water and is catalyzed by the fatty acids; enzymatic hydrolysis is rarely observed (Loncin—*Ind. chim. belge 20, Spec. no.* 883). An activation factor which initiates the acidification is destroyed by heating the oil to 80° (Thuriaux—*Ibid.* 915). When palm oils were acidified through action of natural enzymes, monoglycerides were highest (12.3%) in samples containing 49% free fatty acids, and diglycerides were highest (32%) in samples containing 32.8% free acids (Desnuelle *et al.—Rev. franc. corps gras 4,* 203).

Irradiating fats with β- or γ-rays produces peroxides and carbonyl compounds, and results in odor and flavor changes which do not correlate well with chemical changes (Chipault *et al.—Ind. Eng. Chem. 49,* 1713). With oleic acid, γ-irradiation forms mixtures of 8-, 9-, 10-, and 11-hydroperoxido-öleates and C_8 and C_9 mono- and dicarboxylic acids (Slover & Dugan—*J. Am. Oil Chemists' Soc. 34,* 333). When meat is subjected to γ-radiation for sterilization, carbonyl compounds are formed which are different from those developed during irradiation of fat (Batzer—*J. Agr. & Food Chem. 5,* 700).

p-Aminobenzoic acid was mixed with crude cottonseed oil before refining to form insoluble derivatives of gossypol and related pigments (Dechary *et al.—U. S. 2,787,625*). Thus treated oils refine and bleach easier and are color stable. Color reversion in tallow is inhibited by addition of a small amount of hexamethylenetetramine to the tallow after it has been decolorized with propane (Sims & Nelson—*U. S. 2,783,256*).

Chlorine dioxide treatment of flour does not have a significant effect on the supply of essential fatty acids in the flour and it is thus unlikely that such treatment will result in essential fatty acid deficiency (Fisher *et al.—Chemistry & Industry 1957,* 1179).

Sorbic acid is efficient for inhibiting microbiological spoilage of margarine; it preserves taste; and is physiologically unobjectionable (Becker & Roeder—*Fette-Seifen-Anstrichmittel 59,* 321).

The control of garlic flavor and other flavors in butter has been discussed with regard to removal of the contributing plants with the use of herbicides (Dibbern—*Ibid. 58,* 1043).

The Reaction of Mercaptoacetic Acid with Methyl Linoleate and Linoleic Acid

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DURING THE COURSE of an investigation of the addition of various compounds to the ethylenic bonds of linoleic acid the reaction between mercaptoacetic acid and methyl linoleate was explored, and it appeared to merit more detailed study. Most of the previous work on the addition of mercaptoacetic acid to unsaturated compounds has been confined to addition of the reagent to terminally unsaturated olefins. However Koenig and Swern (6) have studied the addition of mercaptoacetic acid to undecylenic, ricinoleic, and oleic acids, and its addition to peanut oil has been reported (14). Earlier workers (2) reported that mercaptoacetic acid adds quantitatively to both double bonds of methyl linoleate although the reaction product was not isolated. In addition to the isolation and characterization of the di-adduct it appeared to be of especial interest to ascertain the possibility of selective addition of mercaptoacetic acid to methyl linoleate since the preferential addition of bromine to form 12,13-dibromo-9-octadecenoic acid (7) and of thiocyanogen to form 9,10-dithiocyano-12-octadecenoic acid (13) has been reported. Consequently the present investigation was directed toward the preparation, purification, and the characterization of the mono-adduct (carboxymethylthio-octadecenoic acid) and the location of its residual ethylenic bond as well as the characterization of the di-adduct, di(carboxymethylthio)-octadecanoic acid, and its trimethyl ester.

Experimental and Discussion

Analytical Methods

1. The progress of reactions was followed by periodic determination of unreacted mercaptoacetic acid in the reaction mixtures. Mercaptoacetic acid, alone or in reaction mixtures, was determined as follows. An accurately weighed sample of sufficient size to contain 0.7 to 1.0 milliequivalent of mercaptoacetic acid was dissolved in 5 ml. of carbon tetrachloride, 10 ml. of distilled water were added, and the sample was titrated to a permanent yellow color with a standard 0.1 N solution of iodine in glacial acetic acid and back-titrated with standard 0.1 N sodium thiosulfate until the yellow color just disappeared. In the analysis of reaction mixtures containing a large excess of mercaptoacetic acid, determinations were carried out on a scale five times as large as that described above.

