The literature gives pound-cake volume values of around 250 as being the best obtainable. The cake baked with palladium catalyst shortening had a finer texture. This shortening was tested by official Federal Standards for iodine number, acidity, stability, moisture, and smoke point (10). It was satisfactory in all tests.

Summary

Shortening stocks obtained in the pilot plant differ slightly from those obtained in the laboratory under nominally the same conditions. Pilot-plant processing is easily controlled to give a commercially attractive shortening at a cost competitive witb nickel. By repeated re-use 1 g. of 5% palladium on carbon catalyst will hydrogenate about 18 kg. of oil to a satisfactory product, and 1 g. of 2% palladium on carbon catalyst about 11 kg. of oil.

Acknowledgment

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Vinyl Ketostearates. Preparation, Properties, Infrared Spectra, and Analysis of 4- and 12-Ketostearates[1]

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THE PREPARATION of vinyl 4- and 12-ketostearates was undertaken to provide monomers for polymerization and copolymerization investigations, to determine the potential utility of vinyl keto esters as internal plasticizers, and to study the effect of the position of the keto group. Polymerization studies will be reported elsewhere.

Vinyl esters of long-chain fatty acids have generally been prepared either by reacting an excess of vinyl acetate with the fatty acid in the presence of a mercuric sulfate catalyst or by vinylation of the fatty acid with acetylene in the presence of zinc salts (5, 10). 12-Ketostearic and 4-ketostearic acids, which have previously been reported (2), were vinylated with vinyl acetate according to the general procedure of Adelman (1).

The infrared spectra of methyl 4-ketostearate, methyl 12-ketostearate, 4-ketostearic acid, 12-ketostearic acid, vinyl 4-ketostearate, vinyl 12-ketostearate, and the γ-lactone of 4-hydroxy-2-octadecenoic acid were determined in carbon tetrachloride solutions. The absorption bands in the 5.6 micron region (characteristic of the lactone-carbonyl), 5.7 micron region (characteristic of the ester-carbonyl), 5.8 micron region (characteristic of ketone-carbonyl), and 6.1 micron region (characteristic of the vinyl group) were studied and used as a basis for quantitative determination of these groups.

Experimental

Materials. Commercial methyl 12-hydroxystearate obtained from hydrogenated castor oil, Brazilian oiticica oil (*ca.* 56% conjugated triene, calculated as eleostearic acid), Eastman's p-dioxane and practical grade vinyl acetate (freshly distilled), Merck's reagent grade mercuric acetate, Girdler's supported-type (electrolytically precipitated, dry-reduced) nickel catalyst, Baker's reagent grade sodium acetate, chromium trioxide, sulfuric acid, potassium carbonate, glacial acetic acid, methanol, petroleum ether (b.p. 30–60°C.) and acetone, and Johns-Manville's analytical filter-aid (Celite) were used.

Methyl 12-Ketostearate. Commercial methyl 12-hydroxystearate was fractionally distilled under high vacuum. Distillate fractions (b.p. 191°C./0.3. mm., m.p. 54.5–55.4°C.) were oxidized with chromic acid by the general procedure of Rockett (17). To a 5-liter flask, equipped with a mechanical stirrer, a thermometer, and a dropping funnel, were added with stirring 660 ml. of glacial acetic acid and 314 g. (1 mole) of methyl 12-hydroxystearate. The temperature was maintained between 30 and 32°C. while adding dropwise, with stirring, a solution of chromic acid (92 g. of chromic acid, 67 ml. of water, and 1320 ml. of glacial acetic acid) in about 2 hrs. The temperature was maintained between 35 and 40°C. for 90 min. The mixture was poured into 5 liters of water contained in a separatory funnel. After shaking the mixture gently and allowing it to stand for a few hrs., the aqueous layer was drained off. The ester layer was heated to boiling in 3 liters of 6 N hydrochloric acid for 10 min. After siphoning out the aqueous layer, the ester was again heated in 1 liter of 6 N hydrochloric acid for 10 min. The ester was washed twice

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with 3 liters of boiling water. Methyl 12-ketostearate was crystallized from 10 volumes of methanol at 5°C., yield 220 g. Its carbonyl oxygen content (11) indicated it was reasonably pure keto ester.

Anal. Calcd. for $C_{19}H_{36}O_3$: C, 73.03; H, 11.61; carbonyl O, 5.12; sap. equiv., 312.5. Found: C, 73.01; H, 11.36; carbonyl O, 5.10; sap. equiv., 311.6; m.p. 45.3–46°C.; $n^{50/D}$ 1.4391.

