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

HYDROXYSTEARIC ACIDS. II. INFRARED SPECTRA AND X-RAY DIFFRACTION OF 10- AND 12-HYDROXYSTEARIC ACIDS AND METHYL ESTERS, AND OF 9,10-EPOXYSTEARIC ACIDS

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Catalytic hydrogenation of 9,10-epoxystearic acid results in the selective formation of 10-hydroxystearic acid (1). In the important application as a grease stiffener, the lithium salt of this acid has been found, in preliminary tests, to be somewhat less suitable than the 12-hydroxy isomer obtained from castor oil. It is noteworthy that the 12-hydroxystearic acid or its hydrazide invariably formed gels on attempted crystallizations from a wide variety of solvents, whereas the 10-hydroxystearic acid as well as its hydrazide formed well defined crystals from the same solvent. Furthermore, the methyl ester of 12-hydroxystearic acid is easily crystallizable. It appears likely, therefore, that hydrogen bonding might account for the observed gel formation encountered with 12-hydroxystearic acid and its derivatives.

As the purpose of these studies is to develop supplements and replacements for castor oil derivatives, it appeared advisable to investigate further the physical properties of the 12-hydroxystearic acid from castor oil and the 10-hydroxystearic acid from oleic acid. The purpose of this paper is to present the infrared spectra and x-ray diffraction data for 10-hydroxystearic acid, 12-hydroxystearic acid, and for their methyl esters, and the epoxystearic acids from which the 10-hydroxy isomer was prepared.

INFRARED SPECTRA

The infrared spectra of chloroform solutions of the 10- and 12-hydroxystearic acids, their methyl esters, and the epoxy compounds from oleic and elaidic acids are shown in Fig. 1. All spectra were obtained with a model IR-2T Beckman automatic recording infrared spectrophotometer.[2] The instrument was housed in a room maintained at about 23.3° and 20 % relative humidity and its temperature was maintained constant at 25° ± 0.1° by water circulated from a constant temperature bath. The concentrations of the chloroform solutions were all very close to 40 g. per liter and all were measured in a 0.4-mm. rock salt cell against the pure solvent contained in the same cell.

A tabulation of the most intense absorption bands, with their exact wavelength positions of maxima in microns and their intensities expressed as molecular extinction coefficients ϵ,[3] is given in Table I. From a previous study of the

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[2] Mention of names of firms or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

[3] ϵ (molecular extinction coefficient) = $O.D./cl$; where $O.D.$ is the optical density equal