2. Chromatographic separation of adducts was utilized for determination of the approximate amounts of the various components in crude and purified reaction products, and on a larger scale for preparative purposes. A modification of the Ramsey-Patterson procedure (10) for the separation of short chain monocarboxylic acids was employed for analyzing addition products of methyl linoleate and mercaptoacetic acid. The column was prepared as described by Ramsey and Patterson, but the neutralization step was omitted. Since the products were not completely soluble in iso-octane (the mobile phase), samples were added to the column in iso-octane containing about 15% of ether. Methyl linoleate moved rapidly through the column and was eluted principally at an effluent volume of 10 to 20 ml. The threshold volume (the volume at which the band reached the bottom of the column) of the half-ester of the mono-adduct generally amounted to about 40 ml. The monomethyl ester of the di-adduct was not eluted by iso-octane. The amount of mono-adduct was determined directly by titration of appropriate fractions of the eluate. The acid which was not eluted from the column by iso-octane was assumed to be the di-adduct. The amount of unreacted methyl linoleate was determined by subtracting the total calculated weights of mono- and di-adducts from the sample weight. Where the threshold volume of the mono-adduct was large enough to permit good separation from methyl linoleate, the weights

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of the recovered methyl linoleate and mono-adduct fractions were in good agreement with the calculated values, 92–100% and 100–110%, respectively. Since some variation in apparent mono-adduct was observed when samples of different size were analyzed, comparisons of the mono-adduct contents of various reaction products were made on samples of uniform weight (0.2 g.). Application of the Marvel-Rands chromatographic procedure (8) to the free acids obtained from linoleate free reaction products effected the separation of the mono-adduct (peak effluent volume, 30 ml.) from the di-adduct (peak effluent volume, 140 ml.). The amount of each component was determined directly by titration of the eluate.

3. Preformed conjugation was determined by the A.O.C.S. official method (1). Isolated *trans* bonds were determined by the method of Shreve *et al.* (11).

Materials

1. Linoleic acid (iodine value 179.5) was prepared from the free acids of safflower oil by a modification of the urea complexing method of Swern and Parker (12). A 1,000-g. sample of safflower acids was subjected to urea precipitation at about 5°C. from 4,000 ml. of methanol, in which were dissolved 1,600 g. of urea. The urea and methanol-free fraction which had not complexed was then distilled through a 6-in. Vigreaux column. Products with iodine value of 179 were obtained in good yield without difficulty. It was found that the free acids afforded a product of higher purity than that obtained by complexing the methyl esters.

2. Methyl linoleate was prepared by esterification of linoleic acid purified as described above. The methyl linoleate was purified by vacuum distillation through a 6-in. Vigreaux column. The three different preparations of methyl linoleate used in this work had iodine values of 171.7, 170.9, and 167.6 (theory, 172.5).

3. Eastman's practical grade (95%) mercaptoacetic acid was used, in some cases without further purification. However, for the majority of the work, mercaptoacetic acid was distilled (b.p. 101–102°C. at 11 microns) through a 6-in. Vigreaux column. The distilled products analyzed 98% mercaptoacetic acid, as determined iodimetrically.

Reaction Rates. Mercaptoacetic acid and methyl linoleate or linoleic acid are completely miscible. A reaction which is not noticeably exothermic occurs extremely slowly and at varying rates. Although methyl oleate has been reported to be more sluggish in reaction with mercaptoacetic acid than oleic acid (6), linoleic acid and its methyl ester were found to react at approximately equal rates. The rate of reaction appeared to be particularly susceptible to traces of contaminants. Reproducibility was improved somewhat by use of freshly cleaned glassware of known history. Among the other factors investigated, only the amount of excess of mercaptoacetic acid appeared to have any effect on the reaction rate. The time required for saturation of 1 double bond per mole of methyl linoleate was about 250 hrs. when 220% of the amount of mercaptoacetic acid required to react with 1 double bond per mole of methyl linoleate was used and 71 hrs. when 420% of theory was used. In two trials in which 10 times the theoretical amount was used, 5 and 32 hrs. were required to saturate one double bond. The reaction rate was not significantly affected by the addition of catalytic quantities of concentrated sulfuric acid or of peroxides, such as benzoyl peroxide, cumene hydroperoxide, or phenylcyclohexyl hydroperoxide; by exposure to ultraviolet light; by reacting in solution in carbon tetrachloride or in glacial acetic acid; or by varying the temperature from 5 to 70°C.

Preparation of Adducts. Methyl linoleate or linoleic acid (0.07 to 0.14 mole quantities) and distilled mercaptoacetic acid (2.2 or 10.0 moles per mole of linoleate) were mixed in freshly cleaned, glass-stoppered bottles and allowed to react, usually at room temperature. When determination of the amount of unreacted mercaptoacetic acid indicated that the desired amount of reaction had occurred, the reaction mixtures were dissolved in a solvent, usually benzene, and washed repeatedly with water. The washed solutions were dried with sodium sulfate, after which the solvent was removed *in vacuo*.

