oxooctadecanoic acid (IV). The spectral (infrared, nuclear magnetic resonance, mass) properties of oxathiolanes are detailed.

In recent years oxathiolanes have attracted attention due to their pharmaceutical potential (1), antineoplastic activities (2) and as radioprotectants (3). Scanning of the literature revealed that ketones readily condensed with β-mercaptoethanol in the presence of various catalysts (4–6) to furnish oxathiolanes. These sulfur-containing heterocycles also have been reported by the acid catalyzed reaction of TMS enol ethers with β-mercaptoethanol (7).

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The resurgence of interest in oxathiolanes for their pharmacological activities and our derivatization program for the synthesis of fatty heterocycles (8–10) led us to undertake the present work on the synthesis of long chain oxathiolanes. Recently, this type of sulfur heterocycle also has been prepared from α,β-unsaturated oxo fatty esters in our laboratory (11). This paper describes the synthesis and spectral characteristics (IR, NMR, Mass) of chain substituted ethylene oxathiolanes obtained from isolated oxo fatty acids/esters.

EXPERIMENTAL PROCEDURES

All melting points are uncorrected. IR spectra (expressed in cm^{-1}) were obtained on a Pye Unicam SP3-100 spectrophotometer in nujol mulls. NMR spectra were run in $CDCl_3$ on a Varian A60 spectrometer with tetramethylsilane as the internal standard. NMR values are given in ppm δ (s, singlet; br, broad; d, doublet; m, multiplet). Mass spectra were measured with JEOL JMS D-300 at 70 eV. Figures in parentheses after MS values indicate the intensity of a peak relative to the base peak (100) and some indication of its source. TLC plates were coated with silica gel. The spots were visualized by charring after spraying with a 20% aqueous solution of perchloric acid. Anhydrous sodium sulphate was used as a drying agent.

Column chromatography was carried out with silica gel G (60-120 mesh), 25-30 g per g of material to be separated. Elution was usually effected with light petroleum ether (bp 40-60 C) containing increasing proportions of ether.

Preparation of oxo fatty acids (I, II, III, IV). 10-Oxoundecanoic acid (I, mp 58-59 C), 9-oxooctadecanoic acid (II, mp 80-80.5 C), 9,10-dioxooctadecanoic acid (mp 84.5 C) and 2-oxooctadecanoic acid (IV) were prepared as discussed earlier (10). Methyl 9,10-dioxooctadecanoate (III) was prepared by refluxing the acid with absolute methanol containing a catalytic amount of H_2SO_4.

Reaction of I with β-mercaptoethanol and BF_3-etherate. A solution of ketone (I) (2.0 g, 10 mmol) in freshly distilled BF_3-etherate (15 ml) was treated with β-mercaptoethanol (3.12 g, 40 mmol) and left at room temperature for one hr. Methanol (0.5 ml) was added to the solution to stop the reaction. The reaction mixture was poured into water and extracted with ether. The ether layer was washed with water and dried. Evaporation of solvent yielded an oily product. The crude product was chromatographed on silica gel. Elution with light petroleum ether:ether (95:5) afforded the compound V (1.8 g, 70%) as an oil.

$C_{13}H_{24}O_3S$: Calcd. C, 59.97; H, 9.28. Found: C, 59.80; H, 9.20%; IR: 1710 (COOH), 1435 (CH_2—S, deformation), 1250 (CH_2—S, wagging), 1050 (oxathiolane ring); NMR: 4.15 t ($C\underline{H}_2$—O), 2.85 t ($C\underline{H}_2$—S), 2.3 m ($C\underline{H}_2$—COOH), 1.7 t (C_9—$C\underline{H}_2$—), 1.5 s (terminal—$C\underline{H}_3$), 1.3 br,s (chain—$C\underline{H}_2$), 9.1 br,s (COO$\underline{H}$); MS: 260 (M^+, 0.5), 243 (M—OH, 1), 228 (245—OH, 0.6), 217 (245—$[CH_2]_2$, 0.4), 213 (245—S, 0.3), 183 (201—H_2O, 4), 169 (201—S, 1.9), 167 (201—H_2S, 3.5), 152 (169—OH, 10.4), 149 (167—H_2O, 7.6), 87 (115—$[CH_2]_2$ or $C_4H_7O_2$, 12.5), 85 (115—CH_2O, 65), 83 (115—S, 100).