12-Ketostearic Acid. Methyl 12-ketostearate (220 g.) was refluxed with an alcoholic potassium hydroxide solution (700 ml. of 1.5 N potassium hydroxide in 80% ethanol) for 1 hr. The warm soap solution was poured slowly, with vigorous stirring, into 1 liter of 1.5 N hydrochloric acid. The 12-ketostearic acid was filtered off, washed with boiling water, then crystallized from 3 volumes of acetone at 25°C., yield 159 g.

Anal. Calcd. for $C_{18}H_{34}O_3$: C, 72.43; H, 11.48; carbonyl O, 5.36. Found: C, 72.44; H, 11.57; carbonyl O, 5.35; m.p. 82.0–82.5°C.

Vinyl 12-Ketostearate. 12-Ketostearic acid was vinylated, employing a 5-molar excess of vinyl acetate in the presence of a mercuric acetate-sulfuric acid catalyst, according to Adelman's (1) vinyl interchange reaction. To a 1-liter flask, equipped with a thermometer, were added 298 g. (1 mole) of 12-ketostearic acid and 516 g. (6 moles) of vinyl acetate. This mixture was heated to 70°C. while being swirled gently. Then 0.1 g. of copper resinate and 6.0 g. of mercuric acetate were added. When all these materials were in solution, 0.83 ml. of concentrated sulfuric acid was added while the mixture was swirled gently. The reaction mixture was maintained between 38 and 42°C. for 48 hrs. Maximum conversion obtained was 65%. The reaction was stopped by adding 3 g. of sodium acetate and stirring the mixture for 15 min. The reaction mixture was dissolved in 2 liters of diethyl ether and washed twice with 1-liter portions of water. The ethereal solution was then extracted with a slight excess of dilute potassium carbonate (800 ml. of 10% potassium carbonate) to remove the free fatty acids. After distilling the ether and excess vinyl acetate under reduced pressure, the crude vinyl ester was distilled rapidly under high vacuum to remove traces of mercury. Distillate fractions (b.p. 175–200°C./0.3 mm.) were dissolved in 10 volumes of ether and re-extracted with dilute potassium carbonate. After distilling the ether under reduced pressure, vinyl 12-ketostearate was successively crystallized from 3 volumes of acetone at 5°C. in the presence of 0.02% hydroquinone, and from 15 volumes of petroleum ether at −5°C., yield 150 g. Its H.I.V. (hydrogen iodine value) (15) indicated that it was reasonably pure vinyl ester.

Anal. Calcd. for $C_{20}H_{36}O_3$: C, 74.02; H, 11.18; carbonyl O, 4.93; H.I.V., 78.2. Found: C, 73.90; H, 11.16; carbonyl O, 4.95; H.I.V., 78.0; m.p. 48.2–48.8°C.; $n^{50/D}$ 1.4457.

Methyl 4-Ketostearate. One kg. of Brazilian oiticica oil, having a H.I.V. of 185, was hydrogenated in a Parr pressure reaction apparatus at 30 p.s.i. in the presence of 40 g. of supported-nickel catalyst (20% nickel and 80% coconut oil and diatomaceous earth) at about 150°C. during a 24-hr. period, to an H.I.V. of about 5. The hot hydrogenated oil (*ca.* 100°C.) was filtered by suction through a thin layer of hot filter-aid to remove the catalyst. The hydrogenated oil was interesterified with methanol (650 ml., 5-molar excess) in the presence of a 1% sodium methoxide catalyst, at about 70°C. during a 2-hr. period. The warm methyl esters were poured into 500 ml. of N hydrochloric acid contained in a separatory funnel, then the mixture was shaken gently. After the aqueous layer was removed, the esters were washed with a 500-ml. portion of warm distilled water. The crude esters were fractionally distilled under high vacuum. Distillate fractions (b.p. 170–180°C./0.5 mm.) were crystallized from 12 volumes of acetone at 5°C. to precipitate most of the nonketo esters. After the acetone was evaporated under reduced pressure, methyl 4-ketostearate was successively crystallized from 15 volumes of petroleum ether at 5°C. from 15 volumes of methanol at 5°C.