In order to determine whether reaction conditions or purity of the mercaptoacetic acid had any effect on the relative amounts of mono-adduct formed, three crude reaction products freed of mercaptoacetic acid were analyzed chromatographically on a Ramsey-Patterson column after reactions had proceeded to the extent of saturating 1 double bond per mole of methyl linoleate. These were:

1. the product from the reaction at 5°C. of 0.10 mole of methyl linoleate and 0.22 mole of distilled mercaptoacetic acid for 188 hrs.;

2. the product from the reaction at room temperature (about 25°C.) of 0.028 mole of methyl linoleate and 0.28 mole of distilled mercaptoacetic acid for 5 hrs.;

3. the product from the reaction at room temperature of 0.1 mole of methyl linoleate with 1.0 mole of undistilled mercaptoacetic acid for 24 hrs. (The content of mono-adduct in the above products was 39%, 43%, and 30% by weight, respectively. Since the use of undistilled mercaptoacetic acid resulted in a low yield of the mono-adduct, reaction products prepared with distilled mercaptoacetic acid were used as starting materials for the isolation of mono-adduct.)

Purification of Mono-adduct by Alkali Extraction and Distillation. The reaction mixture previously freed from mercaptoacetic acid was extracted with alkali, thereby removing the unreacted methyl linoleate from the mixture of adducts. Some saponification of the ester linkage of the adducts occurred during this step. Attempted vacuum distillation of the ester adduct resulted in decomposition. However vacuum distillation could be effected without apparent decomposition by conversion to the neutral methyl ester. An example of this procedure is as follows. Methyl linoleate (0.10 mole, I.V. 170.9) and distilled mercaptoacetic acid (0.22 mole) were allowed to react at room temperature until half of the unsaturation had disappeared (240 hrs.) The reaction mixture was taken up in ether and freed of excess mercaptoacetic acid by washing with distilled water. The adduct fraction was then extracted with 1% sodium hydroxide solution. The soaps were acidified with hydrochloric acid, extracted with ether, and washed with distilled water until free of mineral acid. The yield of adduct fraction was 28.6 g. Esterification with methanol, using sulfuric acid catalyst, yielded 29.0 g. of methyl esters. A 27.0-g. sample of the methyl esters was distilled from a modified Claisen flask. The middle fraction (b.p. 180–182°C. at 20 microns), $n_D^{20} = 1.4753$, weighed 10.2 g. Anal. Calculated for $C_{21}H_{38}O_4S$: C, 65.96; H, 10.06; S, 8.00; sap. equiv., 200.3. Found: C, 65.48; H, 10.09; S, 8.54; sap. equiv., 201.4. Chromatographic analysis on a Marvel-Rands column, obtained after saponification of the free acids, indicated that the product contained

approximately 91% of mono-adduct. Infrared absorption spectra indicated that about 70% of the residual double bonds have the *trans* configuration, assuming that the sample is approximately 90% mono-adduct and 10% di-adduct.

Purification of the Mono-adduct by Chromatography. Methyl linoleate (0.14 mole, I.V. 167.6) and distilled mercaptoacetic acid (1.4 moles) were allowed to react for 48 hrs. at room temperature. Determination of unreacted mercaptoacetic acid indicated that 1.1 to 1.2 double bonds per mole of methyl linoleate had reacted. The yield of mercaptoacetic acid-free reaction product (53.6 g.), the neutral equivalent (364.6), and the sulfur content (8.94%) were all in good agreement with the values to be expected from a product obtained by addition of 1.1 moles of mercaptoacetic acid per mole of methyl linoleate. Infrared absorption spectra indicated that about 70% of the residual double bonds have the *trans* configuration.

