

lecular reaction, as has been proposed for the non-conjugated linoleate isomers.

Acknowledgment

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Cyclization of Eleostearic Acid¹

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ROSSMAN, in 1933, was the first to consider seriously the cyclization of fatty acids (1). For many years the problem was of only mild academic interest. However in 1951 Professor Crampton and his associates at McGill University began an intensive study of cyclic isomers of linolenic acid (2, 3, 4, 5).

Our own interest began with our earlier work with methyl linoleate (6). It was noted that after prolonged polymerization 60% of the monomer was monoolefinic and did not hydrogenate to methyl stearate. The material was considered to be cyclic. Investigation of this material is now in progress.

This paper describes our study of the cyclic isomer of methyl eleostearate. Eleostearate is known to cyclize readily at temperatures of 250° or less. Linoleate however requires much more drastic conditions (290° or above), and disproportionation or even rupture of carbon to carbon bonds may occur. Hence, since the eleostearate would give a cleaner product and higher yields, it was chosen for our first study. The determination of the structure of cyclic eleostearate was only a secondary purpose. The primary purpose was to develop methods (aromatization, oxidative degradation, etc.) and to obtain data (infrared and ultraviolet spectra, analytical constants, etc.) for use in the study of cyclic materials from other sources.

Experimental

A. Preparation of Alpha-Eleostearic Acid. The acids from 2 kg. of American tung oil (alcoholic KOH saponification, 20-min. reflux) were crystallized from 11.3 liters of Skellysolve Fat -25°. The original oil showed 81% total, 79.9% alpha, and 1.3% beta eleostearic acid. The crystals (m.p. 46°), isolated by inverse filtration (silk bolting cloth on a thistle tube), were recrystallized twice from 7.5 liters of Skellysolve F at +5°. The product was clarified by dissolving it in 2.25 kg. of A. R. acetone, filtering (Buchner), and evaporating the solvent finally at 100°C. with a mechanical pump with swirling (10). Yield was 790 g. (m.p. 49.0-49.5 cor.; literature 48.4 [19]) Infrared showed characteristic bands for *cis*, *trans* conjugation at 10.09 and 10.38 μ (7).

B. Preparation of Methyl Eleostearate. Methyl esters were prepared by esterification (10 vol. methanol, 2% sulfuric acid, 3 hrs. reflux), crystallization, and high vacuum distillation. They showed about 50% β - and 50% α -eleostearate by ultraviolet analyses (8). Both heat and mineral acid catalyze *cis*, *trans* isomerization of the double bonds of eleostearates. In the above case the mineral acid was probably the principal cause.

C. Cyclization of Methyl Eleostearate (Figure 3). The cyclization of the methyl eleostearate was done

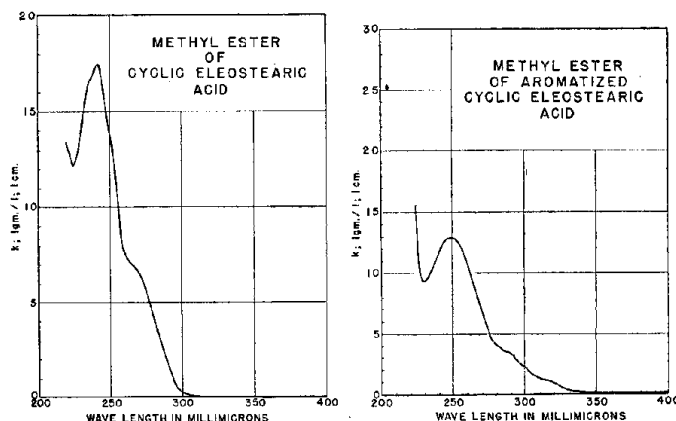


FIG. 1

as a 10% solution in methyl laurate to promote the presumably monomolecular cyclization reaction and to minimize bimolecular reactions, such as dimerization and disproportionation. Thus 58.5 g. (0.2 mole) of eleostearate was heated with 540 g. methyl laurate at 250° C. for 48 hrs. in a sealed, evacuated ampoule. Methyl laurate was stripped off through a short column to a pot temperature of 145° at 0.05 mm. The residue (67.5 g.) showed 39.9% monomer, 48.2% dimer, and 11.9% residual trimer by micromolecular distillation (11). In contrast, undiluted eleostearate would be 80% or more polymerized in only 3 hrs. at only 230°C. (9).