Anal. Calcd. for $C_{19}H_{36}O_3$: C, 73.03; H, 11.61; carbonyl O, 5.12; sap. equiv., 312.5. Found: C, 72.91; H, 11.67; carbonyl O, 5.09; sap. equiv., 312.4; m.p. 47.3–48.0°C.; $n^{50/D}$ 1.4391.

4-Ketostearic Acid. Methyl 4-ketostearate was saponified, the soap solution was acidified, and the fatty acid was crystallized as described for 12-ketostearic acid.

Anal. Calcd. for $C_{18}H_{34}O_3$: C, 72.43; H, 11.48; carbonyl O, 5.36. Found: C, 72.45; H, 11.57; carbonyl O, 5.26; m.p. 96.5–97.1°C.

Vinyl 4-Ketostearate. 4-Ketostearic acid was vinylated, and the vinyl 4-ketostearate was purified as described for 12-ketostearic acid and vinyl 12-ketostearate, respectively.

Anal. Calcd. for $C_{20}H_{36}O_3$: C, 74.02; H, 11.18; H.I.V., 78.2. Found: C, 73.63; H, 11.23; H.I.V., 78.0; m.p. 53.6–54.2°C.; $n^{60/D}$ 1.4411.

γ-Lactone of 4-Hydroxy-2-Octadecenoic Acid. 4-Ketostearic acid was refluxed, in the presence of a sulfuric acid catalyst, for 4 hr. in a dioxane solution (20 g. of 4-ketostearic acid, 60 ml. of dioxane, and 0.5 ml. of sulfuric acid). The mixture was poured into 4 volumes of diethyl ether and extracted three times with 100-ml. portions of 10% aqueous potassium carbonate. After the ethereal solution was evaporated under reduced pressure, the residual material was crystallized from 10 volumes of acetone at −5°C. Infrared and ultraviolet analyses indicated that the γ-lactone of 4-hydroxy-2-octadecenoic acid rather than the γ-lactone of 4-hydroxy-3-octadecenoic acid was formed.

Anal. Calcd. for $C_{18}H_{32}O_2$: C, 77.08; H, 11.50; sap. equiv., 200.08. Found: C, 76.56; H, 12.24; sap. equiv., 195.35; m.p. 48.5–49.3°C.; $n^{50/D}$ 1.4487.

Spectrophotometric Determinations. Complete infrared absorption curves from 2 to 12 microns of all compounds investigated were obtained with a Perkin-Elmer Model 21 infrared spectrophotometer. Settings used were resolution, 927; suppression, 3; gain, 6; response, 1; and speed, 0.5 micron/min. The spectra of the esters, acids, and lactone were obtained in carbon tetrachloride solutions at about 10, 6, and 5 g./liter, respectively, with a 0.48-mm. absorption cell. The absorption of the lactone-carbonyl, ester-carbonyl, ketone-carbonyl, and vinyl group at about 5.6, 5.7, 5.8, and 6.1 microns, respectively, were determined at various concentrations in carbon tetrachloride solutions.

Results and Discussion

Preparation of Compounds. 12-Ketostearic acid was readily prepared by fractionally distilling commercial methyl 12-hydroxystearate, followed by oxidation of the hydroxy ester with a chromic acid solution, saponification of the keto ester, acidification of the soap of the keto ester, and crystallization of the keto acid from methanol. About 65% conversion of the keto acid to the vinyl keto ester was obtained when the keto acid was reacted in the presence of a mercuric sulfate catalyst and an excess of vinyl acetate at 40°C. for 48 hrs. Attempts to purify the reaction mixture by distillation under high vacuum resulted in excessive polymerization. However, after the reaction mixture was dissolved in diethyl ether and the fatty acids and the inorganic materials were extracted with a dilute, aqueous solution of potassium carbonate, distillation was successful. Vinyl 12-ketostearate was readily obtained from suitable distillate fractions by dissolving in diethyl ether and re-extracting with dilute potassium carbonate, to remove traces of keto acid, followed by successive crystallizations from acetone and petroleum ether.