Analysis, using a Ramsey-Patterson column, indicated that this product contained approximately 44% of mono-adduct. A larger quantity of mono-adduct was isolated from the mercaptoacetic acid-free reaction product by using a Ramsey-Patterson type column 70 mm. I.D. containing 468 g. of silicic acid. The proportions of methanol, indicator, ammonia, iso-octane and silicic acid, and the method of packing the column were the same as those employed by Ramsey and Patterson, but the mode of addition of the sample was changed. Small-scale experiments indicated that the crude product was not completely soluble in iso-octane but could be dissolved in a mixture of iso-octane and ether. Since the presence of ether tends to lower the threshold volume of the mono-adduct and could therefore result in poor separation from unreacted methyl linoleate, the sample was introduced in the following manner. A 10.8-g. portion of the crude, mercaptoacetic acid-free reaction product was extracted with three portions, totalling 100 ml., of iso-octane saturated with methanol; and an 80-ml. aliquot of this solution was chromatographed. After elution of the unreacted methyl linoleate band and the principal mono-adduct band with iso-octane, the remainder of the sample was introduced. This was done by dissolving the iso-octane-methanol insoluble residue in 15 ml. of ether, diluting to 100 ml. with iso-octane and adding an 80-ml. aliquot of the resultant solution to the column. Elution with iso-octane was then resumed and continued until a second mono-adduct band was removed. The mono-adduct obtained from combination of the two portions of mono-adduct, 3.32 g., was an odorless, colorless viscous oil $n_D^{24} = 1.4841$. Anal. Calculated for $C_{21}H_{38}O_4S$: C, 65.22%; H, 9.91%; S, 8.29%. Found: C, 65.22%; H, 9.80%, S, 8.03%.

A portion (3 g.) of the mono-adduct was saponified by treatment of the half ester with an excess of 4 N potassium hydroxide (6 ml.) at room temperature, and the acids were recovered from the soaps by acidification with HCl and extraction with ether. The free acid, a colorless oily viscous liquid, $n_D^{26.7} = 1.4908$, was obtained in substantially quantitative yield, and infrared analysis indicated that about 87% of the residual double bonds had the *trans* configuration. Anal. Calculated for $C_{20}H_{36}O_4S$: C, 64.47%; H, 9.74%; S, 8.62%; neutral equivalent, 186.3. Found: C, 64.50%; H, 9.65%; S, 8.51%; neutral equivalent, 188.7.

The methyl linoleate portion recovered from the large column (1.2 g.) contained about 12% of conjugated diene, and infrared analysis indicated that about 40% of the isolated ethylenic bonds were of the *trans* configuration.

An experiment conducted, using catalytic quantities of mercaptoacetic acid (1% by weight), failed to induce any appreciable amount of conjugation or isomerization to the *trans* configuration.

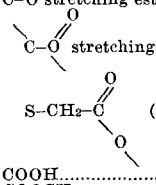
Location of the Position of the Residual Double Bond of the Mono-adduct. This was accomplished by ozonolysis and chromatographic analysis of the resultant acids. A sample (0.5 g.) of the free acid of the chromatographically purified mono-adduct was ozonized in ethyl acetate solution, and oxidation was completed by refluxing with 10 ml. of 30% hydrogen peroxide for 2 hrs. In order to prevent loss of monobasic acids the ozonolysis product was neutralized with aqueous NaOH prior to removal of the solvent. The ozonolysis mixture contained about 20 times the amount of acid to be expected from fission of the ozonide of the mono-adduct, presumably because of the formation of acetic acid from the ethyl acetate. The soaps were diluted to 100 ml. with water, and separate aliquots were used for the determination of caproic and azelaic acids by procedures which gave good recovery of these acids from known mixtures containing appropriate quantities of azelaic, caproic, and acetic acids. For the determination of caproic acid the acids were recovered from their sodium soaps and made up to standard volume in iso-octane and chromatographed by the Ramsey-Patterson procedure.

For the determination of dibasic acids the acids recovered from the sodium soaps were freed of monobasic acids by repeated evaporation to dryness, dissolved in a mixture of 1 ml. tertiary amyl alcohol and 0.1 ml. of water made up to 10.0 ml. with chloroform. An aliquot was analyzed by the method of Higuchi *et al.* (5), modified (4) in the following manner. The silicic acid was oven-dried at 110–115°C. prior to use, 25 g. of silicic acid were admixed with 19 ml. of buffer, 100% chloroform was used in preparing the slurry and as the first eluant; 100 ml. of each eluant were used. The analysis for monobasic acids indicated that the ozonolysis product contained 0.29 milliequivalents of caproic acid (threshold volume, 116 ml.) per mole of mono-adduct ozonized. Although no visible bands for monobasic acids other than caproic were observed, the fraction collected in the range at which enanthic acid would be expected (threshold volume about 90 ml.) contained 0.06 milliequivalent of acid per mole of mono-adduct ozonized. The analysis for dibasic acids indicated the presence of sebacic acid (effluent volume 170–200 ml.) and suberic acid (effluent volume 440–480 ml.) in addition to azelaic acid (effluent volume 240–320 ml.). The amounts of azelaic, sebacic, and suberic acids were 0.38, 0.06, 0.04 mole, respectively, per mole of mono-adduct ozonized. Since the ratio of caproic to azelaic acids was about 1 to 1.2, it was concluded that addition occurred about equally at the 9,10- and the 12,13-ethylenic bonds.