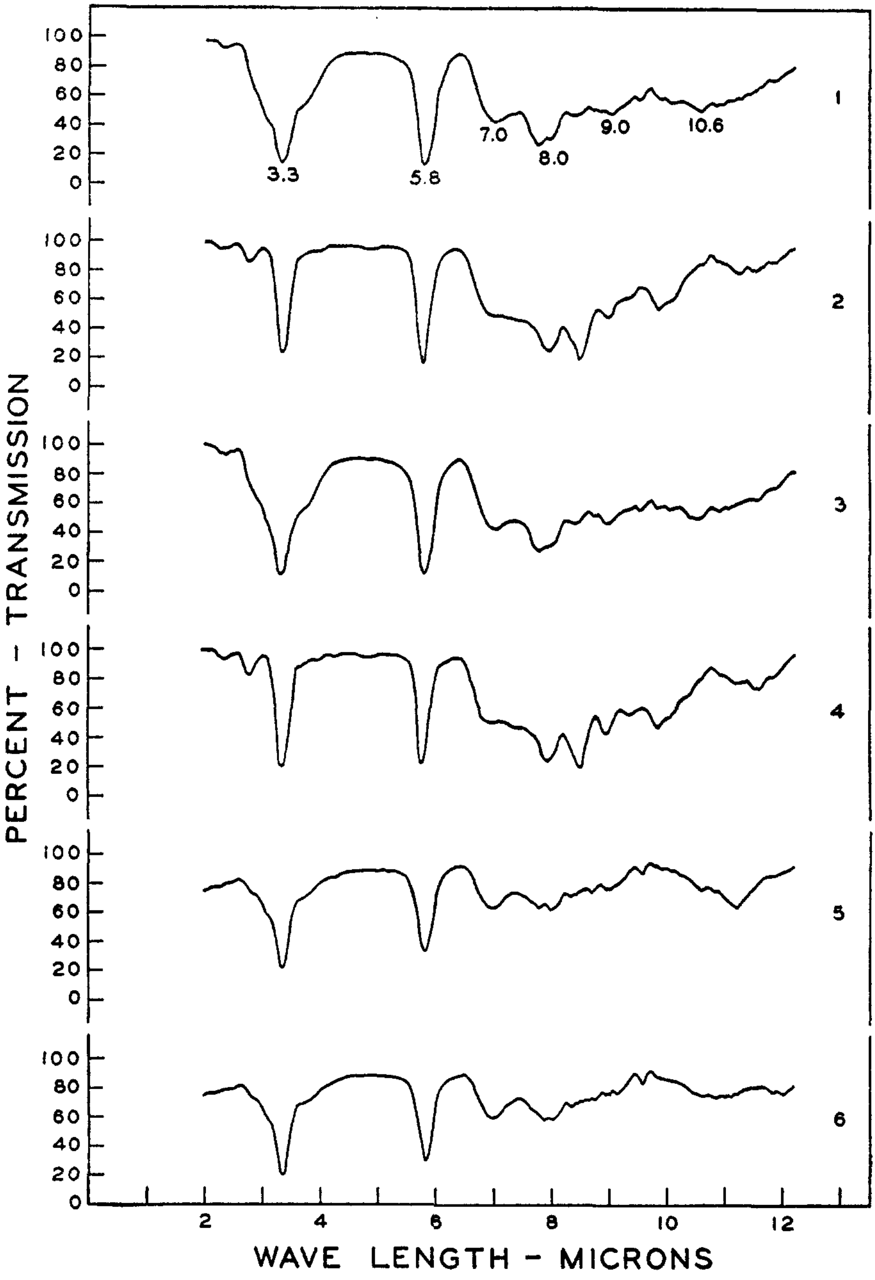


Fig. 1. Infrared Spectra of: 1. 10-Hydroxystearic acid; 2. Methyl 10-hydroxystearate; 3. 12-Hydroxystearic acid; 4. Methyl 12-hydroxystearate; 5. Epoxystearic acid from elaidic acid; 6. Epoxystearic acid from oleic acid (in chloroform solution)

to log 1/T (per cent transmission), *c* is the concentration in moles per liter, and *l* is the cell length in centimeters.

infrared spectra of long-chain fatty acids and esters (2) and from available infrared literature concerned with the generalities of frequency correlations, particularly of oxy- and hydroxy-compounds, most of these bands can be correlated with a particular molecular grouping.

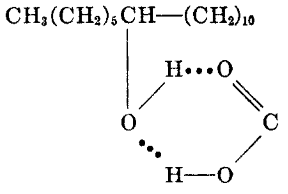
Usually the band due to an O—H stretching vibration, which occurs in the region 2.7 to 3.0 μ, is one of the most prominent in the spectra of hydroxy acids and esters. Reference to Fig. 1, or to the data in Table I, shows that the acids exhibit no bands in this region, indicating that the O—H is hydrogen bonded and the O—H···O band is unresolved from the strong C—H stretching vibration at 3.3 μ. The spectra of successive dilutions of the chloroform solutions fail to reveal evidence of a free O—H bond. This may indicate intramolecular bonding rather than dimer formation between molecules. Such intramolecular bonding would necessitate a hypothesis similar to that advanced to explain the formation of 10-hydroxy acid (instead of both 9- and 10-hydroxy compounds) upon hydrogenation of epoxystearic acid (1). If the COOH group can be thought to curl around toward the OH group, a double bridge bonding of the type illustrated by Smith and Creitz (3) can be formed:

TABLE I

INFRARED SPECTRA OF HYDROXY ACIDS AND THEIR ESTERS AND EPOXY COMPOUNDS

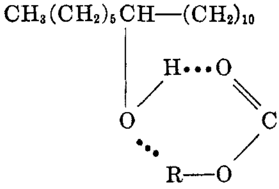
ABSORPTION BAND, μ	10-HYDROXYSTEARIC ACID		METHYL 10-HYDROXYSTEARATE		12-HYDROXYSTEARIC ACID		METHYL 12-HYDROXYSTEARATE		EPOXYSTEARIC ACID FROM ELAIDIC ACID		EPOXYSTEARIC ACID FROM OLEIC ACID	
	μ	ε	μ	ε	μ	ε	μ	ε	μ	ε	μ	ε
2.7			2.78	12.6			2.77	15.7				
3.3	3.37	231.4	3.35	113.2	3.33	168.3	3.35	128.9	3.35	244.7	3.35	253.7
3.6	3.69	51.1			3.65	48.1						
5.8	5.83	264.4	5.78	141.5	5.80	159.2	5.76	122.7	5.82	179.1	5.82	191.0
6.9	6.86	93.2	6.98	56.6	7.00	66.1	6.93	56.6	7.00	74.6	7.00	80.6
7.7–7.9	7.78	99.2	7.93	110.1	7.75	102.2	7.90	116.4	8.00	77.6	8.00	86.6
8.3–8.5	8.40	57.1	8.49	128.9	8.40	60.1	8.49	132.1	8.35	56.7	8.35	62.7
9.0	9.01	57.1	9.00	59.8	8.98	60.1	8.95	69.2	9.02	44.8	8.95	44.8
9.5–9.8	9.50	42.1	9.85	50.3	9.55	45.1	9.85	59.8	9.58	20.9	9.58	26.9
10.7	10.60	51.1			10.60	54.1			10.60	44.8	10.55	47.8
11.2–12.0									11.20	74.6	12.00	44.8

μ = Wavelength in microns. ε = Molecular extinction coefficients.



Such a bonded O—H···O stretching vibration would result in a band above 3.0 μ unresolved, in the present measurements, from the strong C—H stretching vibration at 3.3 μ.

The hydroxy esters would be incapable of forming a double bridge even if the ester group be considered as bending back toward the OH group. However, a single bridge bonding (3) would be expected:



Such a hydrogen bonding would have an O—H stretching vibration which would result in a band at 2.86 μ (3). Examination of the spectra or the tabulated data shows that both the esters, unlike the acids, do exhibit a band at about this region, in agreement with the postulated type of bonding. The somewhat shorter wavelength and somewhat broadened appearance of this maximum, especially in the spectra of the 12-hydroxy ester, may indicate the coexistence of both free O—H and single bonded O—H···O. The infrared spectra, thus interpreted to account for bands arising from O—H stretching vibrations, supports the hypothesis advanced for the formation of the 10-hydroxy acid only. As would be expected, the epoxy compounds exhibit no evidence of O—H bonds.

The strong band at 3.35 μ, due to a C—H stretching vibration, should be expected to be somewhat more intense in the spectra of the acids than the esters, for, in the former, it would be augmented by the unresolved double-bridge bonded O—H···O. Inspection of the spectral data shows that this increase in intensity is exhibited as expected.

Shreve, *et al.* (4) report a weak band in the spectra of long-chain fatty acids at 3.7 μ which they attribute to "A branch of the O—H···O association band" which disappeared on esterification. This band is observed in the spectra of the hydroxy acids, where double-bridge bonding is postulated, but is not found in the hydroxy esters, where free O—H or a single bridge only are believed present. These observations contribute some confirmation to the assignment.

The band at 5.8 μ is attributed to C═O stretching vibration of the COOH or COOR group, shifting to slightly lower wavelengths on esterification. At 6.9 μ a band attributed to C—H bending is exhibited in the spectra of all six compounds. Three bands at 7.7 to 8.0 and at 8.5 μ arise from C—O vibrations, the 7.7 μ band being particularly intense in the spectra of the acids, those at 7.9 and 8.5 μ being more intense in the spectra of the esters (2). Randall, *et al.* (5) assign an unsymmetrical stretching vibration of the C—C—O group to a band about 9.0 μ. This band occurs in the spectra of the compounds studied here in about equal intensity. Weak bands characteristic of the acids at 9.55 μ and of the esters at 9.85 μ, observed in these spectra, are analogous to those exhibited in the spectra of the saturated long-chain fatty acids and esters (2).

Above 10 μ the spectra of the epoxy compounds become the more interesting. The band at about 10.7 μ has been assigned to a vibration of the hydroxy of the carboxyl group and disappears on esterification. Shreve, *et al.* (6) assign a band at 11.2 μ in the spectra of epoxy compounds to the oxirane ring derived from long chain, internal monounsaturated compounds having the *trans* configuration at the double bond. The corresponding *cis* configuration gives rise, in the spectra of the epoxy derivatives, to a band at 12.0 μ. These correlations are confirmed by the infrared measurements reported here. The epoxy acid from oleic acid (*cis*) has a band at 12.0 μ and only a weak shoulder at 11.1 μ, while the epoxy compound from elaidic acid (*trans*) exhibits only a band at 11.2 μ.