Methyl 4-ketostearate was prepared from Brazilian oiticica oil with some difficulty. A considerable amount of polymerized material was present in the processed oil, thus decreasing the amount of available licanic acid (4-keto-9,11,13-octadecatrienoic acid, the principal component of oiticica oil). Lactonization of the 4-keto acid (which produced two γ-lactones) occurred during hydrogenation, and only a small amount of the γ-lactones was hydrolyzed during the interesterification of the hydrogenated oil with methanol. Attempts to purify the crude methyl esters by prolonged fractional distillation, through a packed column under high vacuum, resulted in excessive decomposition. However suitable fractions of methyl 4-ketostearate were obtained by rapid distillation under high vacuum. This concentrated the nonketo esters in the early fractions, gave a heart cut of keto ester, and left the more highly unsaturated and polymerized materials in the pot residue. The suitable fractions were crystallized from acetone to precipitate the remaining nonketo esters. After the acetone was evaporated under reduced pressure, methyl 4-ketostearate was obtained by successive crystallizations from petroleum ether and methanol.

A considerable amount of lactonization occurred during the vinylation of the 4-ketostearic acid. However relatively pure vinyl 4-ketostearate could be obtained by dissolving the vinylated mixture in diethyl ether and extracting the fatty acids with a dilute aqueous solution of potassium carbonate, followed by rapid distillation under high vacuum to remove traces of mercury. Suitable fractions were successively crystallized from acetone and petroleum ether.

Since it was impossible to duplicate the saponification equivalents of the vinyl esters, they are not reported. In saponification acetaldehyde, the tautomer of vinyl alcohol, apparently reacts with some of the alkali, thus indicating abnormally high saponification equivalents. Vinyl 4-ketostearate was slowly hydrolyzed in an aqueous-alcoholic solution of hydroxylamine hydrochloride. Therefore its carbonyl oxygen value is not reported since the acetaldehyde formed during the hydrolysis also reacted with the hydroxylamine.

Infrared Spectra. Fischmeister (7) in a note discussed briefly the infrared absorption of the methyl esters of monoketostearic acids. Progression bands (9, 12) were found in KBr disc spectra between 7.4 and 8.4 microns, which permitted complete identification of the different positional isomers. These bands were determined mainly by the distance between the carbomethoxy and keto groups. No solution-spectra data were reported.

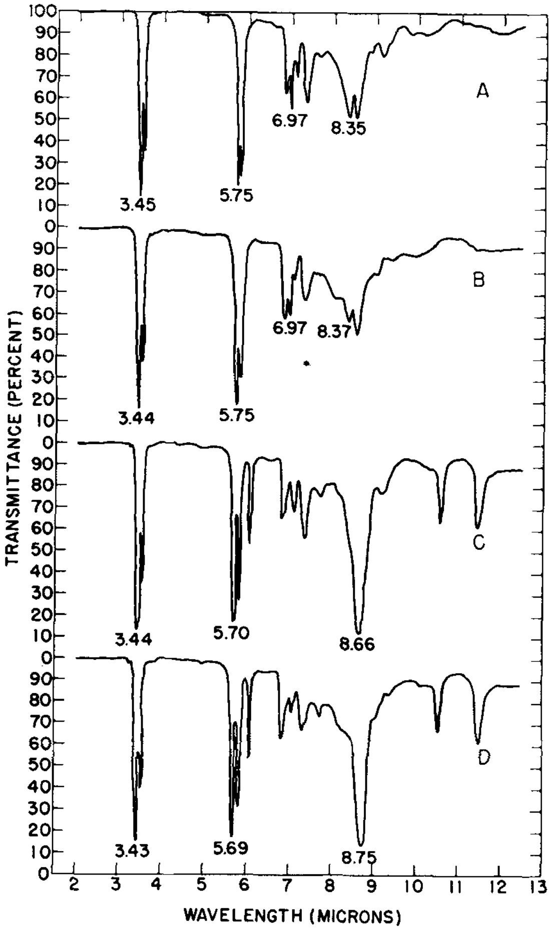

FIG. 1. Infrared spectra of methyl and vinyl ketostearates in carbon tetrachloride solution. A, methyl 4-ketostearate; B, methyl 12-ketostearate; C, vinyl 4-ketostearate; D, vinyl 12-ketostearate.

Carbon tetrachloride solution spectra of methyl 4-ketostearate, methyl 12-ketostearate, vinyl 4-ketostearate, and vinyl 12-ketostearate are given in Figure 1. The spectra of 4-ketostearic acid, 12-ketostearic acid, and the γ-lactone of 4-hydroxy-2-octadecenoic acid are given in Figure 2. From previously reported investigations of long-chain compounds (14) correlations of the bands which appear in these spectra with vibrational groups giving rise to them can be made with considerable degree of certainty. Table I lists the wavelength positions of absorption maxima for all bands with absorptivities of *ca.* 0.05 or more, with their most probable assignments for the seven compounds.