Further elution with light petroleum ether:ether (80:20) gave VI (0.57 g, 20%) as a liquid product.

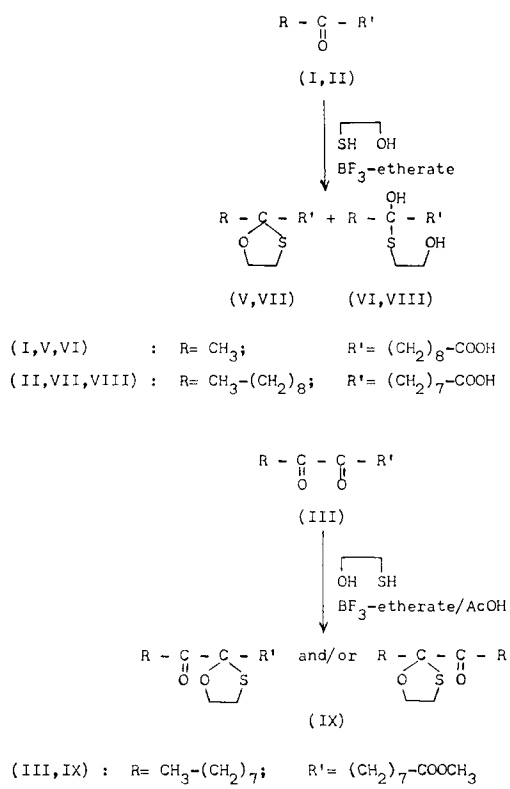
$C_{13}H_{26}O_4S$: Calcd. C, 56.09; H, 9.40. Found: C, 56.18; H, 9.25%; IR: 3440 (OH), 1715 (COOH), 1455, 1260 (CH_2—S); NMR: 4.22 t ($C\underline{H}_2$—OH), 3.9-3.6 br, m (2 × O$\underline{H}$, D_2O exchangeable), 2.85 t ($C\underline{H}_2$—S), 2.35 *m* ($C\underline{H}_2$—COOH), 1.7 m (C_9—$C\underline{H}_2$—), 1.55 s (terminal—$C\underline{H}_3$), 1.25 br,s (Chain—$C\underline{H}_2$) 9.1 br, s (COO$\underline{H}$).

Reaction of II with β-mercaptoethanol and BF_3-etherate. Under the same reaction conditions the oxo acid (II) (2.98 g, 10 mmol) afforded an oily product, which on silica gel column chromatography and elution with light petroleum ether:ether (95:5) gave VII (2.15 g, 60%) as a major oily product.

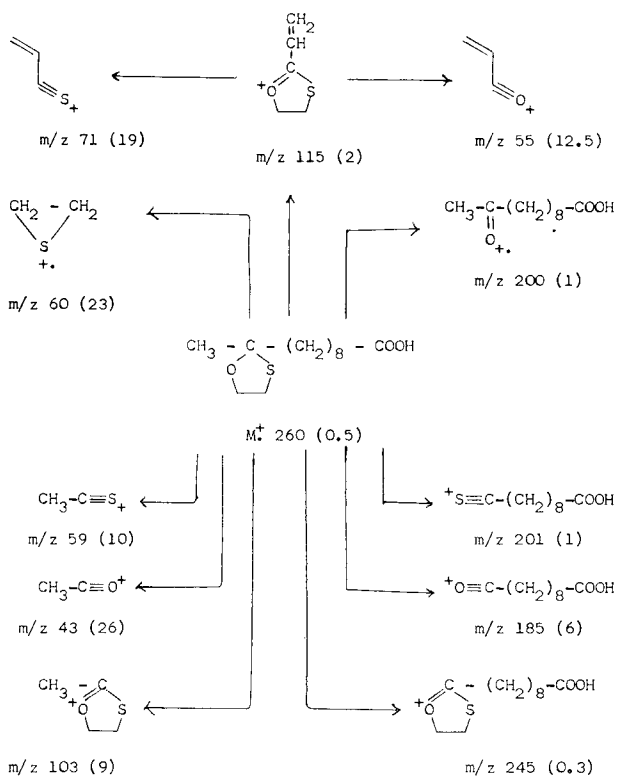
$C_{20}H_{38}O_3S$: C, 66.99; H, 10.67. Found: C, 66.85; H, 10.65% IR: 1705 (COOH), 1440, 1255 (CH_2—S), 1045 (oxathiolane ring); NMR: 4.15 t ($C\underline{H}_2$—O), 2.8 t ($C\underline{H}_2$—S), 2.28 m ($C\underline{H}_2$—COOH), 1.7 m (C_8 and C_{10}—$C\underline{H}_2$—), 1.32 br, s (Chain—CH_2)—, 0.85 t (terminal—$C\underline{H}_3$), 10.1 br, s (COO$\underline{H}$); MS: 358 (M^+, 0.5), 341 (M—OH, 0.5), 326 (M—S, 0.4), 281 (298—OH, 13), 201 (231—CH_2O, 0.5), 183 (215—S, 6), 167 (201—H_2S, 40), 149 (167—H_2O, 100), 43 (CH_3CO^+, 85).