Cyclized eleostearate was concentrated from this residue by removal of noncyclic material as urea adducts (5), followed by distillation to separate it from polymers. Thus 64 g. of the residue in methanol (*ca.*

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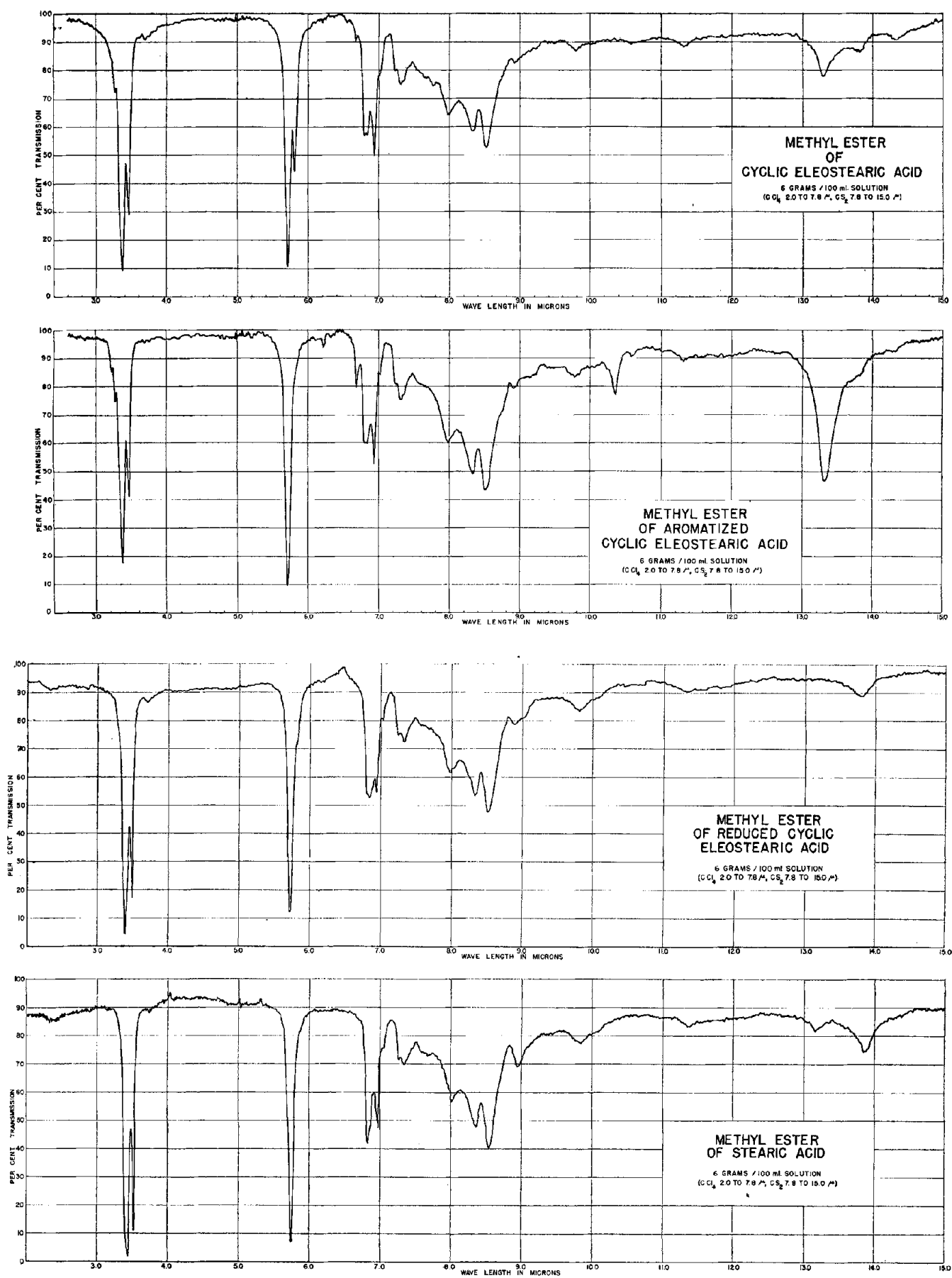