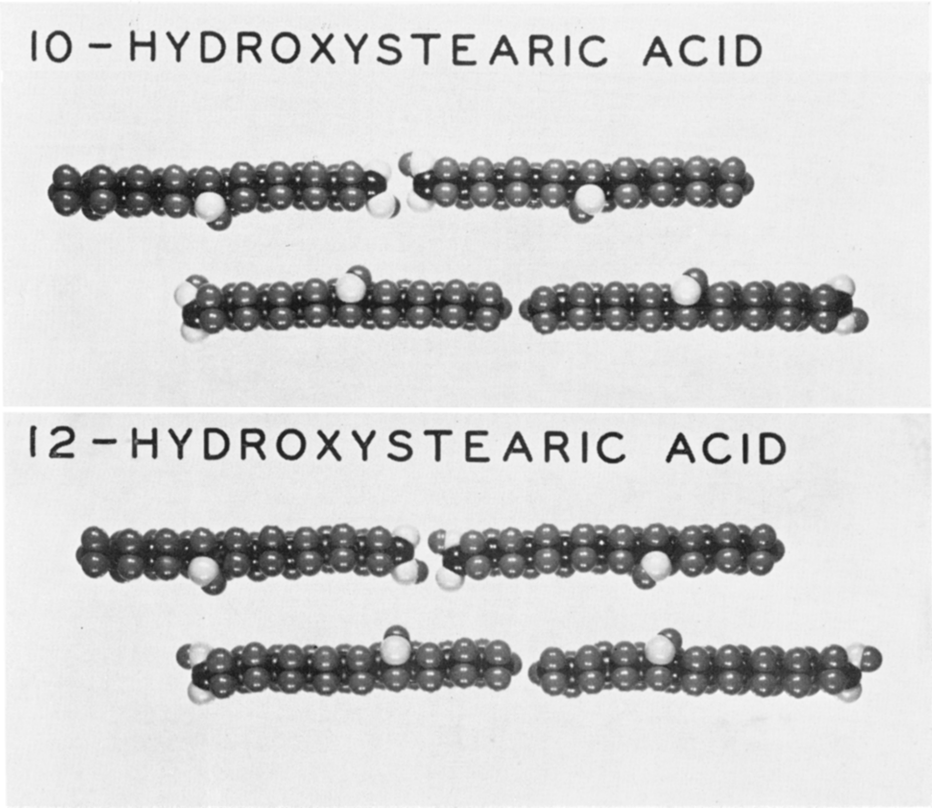


Fig. 2. Comparison of Molecular Models of 10- and 12-Hydroxystearic Acids Showing Possible Orientation to Achieve Maximum Intermolecular Hydrogen Bonding

These epoxy compounds could provide an alternate method of detecting and determining isolated *cis* and *trans* double bond configurations. Isolated *trans* double bonds are usually detected and measured by the C—H bending about the C=C (*trans*) of the internal unsaturated RCH=CHR′ group at 10.3 μ. Formation of the corresponding epoxy compound and observation and measurement of intensities of the 11.1 or 12.0 μ bands would afford a measurement of *cis* and *trans* double bonds in those cases where the 10.3 μ band is masked by a stronger nearby band such as that of an unsaturated cyclic group. Application of a use of the infrared spectra of epoxy compounds for this purpose will be given in a subsequent paper from this laboratory.

SUGGESTED EXPLANATION FOR THE GELLING EFFECT OF HYDROXYSTEARIC ACID

The above interpretation regarding intramolecular bonding has been derived from data obtained with the use of comparatively dilute solutions of the hydroxy acids and esters. It is also evident that on further dilution of these solutions no differences occur in the nature and character of the hydrogen bonding. However, in saturated solutions, from which crystallization would normally be expected to occur, it is conceivable that intermolecular bonding would predominate. Furthermore, it is evident that the hydrogen bond, while admittedly not a strong bond, is of sufficient strength to overcome the elongation tendency of long-chain molecules. However, in concentrated solutions of the hydroxy acids conditions are favorable for satisfying the elongation tendency of the molecule as well as its bonding tendency. This is undoubtedly accomplished through intermolecular bonding and, except in very specialized cases, these conditions are conducive to crystal formation. This is demonstrated by the fact that both 10-hydroxystearic acid and its methyl ester, as well as the methyl ester of 12-hydroxystearic acid, readily forms well defined crystals. However, attempts to crystal-