Further elution with light petroleum ether:ether (80:20) furnished VIII (0.95 g, 25%) as a minor product.

$C_{20}H_{40}O_4S$: Calcd. C, 63.79; H, 10.70. Found: C, 63.65; H, 10.60%; IR:3490 (OH), 1710 (COOH), 1445, 1250 (CH_2—S); NMR: 4.24 t ($C\underline{H}_2$—OH), 2.8 t ($C\underline{H}_2$—S), 2.7-2.5 br,m (2 × O$\underline{H}$, D_2O exchangeable), 2.3 m ($C\underline{H}_2$—COOH),



SCHEME 1



SCHEME 2. Mass fragments of the compound V.

1.7 m (C_8 and C_{10}—C<u>H</u>$_2$), 1.3 br,s (chain—C<u>H</u>$_2$), 0.9 t (terminal—C<u>H</u>$_3$), 10.1 br,s (COO<u>H</u>).

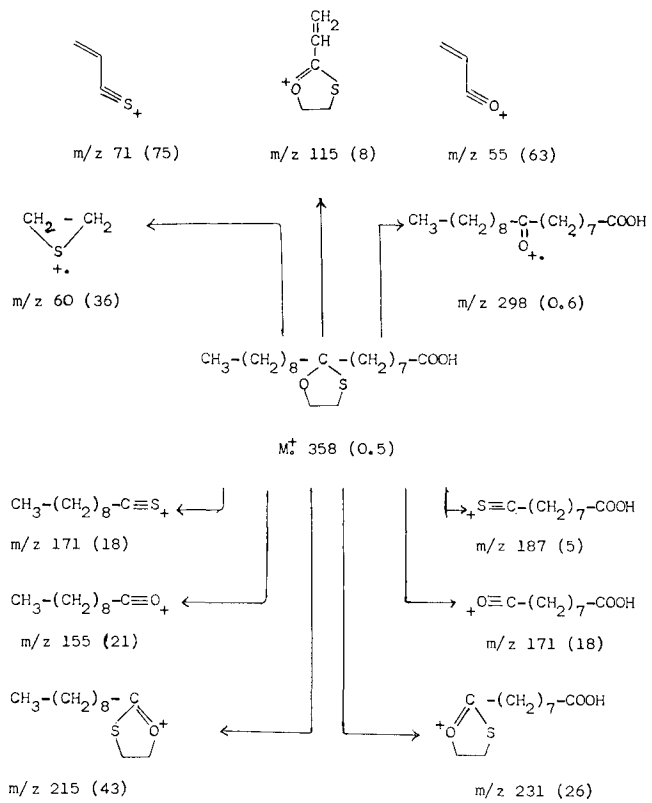
Reaction of III with β-mercaptoethanol, BF_3-etherate and acetic acid. A solution of methyl 9,10-dioxooctadecanoate (III) (3.26 g, 10 mmol) in acetic acid (5 ml) was treated with β-mercaptoethanol (3.12 g, 40 mmol) and freshly distilled BF_3-etherate (15 ml). The mixture was left at room temperature for four hr. Methanol (0.5 ml) was then added and the reaction mixture was poured into water and extracted with ether. The ether layer was washed successively with water, sodium bicarbonate (5%), water and dried. Evaporation of solvent and purification by column chromatography yielded an oily product IX (3.0 g, 50%).