The different classes of compounds can readily be identified by their infrared absorption spectra. Methyl esters are characterized by the C—H deformation ($COOCH_3$) band at 6.97 microns; the vinyl esters are characterized by the C—H deformation ($CH_2{=}CH$) bands at 6.07, 10.53, and 11.49 microns; the keto acids are characterized by the O—H deformation (COOH) band at 10.74 microns (13); and the γ-lactone is characterized by the vibration (lactone ring) band at 10.99 microns and the C=O stretching at 5.6 microns.

The stretching of the lactone-carbonyl, ketone-carbonyl, ester-carbonyl, and vinyl group were easily resolved in carbon tetrachloride solution. Their ab-

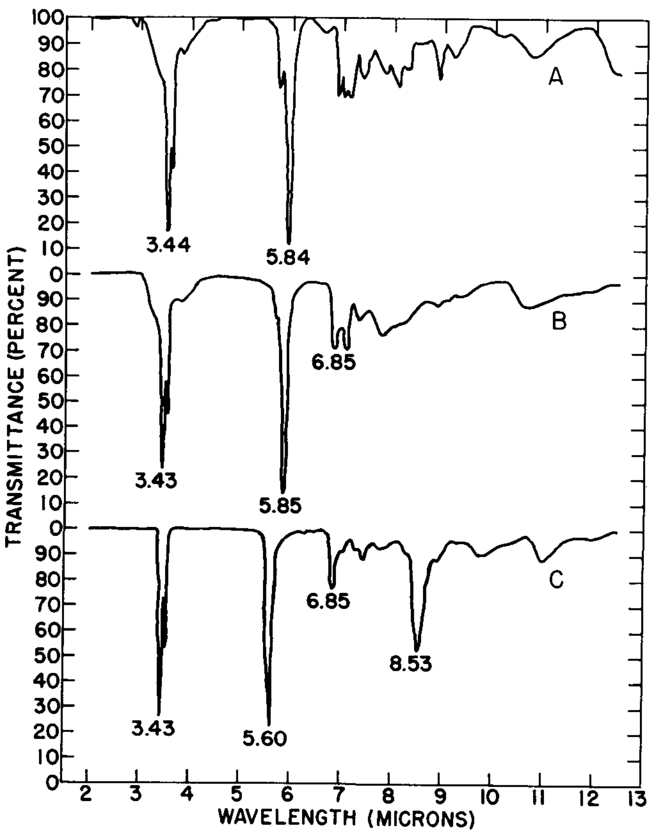

Fig. 2. Infrared spectra of ketostearic acids and the lactone of 4-ketostearic acid. A, 4-ketostearic acid; B, 12-ketostearic acid; C, γ-lactone of 4-hydroxy-2-octadecenoic acid.

sorption bands were used for quantitative determination of γ-lactone ($\Delta^{\alpha,\beta}$-butenolide), methyl keto ester and vinyl keto ester. As shown in Figure 3, the absorptions of these various carbonyl groups and vinyl group obey the Lambert-Beer law over a wide range of concentrations. Lactonization of 4-ketostearic acid during hydrogenation of the oiticica oil and during vinylation of the 4-ketostearic acid, and purification of the methyl keto esters and vinyl keto acids were conveniently followed by infrared analyses. In addition, infrared analyses help to establish the structure of the two γ-lactones formed during the lactonization of 4-ketostearic acid.

Previous investigators (4, 6, 8, 16, and 18) have found that $\Delta^{\alpha,\beta}$-butenolides absorb in the infrared region at about 1750 cm.$^{-1}$ (*ca.* 5.7 microns) and in the ultraviolet region between 200 and 220 millimicrons and that $\Delta^{\beta,\gamma}$-butenolides absorb in the infrared region at about 1800 cm.$^{-1}$ (*ca.* 5.55 microns). Therefore the lactone which absorbed at 5.6 microns was assigned the structure of the γ-lactone of 4-hydroxy-2-octadecenoic acid (γ-tetradecyl-$\Delta^{\alpha,\beta}$-butenolide) and the lactone which absorbed at 5.53 microns was assigned the structure of the γ-lactone of 4-hydroxy-3-octadecenoic acid (γ-tetradecyl-$\Delta^{\beta,\gamma}$-butenolide). This was confirmed by ultraviolet analyses as the $\Delta^{\alpha,\beta}$-butenolide absorbed at 214 millimicrons and the $\Delta^{\beta,\gamma}$-butenolide did not have any absorption peak in that region. When a mixture of the two lactones was heated, the $\Delta^{\beta,\gamma}$-butenolide isomerized to the $\Delta^{\alpha,\beta}$-butenolide, as indicated by a decrease in absorption at 5.53 microns and an increase in absorption at 5.6 microns. This is consistent with the find-