FIG. 2

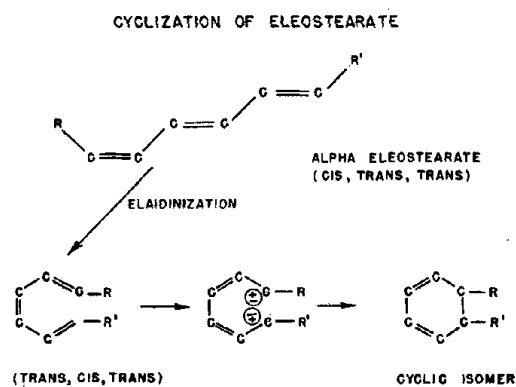


FIG. 3

20 cc./g.) was saturated with urea at reflux, cooled to room temperature, and filtered. This was repeated two more times, cooling to -25°C . each time. The final filtrate afforded 22.6 g. of ester upon evaporation and washing free of urea (in Skellysolve B, with dilute sulfuric acid). This material on distillation (to pot temperature of 180°C . at 0.05 mm.) gave 16.04 g. of distillate, or 29% on original eleostearate. This material showed $n_D^{20} = 1.4761$. The ultraviolet curve is shown in Figure 1 with peak at $241\text{ m}\mu$ with a k value (k g./1,000 cc., 1 cm.) of 16.8. Infrared absorption spectrum (Figure 2) showed bands at 6.7, 13.3, and $14.3\ \mu$. Spectral analysis (8) indicated 4.2% total, 1.6% α - and 2.0% β -eleostearate. A free acid contaminant is indicated by the band at $5.8\ \mu$. This is probably lauric acid as shown in Part D.

It might have been preferable to use a higher boiling diluent (such as methyl arachidate or behenate) so that the cyclic (and other) monomeric material could be separated directly from both diluent and polymers by a fractional distillation.

The cyclic isomer had a micro-hydrogenation iodine value of 159 (5% Rh on alumina in butanol, 2 parts catalyst to 1 part sample). The theoretical value for the cyclohexadiene is 173.6. Approximately 0.5 g. was hydrogenated, using a gram of the catalyst (Baker's No. 310). In 30 hrs. 73% of the theoretical amount of hydrogen was taken up. The reduced ester was distilled at 0.1 mm. The I. R. curve of this is shown in Figure 2. There is somewhat less than the normal amount of absorption in the $13.9\ \mu$ region (chain of 4 CH_2) as compared with methyl stearate. Also there is an extra band in the $6.9\ \mu$ region (C-H bending) and in the $9\ \mu$ region.

D. *Aromatization of Cyclic Eleostearate* (Figure 4). The cyclic isomer is assumed to be mostly a dialkyl cyclohexadiene. Nine grams of the cyclic concentrate (approx. 0.03 mole) were dissolved in 90 ml. of benzene. To this was added 0.03 mole or 5.34 g. of N-bromosuccinimide. The mixture was heated to reflux for 2 hrs. The solution was cooled, and most of the succinimide was precipitated out on the walls of the flask. The solution was decanted from the solid succinimide. The weight of the solid was 2.68 g., or approximately 0.027 moles (0.03 g. of the succinimide is apparently soluble in the 90 ml. of benzene at room temperature). The succinimide was washed with fresh benzene, and this was added to the benzene solution. The combined solution was transferred to an ampule (approximately 150-ml. capacity). The benzene was stripped off under vacuum. To the resi-

due, presumably the bromo diene, were added 100 ml. of fresh 2,4,6-collidine. The ampule was sealed with a flame while under a water pump vacuum. The sealed ampule was then heated in an aluminum block for 4 hrs. at 150°C . presumably to dehydrohalogenate the diene to the benzene derivative. The ampule was cooled and opened, and the excess collidine was stripped off at room temperature by swirling (10) overnight under high mechanical vacuum.

The residue of collidine-hydrobromide plus some succinimide was extracted several times by Skellysolve B by decantation. The Skellysolve solution was washed five times with dilute HCl, five times with water, five times with more dilute HCl, and finally five times with water. The solution was dried by filtration through a column of anhydrous Na_2SO_4 . The solvent was stripped off to give a dark oil weighing 8.21 g. This was flash-distilled, giving 7.29 g. of distillate. [Note: During the early part of the distillation some distillate crystallized when cooled. Crystallization of 2 g. of the total distillate from 20 ml. of ethanol at -60°C . gave a product which after two more crystallizations weighed 0.09 g. and melted at 44.4 to 44.9°C . (corrected). Two parts of this with one part of pure lauric acid showed no depression of melting point. It was concluded that the impurity was lauric acid, which had concentrated from the original methyl laurate used as the polymerization diluent. It has been recently shown that acids have much less tendency to form urea adducts than do the methyl esters (12).]