$C_{21}H_{38}O_4S$: Calcd. C, 65.25; H, 9.90. Found: C, 65.15; H, 9.84%; IR: 1735 ($COOCH_3$), 1715 (CO—CH_2—), 1435, 1230 (CH_2—S), 1025 (oxathiolane ring); NMR: 4.12 t (C<u>H</u>$_2$—O), 3.6 s (COOC<u>H</u>$_3$), 2.72 (C<u>H</u>$_2$—S), 2.3 m (C_2 and C_{11} and/or C_8—C<u>H</u>$_2$), 1.65 m (C_8 or/and C_{11}—C<u>H</u>$_2$—), 1.3 br,s (chain—C<u>H</u>$_2$), 0.9 t (terminal—C<u>H</u>$_3$); MS: 386 (M^+, 28), 369 (M—OH, 61), 342 (M—$[CH_2]_2O$, 4), 325 (M—$[CH_2]_2SH$, 6), 261 (275—CH_2, 34), 243 (275—S or CH_3OH, 18), 217 (245—$[CH_2]_2$, 44), 171 (201—CH_2O, 22), 157 (201—$[CH_2]_2O$, 10), 71 (CH_2=CH—C≡S, 22), 60 (CH_2—CH_2, 40), 55 (CH_2=CH—C≡O, 81), 43 (CH_3—C≡O, 100).

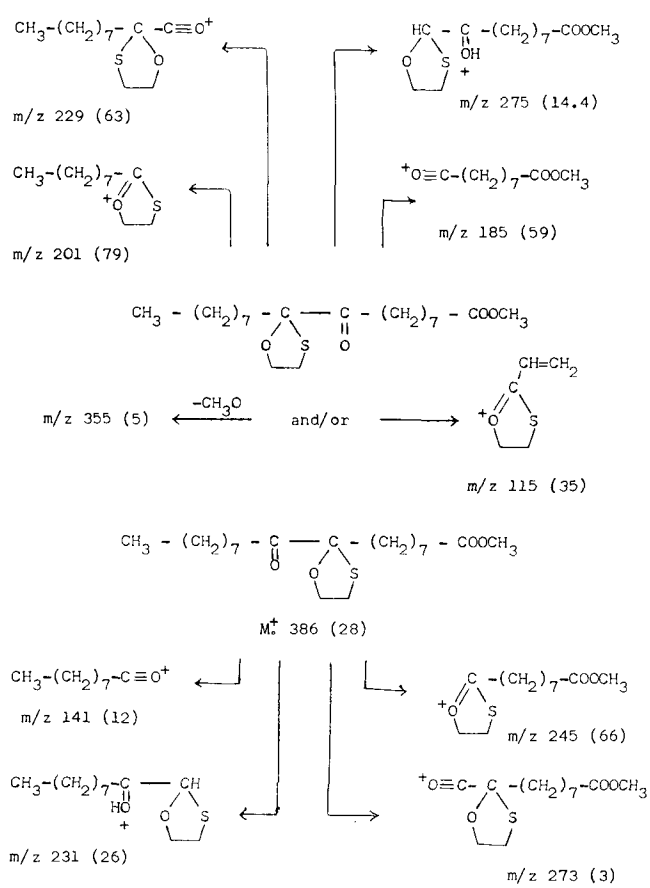
Reaction of IV with β-mercaptoethanol, BF_3-etherate. A similar reaction of 2-oxooctadecanoic acid (IV) (2.98 g, 10 mmol) with β-mercaptoethanol did not show any change in R_f value on a TLC plate even on prolonged refluxing. Final work-up regenerated the original 2-oxo acid as evidenced by co-TLC with authentic sample and spectral behavior.