Preparation of Di-adduct. Linoleic acid (20 g., 0.07 mole) and mercaptoacetic acid (65 g., 0.7 mole) were allowed to react at room temperature for 144 hrs. Analysis for mercaptoacetic acid indicated that 0.14 mole had reacted. The yield of mercaptoacetic acid-free reaction product was 96% of theory. The product, a nearly colorless, viscous oil, (η = approx. 110 poises of 25°C.), $n_D^{26.5} = 1.5071$, $d_{30}^{30} = 1.110$. Anal. Calculated for $C_{22}H_{40}O_6S_2$: C, 56.86%; H, 8.68%; S,

TABLE I

Absorption Bands in the Infrared Spectra of Linoleic Acid, Methyl Linoleate, and Their Mercaptoacetic Acid Derivatives

Curve ⟶	Wavelength position (μ) of maxima							
	A	B	C	D	E	F	G	H
Functional group								
1. O–H . . . O stretching (bonded)	3.25	.....	.....	3.25	3.21–.29	.....	3.24	.....
2. C–H stretching (–CH_3)	3.46	3.43	3.46	3.45	3.41	3.41	3.45	3.45
3. C–H stretching (–CH_2)	3.51	3.50	3.51	3.50	3.50	3.48	3.51	3.51
4. C–H, O–H . . . O combination band	3.77	.....	.....	3.76	3.76	.....	3.77	.....
5. C=O stretching (ester *ca.* 5.75)	.....	5.78	5.80	.....	5.76–.83	5.75	.....	5.75–.80
6. C=O stretching (acid *ca.* 5.85)	5.84	.....	.....	5.82–.87	.....	.....	5.80–.90	.....
7. C–H deformation (–CH_2, –CH_3)	6.85	6.83	6.86	6.86	6.84	6.84	6.88	6.87
8. –CH_3 symmetrical deformation ($COOCH_3$)	.....	6.95	6.96	.....	6.94	6.94	.....	6.97
9. Unassigned	7.09	7.15	.....	7.10	7.06	.....	7.10–.12	.....
10. –CH_3 asymmetrical deformation ($COOCH_3$)	.....	7.33	7.32–.39	.....	7.30	7.31	.....	7.33–.38
11. C–O and C–S(?) (see text)	7.80	7.89	7.95–8.03	7.72–.77	7.77–.78	7.76–.79	7.72–.80	7.80
12. C–O stretching ester	.....	8.55	8.58	.....	8.56	8.60	.....	8.65–.69
13.  (see text)	8.85	8.88–.92	.....	8.80	8.80–.84	8.80	8.82	8.82
14. COOH	9.65	.....	.....	9.63–.68	9.60–.64	.....	9.66	.....
15. $COOCH_3$	.....	9.86	9.92	.....	9.90	9.87	.....	9.93
16. C–H bending about *trans* C=C	.....	.....	10.28	10.32	10.26	10.27	.....	10.25

Infrared absorption spectra (in $CHCl_3$ solution) of linoleic acid, methyl linoleate, and reaction products with mercaptoacetic acid: A, linoleic acid; B, methyl linoleate; C, unreacted methyl linoleate recovered from reaction product; D, free acid of mono-adduct; E, half ester of crude mono-adduct, ester on fatty acid moiety; F, dimethyl ester of mono-adduct; G, free acid of di-adduct; and H, trimethyl ester of di-adduct.

13.80%; neut. equiv., 154.9. Found: C, 56.68%; H, 8.55%, 8.93%; S, 13.42%; neut. equiv., 161.

The trimethyl ester was obtained in good yield by esterification with methanol, using 1% H_2SO_4 as a catalyst. The ester was a nearly colorless oil, having a viscosity of 0.5 poise at 25°C., $n_D^{25} = 1.4861$, and $d_{30}^{30} = 1.051$. Anal. Calculated for $C_{25}H_{46}O_6S_2$; C, 59.25%; H, 9.15%; S, 12.65%; sap. equiv., 168.9. Found: C, 59.60%; H, 9.14%; S, 12.41%; sap. equiv., 171.6.

Infrared Spectra

The infrared spectra of pure linoleic acid and methyl linoleate and of several products of the reaction of these compounds with mercaptoacetic acid are shown in Figure 1. Principal absorption bands in these spectra, those with absorptivities of 0.10 or more, are compared in Table I. Most of the observed bands can be correlated with vibrations of functional groups which give rise to them, and the correlations support the postulated structures of the reaction products.