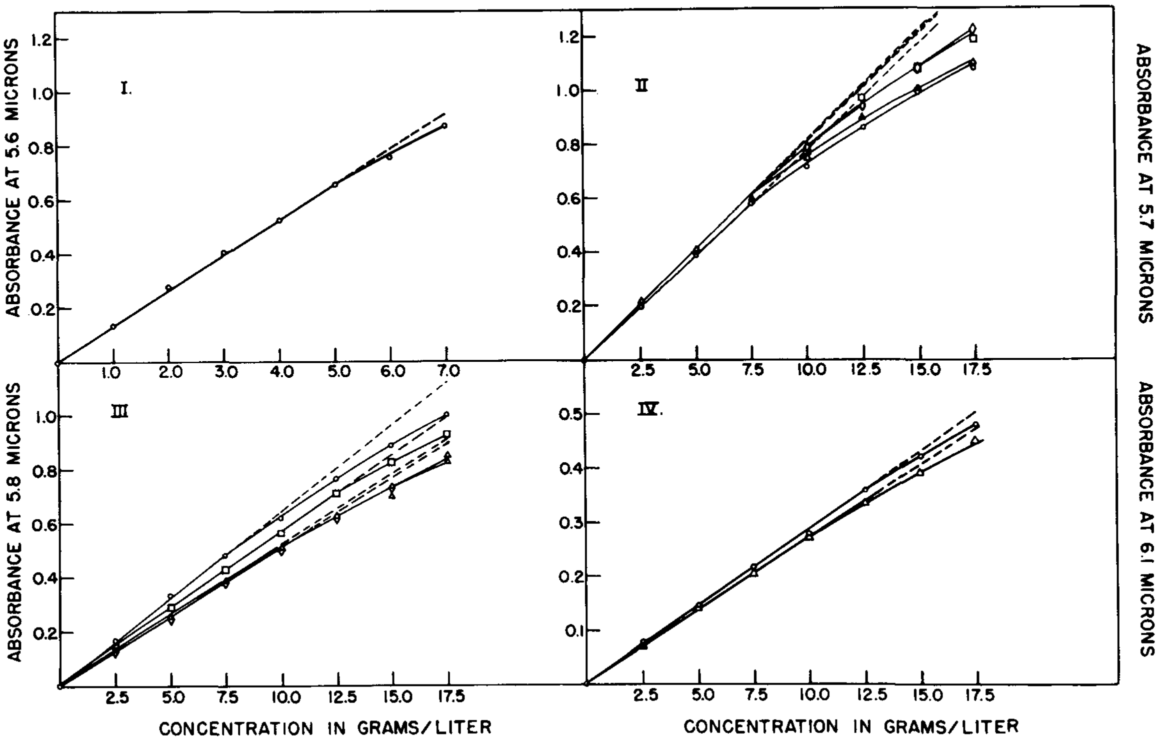

Fig. 3. Relationship between the absorbance of various carbonyls and vinyl groups of ketostearic acids and some of their derivatives.

I. ○, γ-lactone of 4-hydroxy-2-octadecenoic acid
II. ○, methyl 4-ketostearate
△, methyl 12-ketostearate
□, vinyl 4-ketostearate
◇, vinyl 12-ketostearate
III. ○, methyl 4-ketostearate
△, methyl 12-ketostearate
□, vinyl 4-ketostearate
◇, vinyl 12-ketostearate
IV. ○, vinyl 4-ketostearate
△, vinyl 12-ketostearate

ings of Cocker *et al.* (3) that the $\Delta^{\alpha,\beta}$-butenolides are more stable than the $\Delta^{\beta,\gamma}$-butenolides. The γ-lactone of 4-hydroxy-2-octadecenoic acid was isolated in relatively pure form, but the γ-lactone of 4-hydroxy-3-octadecenoic acid was merely concentrated.