RESULTS AND DISCUSSION

The formation of oxathiolanes and hemimercaptals from oxo fatty acids/ester is outlined in Scheme 1. IR spectra of oxathiolanes (V, VII, IX) showed a diagnostic band ranging from 1050-1025 cm^{-1} as characteristic of oxathiolane function. The two bands appearing at ~1250 (CH_2—S, wagging) and ~1440 cm^{-1} (CH_2—S deformation) indicated the presence of sulfur in all the compounds (V-IX). Product IX showed a band at 1715 cm^{-1} for C-9 or C-10 free carbonyl function. The NMR spectra of oxathiolanes gave three characteristic signals at δ 4.15 (C<u>H</u>$_2$—O, of ring), 2.85 (C<u>H</u>$_2$—S, of ring) and 1.7 (methylene protons α- to oxathiolane ring). The NMR spectrum of V showed an additional signal at δ 1.5 for methyl protons α- to the oxathiolane ring. In hemimercaptals, 10-hydroxy-10-(2′-hydroxyethylmercapto) undecanoic acid (VI) and 9-hydroxy-9-(2′-hydroxyethylmercapto) octadecanoic acid (VIII), all the signals are the same except D_2O exchangeable signals at δ 3.9-3.6 and 2.7-2.5 as broad multiplets due to the —OH group. The identity of hemimercaptals was established on the basis of their chromatographic (high polar), IR (3440-3490 cm^{-1}



SCHEME 3. Mass fragments of the compound VII.



SCHEME 4. Mass fragments of the compound IX.

for —OH group) and NMR (D_2O exchangeable signals) behavior.

Mass spectra of oxathiolanes (V, VII, IX) showed small molecular ion peaks. The ion peaks obtained due to the α-cleavages to the oxathiolane ring confirming the position and nature of the ring also were observed. A characteristic mass ion at m/z 115 observed in all the spectra, has been reported earlier as characteristic of oxathiolane grouping (12). The isomeric nature of IX was confirmed by mass fragmentation data shown in Scheme 4. Other prominent mass ions substantiating the structures have been elaborated in Schemes 2-4.

Here we observed that β-mercaptoethanol reacts with only one oxo group of methyl 9,10-oxooctadecanoate (III), whereas the ethane dithiol condenses with both the ketones of III as described earlier (8). This observation apparently is due to the difference in the reactivity of β-mercaptoethanol and ethanedithiol.

The formation of hemimercaptals (VI, VIII) from I, II respectively is explained in terms of lesser nucleophilicity of oxygen than of sulfur. Acetic acid was used in the reaction of III in order to dissolve the reactant, while I, II were found readily soluble in BF_3-etherate. There was no reaction of IV with β-mercaptoethanol in BF_3-etherate. The inductive effect caused by the chain and acid carbonyl group makes this oxo function less reactive. Steric hindrance may also play an important role in the nonreactivity of this acid.

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The Ionic Modification of the Surface Charge and Isoelectric Point of Soy Protein

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The effect of anionic and cationic binding on the surface charge of soy proteins was measured by electrokinetic analysis. All of the ions investigated suppressed the surface charge of the protein; however, certain multivalent ions such as Al (III), Fe (III), hexametaphosphate and tripolyphosphate also altered the isoelectric point of the protein. The results indicated the unpredictability of ionic effects on protein functionality, thus emphasizing the importance of making measurements of protein charge.

Much effort has been given to understanding of the functional properties of proteins. Functional properties of proteins are dependent on their physicochemical characteristics. For example, effects of ion binding to polyelectrolytes have been determined by emulsion rheology studies (1). The effect of pH and ionic strength on protein solubility has been determined (2) and is well known. In the food industry, the emphasis has been on studying the functional properties of the proteins rather than on measurements of the underlying physicochemical properties that actually control protein functionality. Because binding of either hydrogen ions or salts affects protein functionality by modifying the electrical properties of the protein, a method was used to measure these electrical properties. The method chosen was electrokinetic analysis (3,4), and the results of an electrokinetic study on the effect of pH and ionic modification of soy protein isolate are reported herein.

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MATERIALS AND METHODS

Soy isolate was from Kraft, Inc., Glenview, Illinois. Other chemicals were of reagent grade. Electrokinetic analysis was performed either by a System 3000 Electrokinetic Analyzer (PenKem, Inc., Bedford Hills, New York) or by a Zeta Meter, (Zeta Meter, Inc., New York, New York). The methods described in the instruction manuals (3,4) for the electrokinetic equipment were followed to make mobility determinations. The ionic strength of solutions was measured as specific conductance (micromhos/cm) using either the System 3000 Electrokinetic Analyzer or the Zeta Meter.

Soy protein isolate concentration was 0.28 mg/ml (solids basis) in distilled water. About 50-100 ml of