The region about 7.7 to 8.9 microns is of special interest. Bands are observed between 7.7 to 7.95 μ and between 8.8 and 8.95 μ in the spectra of all the samples. Koenig and Swern (6) suggest a correlation between bands in the range 1271–6 cm.$^{-1}$ (7.84–7.87 μ) and 1128–32 cm.$^{-1}$ (8.83–8.87 μ) and the carbalkoxymethylthio (–SCH_2COOR) group. They report that these bands do not occur in compounds which contain carboxymethylthio (–SCH_2–COOH) group. The data in Table I do not appear to support these specific correlations. From a study of the infrared spectra of long chain fatty acids and their esters, in CS_2 solution or as the pure liquids, Shreve *et al.* (11) reported strong C–O vibrations at about 7.8 and 8.0 μ for the acids and three bands at about 8.0, 8.3, and 8.5 μ in the spectra of the esters. O'Connor, Field, and Singleton (9), from similar measurements in $CHCl_3$ solution, reported C–O stretching bands for the acids at 7.75–7.80 and 8.40–8.45 μ and at 7.90–7.95 and 8.48–8.50 μ for the methyl esters. In the chloroform solution spectra reported here, C–O stretching would appear to account for the bands at 7.7–7.95 μ, a band appearing between about 7.7–7.8 μ for the acids and 7.8–8.0 μ for the methyl esters. Bellamy (3) has emphasized that the C–O stretching mode is very sensitive to change in mass and nature of attached groups. A consideration of the intensities of these bands however indicates that another absorption band, probably arising from a C–S stretching, is unresolved from the C–O absorption at these wavelengths. In Table II bands between 7.7 and 7.9 μ are tabulated with their intensities, as molecular absorptivities. Compounds in Group I (Table II) contain one C–O and no C–S groups, Group II, two C–O and one C–S group, and Group III, three C–O and two C–S linkages. A doubling and tripling of the observed intensities in Group I is not sufficient to account for the observed intensities in Groups II or III. Postulation of an unresolved C–S stretching results in somewhat better agreement although such a hypothesis would require that the C–S stretching vibration be somewhat weaker than that of the C–O stretching and that the two stretching vibrations occur at almost identical wavelengths.

TABLE II

Intensities of Bands at Approximately 7.8 and 8.8 Microns

Compound	*ca.* 7.8 microns			*ca.* 8.8 microns		
	λ	a	ϵ	λ	a	ϵ
	Group I					
Linoleic acid	7.80	0.31	93	8.85	0.13	39
Methyl linoleate	7.89	0.28	84	8.88–.92	0.11	33
	Group II (Mono-adducts)					
Free acid	7.72–.77	0.59	236	8.80	0.24	96
Half ester	7.77–.78	0.56	224	8.80–.84	0.33	132
Diester	7.76–.79	0.60	240	8.80	0.41	164
	Group III (Di-adducts)					
Triacid	7.72–.80	0.65	325	8.82	0.30	150
Triester	7.80	0.71	355	8.82	0.50	250