The distillate was dissolved in 200 ml. of Skelly B and extracted carefully with a 2-3% solution of K_2CO_3 in 50% methanol. The acid-free ester solution was dried with anhydrous Na_2SO_4 , and the solvent was stripped off. The esters weighed 6.00 and had a n_D^{20} of 1.4946. The ultraviolet and infrared absorption curves are shown in Figures 1 and 2.

E. *Oxidation of the Dialkyl Benzene to Ortho Phthalic Acid* (Figure 4). Next 0.59 g. of the aromatic ester (0.002 moles) was dissolved in 4 ml. of benzene containing 0.712 of N-bromosuccinimide (0.004 moles). This was heated at reflux for 3 hrs. presumably to substitute bromine atoms in the alkyl side chains on carbon atoms alpha to the benzene ring. The solvent was then stripped off with vacuum. The yellow solid was then extracted with 10 ml. of Skellysolve B (by refluxing 5 min., cooling, and decanting). The extraction was repeated 4 more times. The residual succinimide weighed 0.37 g. (0.0037 moles). The solvent was stripped from the combined decantings to give 0.89 g. of the dibromo ester. The 0.89 g. of dibromide was heated at reflux for 6 hrs. with swirling (10) with 2.5 g. of anhydrous Na_2CO_3 dissolved in approximately 50 ml. of water. The partially dissolved and emulsified material was neutralized with 5-ml. concentrated H_2SO_4 dissolved in 100

AROMATIZATION AND OXIDATION

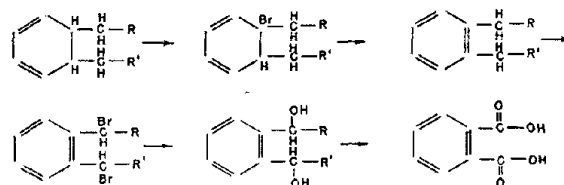


FIG. 4

ml. of water. The fatty material was extracted with 3 portions of ethyl ether totalling 125 ml. The ether solution was washed once with dilute H_2SO_4 , then several times with Na_2SO_4 solution, and finally several times with water. The solvent was stripped off with vacuum. The presumably dihydroxy material weighed 0.64 g. and was insoluble in Skellysolve B.

This was dissolved in approximately 100 ml. of A. R. acetone. To the approximately 2 millimoles was added 1.68 g. of $KMnO_4$ (10.6 millimoles) in increments of about 0.1 g. The $KMnO_4$ was decolorized rapidly at first while the last 0.1 g. required about 2 hrs. The acetone was stripped off with vacuum. The 10.6 millimoles of MnO_2 were reduced with the equivalent amount of $NaHSO_3$, plus 10% excess, or 1.22 g., in 20 ml. of water containing 2 ml. of concentrated H_2SO_4 . The water and other volatiles were stripped off with high vacuum. The residual salts were extracted repeatedly with small amounts of ethyl ether. Any mineral acid present was washed from the combined ether solutions (200–300 ml.). The ether was stripped off, and the residue was sublimed at atmospheric pressure to give 0.09 g. of sublimate (m.p. 131.5–133.0°). This is a 20% yield as phthalic anhydride, based on the concentrate which was obtained in 29% yield from eleostearate. It was resublimed to a small cold finger condenser to give 0.07 g. (softened at 125°, melted at 130.5°).

After several months' storage at 4°C., 0.05 g. of the material was distilled under high vacuum from a 50-ml. graduated centrifuge tube to a small cold finger (air) condenser. Heat was supplied by an aluminum block bored to receive the tube. Distillation temperature was 65°C. After 1½ hrs. 25 mg. remained as the residue. The sublimate contained some liquid impurity. It was crystallized from 0.5 ml. of CCl_4 . The mother liquor was removed with a fine capillary eyedropper. The crystals were washed with a few drops of fresh CCl_4 . Removal of the solvent gave 15 mg. of phthalic anhydride (m.p. 130.0–131.3, remelt 130.0–130.5). (Mixture with pure P.A. melted 130.5–132.0°.) The ultraviolet absorption spectrum was identical with that of pure phthalic anhydride.