Summary

Vinyl 12-ketostearate and vinyl 4-ketostearate were prepared by vinylating 12-ketostearic and 4-ketostearic acids, respectively, with vinyl acetate in the presence of a mercuric sulfate catalyst. The crude vinyl esters were purified by extracting the free fatty acids with dilute potassium carbonate, removing the mercury by distillation, and crystallizing successively from acetone and petroleum ether.

Infrared analyses revealed that lactonization occurred with the 4-ketostearic acid during the hydrogenation of the oiticica oil and during the vinylation of the keto acid. Two γ-lactones were produced. The γ-lactone of 4-hydroxy-2-octadecenoic acid was isolated in relatively pure form, and evidence was obtained for the concurrent formation of the less stable γ-lactone of 4-hydroxy-3-octadecenoic acid. The infrared spectra of the methyl keto esters, keto acids, vinyl keto esters, and the γ-lactone of 4-hydroxy-2-octadecenoic acid were determined in carbon tetrachloride solutions. It was found that the characteristic absorbances for the lactone-carbonyl, ester-carbonyl, ketone-carbonyl, and the vinyl group at about 5.6, 5.7, 5.8, and 6.1 microns, respectively, obey the Lambert-Beer law over a wide range of concentrations.

TABLE I

Absorption Bands in the Infrared Spectra of 4- and 12-Ketostearic Acids and Some of Their Derivatives

Functional group	Wavelength position of maxima (microns)[a]						
	A	B	C	D	E	F	G
C—H stretching	3.45	3.44	3.44	3.43	3.44	3.43	3.43
C—H stretching	3.52	3.51	3.53	3.51	3.52	3.51	3.51
C=O stretching ($\Delta^{\alpha,\beta}$-butenolide)	......	......	......	......	......	......	5.60
C=O stretching (acid)	......	......	......	......	5.70 5.84	5.70 5.85	......
C=O stretching (ester)	5.75	5.75	5.70	5.69	......	......	......
C=O stretching (ketone)	5.82	5.83	5.82	5.82	......	......	......
CH_2=CH stretching	......	......	6.08	6.07	......	......	......
C—H deformation	6.85	6.85	6.84	6.84	6.85	6.85	6.85
C—H deformation ($COOCH_3$)	6.97	6.97	......	......	......	......	......
C—H deformation	7.10	7.10	7.11	7.09	7.08	7.07	7.04
C—H deformation	7.37	7.35	7.37	7.34	7.32	7.31	7.42
C—O stretching	8.35 8.54	8.37 8.58	8.66	8.75	7.80	7.81	7.83 8.53
C—O—C stretching	9.16	9.04	9.17	9.04	......	......	8.89
Unassigned	9.84	9.80	......	......	......	......	9.81
CH_2=CH deformation	......	......	10.56 11.49	10.54 11.49	......	......	......
O—H deformation (COOH)	......	......	......	......	10.74	10.74	......
Lactone ring	......	......	......	......	......	......	10.99

[a] A, methyl 4-ketostearate; B, methyl 12-ketostearate; C, vinyl 4-ketostearate; D, vinyl 12-ketostearate; E, 4-ketostearic acid; F, 12-ketostearic acid; G, γ-lactone of 4-hydroxy-2-octadecenoic acid.

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The Fatty Acid Composition of Clothes Soil

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CLOTHES SOIL is a complex mixture of inorganic and organic materials. The nature of soil on clothes varies with the occupation and environment of the wearer. To attempt an analysis of all the components that occur as soil on clothing would be an impractical, if not impossible, task. The analysis can be simplified however if only the problem soils are considered. These are materials that are not removed by normal laundering procedures. Accumulated soil causes the yellowish-grey cast associated with the gradual deterioration in appearance of white garments (Figure 1). Previous work in our laboratories has shown that a major inorganic component of soil retained on clothing are clay particles that average about 0.1 μ in diameter (7). Concurrently there is an accumulation of organic material on the surface of the cotton fibers (Figure 2).

Information on the composition of this organic material is limited. Brown (1) and Oldenroth (5) extracted and analyzed freshly-adsorbed organic material from soiled garments. Brown (1) reported about 60% of the extracted soil to be free and combined fatty acids. In addition to fatty acids, he found about 15% cholesterol and fatty alcohols and 21% hydrocarbons. Oldenroth (5) reported 60–70% saponifiable material and about 8% cholesterol.

Yellowing of garments in areas that are in contact with the skin has been reported (5, 8, 10). These