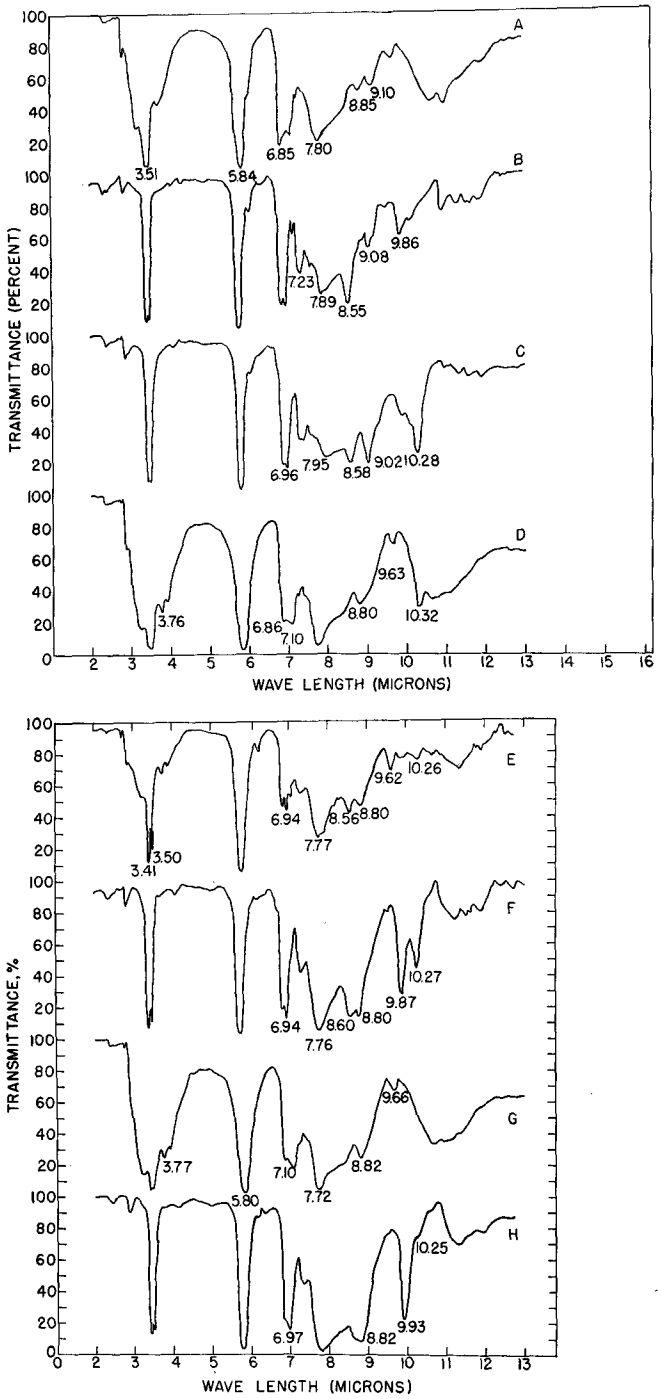


FIG. 1. Infrared absorption spectra (in $CHCl_3$ solution) of linoleic acid, methyl linoleate, and reaction products with mercaptoacetic acid: A, linoleic acid; B, methyl linoleate; C, unreacted methyl linoleate recovered from reaction product; D, free acid of mono-adduct; E, half ester of crude mono-adduct, ester on fatty acid moiety; F, dimethyl ester of mono-adduct; G, free acid of di-adduct; and H, trimethyl ester of di-adduct.

For example, the band at 7.80 μ in the spectrum of the trimethyl ester of the diadduct, with two C–S and three C–O groups, is rather sharp. Analysis of the absorptivities at *ca.* 7.8 μ (Table II) fails to reveal any particular evidence for an absorption arising from the carbalkoxymethylthio rather than the carboxymethylthio group.

Bands at about 8.7 and 9.0 μ for the long-chain fatty acids and at 8.9–9.0 μ only for the esters have been reported by O'Connor *et al.* (9). In all the spectra measured in the present investigation a band is observed between 8.80 and 8.90 μ although in the spectra of the pure methyl linoleate this band is weak. At the resolution of these measurements this band could not be used to identify a sulfur-containing group. Again a study of intensities, Table II, indicates that the vibration of the $-\overset{O}{\overset{\|}{C}}-OR$ may be unresolved from some vibration of the $-S-CH_2-\overset{O}{\overset{\|}{C}}-O-R$. There is no evidence for a differentiation between carbalkoxymethylthio and carboxymethylthio groups although the absorption of the esters of the sulfur compounds is distinctly more intense than is the absorption of the free acids; and the contribution, to the absorption, of the sulfur-containing moiety seems to be greater in this region than it is in the 7.7–7.9 micron region.

At about 10.3 μ the C–H bending about the *trans* C = C, which has been used for the quantitative estimation of this group, is seen in all the unsaturated reaction products, including the recovered methyl linoleate. Obviously a considerable proportion of the *cis* bonds originally present in the methyl linoleate has been isomerized to the *trans* isomer during the reaction with mercaptoacetic acid.

Summary

The reaction of mercaptoacetic acid with methyl linoleate and with linoleic acid was investigated. The reaction proceeded at low and erratic rates, with and without catalysts, such as peroxides at various temperatures, but could be accelerated by use of a large excess of mercaptoacetic acid.

Addition of 1 mole of mercaptoacetic acid to 1 mole of methyl linoleate resulted in a product containing about 40% of mono-adduct. Ozonolysis of the purified mono-adduct yielded approximately equimolar quantities of caproic and azelaic acids, indicating that addition occurred about equally at the 9,10- and 12,13-ethylenic bonds. The dicarboxylic acid and the dimethyl ester of the mono-adduct and the tricarboxylic acid and trimethyl ester of the di-adduct of linoleic acid and mercaptoacetic acid were prepared, and the infrared spectra and some physical and chemical characteristics of these products were determined.

The infrared spectra of the reaction products were obtained and correlated with functional groups which give rise to them. Bands at about 7.8 and 8.8 μ, commonly observed in long chain acids and esters and ascribed to C–O vibrations, are intensified in the sulfur-containing reaction products, suggesting characteristic absorption of C–S compounds at almost identical wavelengths.

The formation of adducts was accompanied by a high degree of isomerization of the unreacted ethylenic bonds from the *cis* to the *trans* form both in the mono-adduct and in unreacted methyl linoleate. The methyl linoleate recovered contained about 12% diene conjugation, but catalytic quantities of mercaptoacetic acid were not effective in inducing conjugation.