F. *Derivatives of phthalic anhydride* (P.A.). Several derivatives of P.A. were examined to determine their value for purposes of characterization. That easiest to prepare pure and in high yields was the imide.

About 5 mg. of the P.A. were heated with 1 ml. of concentrated NH_4OH on the steam bath. After 30–40 min. all liquid was gone, and another 1 ml. of NH_4OH was added. After 30 min. the excess NH_4OH and water were removed with vacuum at room temperature. About 5 mg. of the monoamide, monoammonium salt remained.

This apparently converted to the imide before melting. It melted at 232.4° to 233.5°C. A mixture with pure imide melted at 233.0° to 233.5°C.

It was therefore concluded that the cyclic product from methyl eleostearate consisted largely of an ortho dialkyl substitute cyclohexadiene. The infrared absorption curve indicates the presence of some aromatic molecules apparently due to hydrogen transfer after cyclization (Figure 2).

Discussion

Examination of molecular models (Fisher-Hirschfelder-Taylor) of unsaturated fatty acids reveals that

cyclization is sterically possible in numerous ways. Indeed, the possibilities could be a study in itself. The routes that any particular isomer would prefer however are probably limited. In the case of the conjugated triene (eleostearate and its isomers) one mechanism is immediately apparent (Figure 3). This is the one which yields the dialkyl cyclohexadiene.

The sole requirement for a conjugated triene to approach the position necessary for cyclization to occur seems to be a *cis* configuration at the central double bond. Zechmeister (13) has shown that the central double bond of a conjugated system has the smallest amount of double bond character and that less activation energy is necessary for its isomerization. Of the three possible isomers with a *cis* central bond, the *trans, cis, trans* shows the least steric hindrance. The two alkyl groups of the resultant cyclohexadiene would be *trans* to each other about the ring. The *cis, cis, cis* isomer exhibits the most hindrance and would give the same *trans* isomer. The *cis, cis, trans* (or *trans, cis, cis*) would give the *cis* isomer.

A more probable mechanism however involves the ionic intermediate shown (Figure 3). Models of this intermediate exhibit no hindrance whatsoever. The alkyl groups would be either *cis*, or *trans* to each other about the ring with the *trans* form probably predominating. No experimental attempts were made to separate any of the isomers. The cyclic concentrate is no doubt a mixture of double bond positional isomers formed after cyclization.

Tung oil is known to polymerize at temperatures as low as 125° (14). It would be interesting to repeat this work at low temperatures where the chances of secondary isomerizations would be minimized.

Chis Chin (14, 15) has recently published comprehensive accounts of the polymerization and isomerization of tung oil, alpha and beta eleostearic acids, and methyl beta eleostearate and of structural studies on the products. It would be highly desirable to have these papers republished in an Occidental language.

It is probable that cyclic isomers of the common unsaturated fatty acids are of more significance in industrial operations and are more widely distributed in processed fatty materials than might previously have been supposed. The following discussion is entirely an extrapolation of our present knowledge. These suggestions may be useful to other workers.

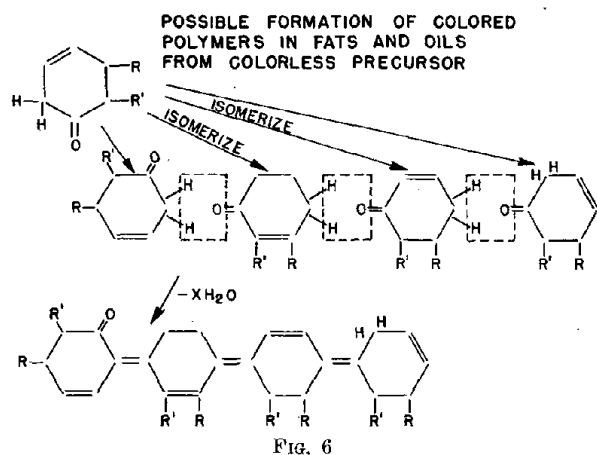
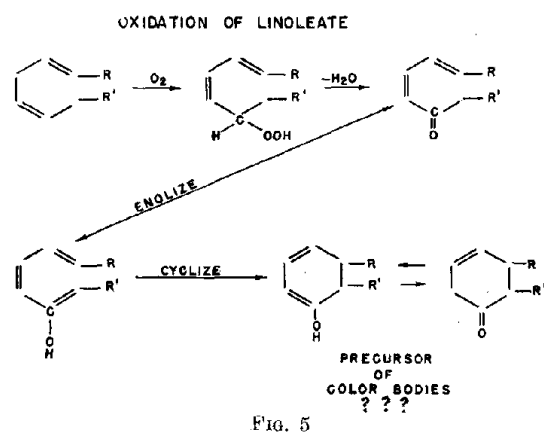
One would expect acid or base to catalyze cyclization. The difficulties of converting pure eleostearic acids to their methyl esters have already been mentioned (9). The usual method employing sulfuric acid in refluxing methanol yields a mixture of isomeric esters. Chis Chin (15) has gone one step further and actually prepared concentrates of the cyclic isomer by lengthy heating in ethanolic H_2SO_4 . Also α -eleostearic acid appears to be a strong enough acid to catalyze its own elaidinization even under vacuum at subzero temperature. The esters are relatively stable. Then, too, in the laboratory preparation of pseudo-eleostearic acid from normal linolenic acid we have found the recommended alkali isomerization time to be many times too long. If the literature instructions are strictly followed, the resultant product is so contaminated with what appears to be a cyclic isomer that high purification of the conjugated triene in reasonable yields is virtually impossible.