TABLE II

INTERPLANAR SPACINGS

10-HYDROSXYSTEARIC ACID				12-HYDROXYSTEARIC ACID			
Acid		Methyl ester		Acid		Methyl ester	
"d" spacing	Intensity	"d" spacing	Intensity	"d" spacing	Intensity	"d" spacing	Intensity
4.37	F	8.01	F	4.55	S	8.28	M
4.14	VS	4,42	M	3.85	S (Broad)	6.27	M
3.81	M	4.12	S	2.40	F	4.79	F
3.36	F	3.79	S	2.21	F	4.54	F
3.02	F	2.56	F			4.11	VS
2.46	F					3.85	S
2.25	F					3.58	M
2.19	F					3.39	F
						3.13	F
						3.02	F
						2.64	F
						2.44	M
						2.33	F
						2.21	S
						2.06	F
						2.01	F
						1.97	F
						1.83	F
						1.77	F
						1.72	F

lize 12-hydroxystearic acid result in gel formation and this may be accounted for on the basis of a certain peculiarity in its molecular structure. Assuming that the two functional groups in one molecule can each bond with hydroxyl groups from two other molecules, then a symmetrical pattern can be obtained as illustrated by the model shown in Fig. 2.

It can be seen that this pattern can be extended to include other molecules to the limit where the hydrogen bonding is no longer effective, and, in so doing, produce colloidal particles. Reference to molecular models (Fig. 2) clearly demonstrates that it is impossible for 10-hydroxystearic acid to fall into such a pattern and at the same time demonstrates the relative ease with which 12-hydroxystearic acid can form this pattern. Obviously, the production of such a pattern is dependent upon the presence of two functional groups within the molecule, both of which are capable of forming a hydrogen bond. Thus it would be impossible for esters to enter into gel formation in this manner. However, lithium soaps could undoubtedly form a similar double-bridge bond.

X-RAY DIFFRACTION POWDER PATTERNS

X-ray diffraction patterns have been obtained of the two hydroxystearic acids and of their methyl esters. From these powder patterns the "d" or interplanar spacings were calculated and their relative intensities estimated. The diffraction photographs were obtained with a General Electric diffraction X-ray unit, Model XRD,[2] using CuK$_\alpha$ radiation with a nickel filter (0.0007 inch thick). The spacing lines and their intensities are recorded in Table II.

EXPERIMENTAL

The perbenzoic acid oxidation of oleic and elaidic acids was selected as the best method for the preparation of epoxy compounds which were to be used as primary standards for this and the work previously reported (1). This method was chosen because the course of the reaction can be readily followed by chemical means and also because there are no fatty byproducts produced in side reactions.

9,10-Epoxystearic acid (*cis*). Oleic acid (5.0233 g., 0.018 mole) (iodine value, 89.2) was weighed into a 250-ml. glass-stoppered flask and 50 ml. of 0.4078 *N* perbenzoic acid in chloroform solution (7) (0.020 mole, 10% excess) was added. This solution was maintained at 0° for 21 hours during which time 98.4% of the calculated amount of oxygen was absorbed. The excess perbenzoic acid was removed by passing isobutylene through the solution. After removal of the chloroform, the solid residue was triturated with 50 ml. of light petroleum ether to effect a partial separation of the epoxystearic acid from the benzoic acid. This operation was then repeated yielding 2.2 g. of a white solid melting at 57.5°. After recrystallization from 15 ml. of absolute ethanol at 0°, 1.5 g. of pure 9,10-epoxystearic acid (*cis*) (m.p. 59°) was recovered.

Anal. Neut. equiv.: Calc'd, 298. Found, 297.3.

9,10-Epoxystearic acid (*trans*). Pure elaidic acid (m.p. 44.5°) (5.0088 g., 0.018 mole) was dissolved in 50 ml. of 0.4078 *N* perbenzoic acid chloroform solution and maintained at 0° for 21 hours after which 99% of the theoretical amount of oxygen was absorbed. The excess peroxide was removed with isobutylene and the chloroform was removed by evaporation. The solid residue was washed with 50 ml. of light petroleum ether and the resulting filtrate on standing at 0° overnight deposited 1.5 g. of pure 9,10-epoxystearic acid (*trans*) (m.p. 55.5°).