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Observations on the Permanganate Oxidation of Unsaturated Esters[1,2,3]

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THE OXIDATION of fats with potassium permanganate to convert the unsaturated glycerides to azelaoglycerides was originally suggested by Hilditch and Lea (1). Kartha has suggested (2) that Hilditch's procedure (3) can be improved by conducting the oxidation in the presence of acetic acid. Kartha has pointed out that, during the permanganate oxidation of fats in acetone, alkaline products accumulate which may hydrolyze the ester groups of the fat. He believes that the ester linking the azelaic acid moiety to the glycerol is especially easily hydrolyzed under these conditions. Hilditch has expressed doubt that the hydrolysis which might occur during the permanganate oxidation is significant, especially when compared with that which might occur during subsequent alkaline extractions of the product. There have been exchanges of view-point in the literature (4, 5, 6).

Recently work has been started in this laboratory to try to improve the present methods of glyceride analysis. One approach that appeared feasible was to try to improve the methods of separating the azelaoglycerides and fully saturated glycerides obtained after permanganate oxidation of fat. However some of the products obtained by potassium permanganate oxidation according to Kartha's procedure were found to have an unexpectedly high proportion of ester groups. This led to a critical study of Kartha's procedure and other procedures on some known compounds. The results of this study are reported below.

Materials and Methods

Undecylenic acid (Eastman practical) was converted to the methyl ester by refluxing for six hours with an excess of methanol and a sulfuric acid catalyst.[4] The methyl undecylenate was freed from acid by washing with 3% aqueous sodium carbonate and was distilled through a Vigreaux column 25 cm. long at 1-mm. pressure. The fraction boiling between 80.2 and 80.5°C. amounted to about 80% of the charge. It gave the following analysis: n_D^{20} 1.4390, saponification value 283.4 (theory 282.9), iodine value 127.6 (theory 128.0), d^{20} 0.88414 g./cc. When hydrogenated, the product had n_D^{20} 1.4292 [calculated value 1.4291 (7)].

Triundecylenin was made by reacting 347 g. of the above methyl undecylenate with 127 g. of triacetin (Eastman), using 2.3 g. of sodium methylate as a catalyst. The reaction mixture was stirred with a magnetic stirrer, and nitrogen was bubbled through it. The pressure was reduced from 40 mm. to 5 mm. over several hours, and the mixture was left under 5 mm. of pressure over-night. Next day the pressure was reduced to 0.2 mm. for a few hours. The methyl acetate which distilled was caught in a dry ice trap and amounted to 93% of theory. The catalyst was destroyed with 3 ml. of acetic acid and 500 ml. of water. The product was washed free from acids with aqueous sodium carbonate. The product (349 g.) was crystallized from 1,750 ml. of ether at —65°C. The crystalline residue, which weighed 135 g., was crystallized from 1,350 ml. of methanol-ether (4:1) at —30°C. The product weighed 115 g. It gave the following analysis: saponification value 287.2 (theory 284.9), hydroxyl value zero, iodine value 128.1 (theory 128.9) n_D^{20} 1.4650, d^{20} 0.94416 g./cc., m.p. 8.0–8.3°C. When hydrogenated, the product had a m.p. 30.15–30.40°C. [reported for triundecanoin 30.50°C. (8)] and a n_D^{20} 1.4541.

Methyl oleate was prepared as follows. A commercial oleic acid was purified with urea by the method of Swern and Parker (9). The oleic acid was then esterified with methanol, using a sulfuric acid catalyst, and the product was washed free of oleic acid with aqueous sodium carbonate solution. The methyl oleate was then distilled at 3 mm. through a three-foot column packed with glass helices. The fraction, whose boiling point indicated an 18-carbon chain, was collected and dissolved in 10 volumes of methanol. The portion crystallizing from the methanol at —30°C. was discarded. The methyl oleate recovered from the methanol filtrate gave the following analysis: saponification value 189.6 (theory 189.2), iodine value 85.2 (theory 85.6), n_D^{20} 1.4528 [calculated 1.4520 (7)]. Alkali isomerization (10) and

[1] A report of this work was given at the American Dairy Science Association meetings, Stillwater, Okla., in June, 1957.
[2] Journal Paper No. J-3245 of the Iowa Agricultural and Home Economics Experiment Station, Ames, Ia., Project No. 1128.
[3] Supported in part by a grant from the American Dairy Association.
[4] During the preparation of this and the other unsaturated esters, the fatty acids were protected from autoxidation by oxygen-free nitrogen.