Anal. Hydrogenation equiv.: Calc'd, 298. Found, 297.

10-Hydroxystearic acid. This compound was prepared through catalytic hydrogenation of 9,10-epoxystearic acid (*cis*) as previously described by Mack, *et al.* (1) (m.p. 81°) and mixture melting point with authentic 10-hydroxystearic acid, 81°.

Anal. Neut. equiv.: Calc'd, 300. Found, 300.

Methyl 10-hydroxystearate. This ester was also prepared by means of catalytic hydrogenation (1) (m.p. 51°). This ester gave a *hydrazide*, m.p. 112°, crystallized from alcohol.

Anal. Calc'd for $C_{18}H_{38}N_2O_2$: N, 8.91. Found: N, 8.89.

Saponification of the ester gave 10-hydroxystearic acid, m.p. 81°, mixture m.p. with authentic acid, 81°.

Methyl 12-hydroxystearate. Castor oil (900 g.) was extracted five times with 500-ml. portions of light petroleum ether. The residue, freed from solvent on the water bath *in vacuo*, was saponified by refluxing for 3 hours with 250 g. of potassium hydroxide in three liters of 95% ethanol. The acids were liberated in the usual manner and the oil layer was separated and dried over sodium sulfate. The fatty acids were esterified by refluxing with seven liters of absolute methanol and 240 ml. of conc'd sulfuric acid for 3 hours. The methyl esters were recovered by dilution of the esterification mixture with water, extraction with ether, washing free of acid and drying the ethereal extract over sodium sulfate. After removal of the ether, the methyl esters (800 g.) were fractionally distilled in a 15-inch Vigreaux column which was wrapped with resistance wire for supplemental heating. Five fractions were collected, and fraction three (200 g.) having a narrow boiling range (172–174°) at 2 mm. pressure was found to be pure methyl ricinoleate and was selected for hydrogenation. Methyl ricinoleate (32 g.) was dissolved in 200 ml. of absolute ethanol, 3 g. of palladium catalyst was added, and the mixture was hydrogenated in a Parr hydrogenator until theoretical hydrogen absorption was noted. The catalyst was removed and the filtrate maintained at 0° overnight. There was deposited 12 g. of nearly pure methyl 12-hydroxystearate, m.p. 56.5°. This material was recrystallized from light petroleum ether followed by a second recrystallization from absolute methanol yielding pure methyl 12-hydroxystearate, m.p. 57.5° (8).

12-Hydroxystearic acid. Pure methyl 12-hydroxystearate (4 g.) was saponified in 50 ml. of 95% ethanol containing 3.0 g. of potassium hydroxide by refluxing for one hour. The alcohol was removed by vacuum distillation at temperatures under 50°. The soap was dissolved in 300 ml. of water and was acidified with hydrochloric acid. The liberated acid gelled and was separated with vacuum filtration. The precipitate was washed with about three liters of warm water to remove all traces of mineral acid and alcohol, after which it was vacuum-dried. Yield, 3 g. Attempts to crystallize the product resulted in gel formation irrespective of the solvent used. Finally a sample of the material was dissolved in methanol, cooled to 0°, and the resulting gel was subjected to centrifugation to remove the solvent. It was finally freed from all traces of solvent by drying under a high vacuum, m.p. 80°.

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SUMMARY

The infrared absorption spectra of 10- and 12-hydroxystearic acids, their methyl esters, and the 9,10-epoxystearic acids from elaidic and oleic acids were determined. Correlations of the most prominent bands in these spectra with molecular groupings most likely responsible for them have been made.

The hypothesis previously proposed to explain the formation of 10-hydroxystearic acid rather than a mixture of the 9- and 10-isomers upon hydrogenation of 9,10-epoxystearic acid has been supported by infrared interpretations, and a

possible explanation for the gelling tendency of 12-hydroxystearic acid as compared to the nongelling tendencies of 10-hydroxystearic acid and the methyl esters has been given.

The x-ray diffraction patterns for the two hydroxystearic acids and for their methyl esters have been obtained, and the interplanar spacings measured from them are given along with their relative intensities.

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