In the commercial isomerization for improving the drying properties of unsaturated oils or fatty acids,

mixtures of linoleic and linolenic or other acids are frequently employed. The more highly unsaturated acids conjugated readily but are further exposed to the time and temperature conditions necessary to conjugate a reasonable amount of the diene. During this over-exposure the triene and more highly unsaturated materials no doubt undergo considerable cyclization. Chis Chin has shown that cyclic isomers of eleostearic acid are very reluctant thermally to polymerize (14). The drying power of these materials is not known, but one would expect it to be weak. One would also expect that the cyclic isomers would plasticize and soften films.

Slansky has recently reported an alkali-induced isomerization of linseed oil (16), using glycerine as the solvent. Approximately 50% of the total fatty acids were conjugated. It was noted that the film-forming properties were not very different from those of the untreated linseed oil. Considerable stearic acid was also formed during the isomerization reaction. No doubt, cyclization and hydrogen transfer had both occurred. Hydrogen transfer has been noted before during thermal polymerization and in this case involved largely cyclic polymers and unsaturated monomers (6).

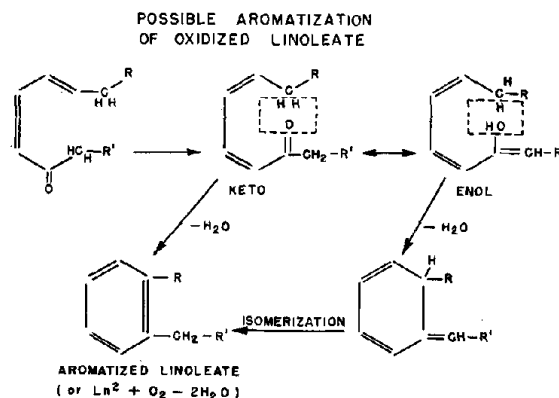
Color formation in fatty acids and oils is a serious problem to industry. It is suggested that cyclization is involved (Figure 5). The reaction sequence for linoleate would be a) hydroperoxide formation, b) dehydration as suggested by Lea (17) to the conjugated ketone, c) enolization to the conjugated triene, d) cyclization as with eleostearic acid, and e) polymerization of the resultant unsaturated cyclic ketone to colored products (Figure 6). It is also conceivably



possible for an oxidized linoleate to aromatize by the elimination of 2 molecules of water as shown in Figure 7.

The formation of triene conjugation in the alkali isomerization of oxidized linoleate has been reported by Privett and Lundberg (18). This is a common source of error in the spectrophotometric analysis of oxidized materials.

The color problem is well known to manufacturers of saturated fatty acids. The small amounts of unsaturated acids are readily oxidized, especially in the solid form where oxygen can readily penetrate the crystal structures. Since they are highly diluted, they tend to cyclize when heated rather than to polymerize.



The result is a color precursor which tends to distill with the main product and which is not readily removed by adsorbants. Crystallization from polar solvents (methanol, acetone, etc.) appears to be the best method of purification of the saturates. With unsaturates, such as oleic or especially with linoleate, crystallization is not practical. The solution would seem to be in selection of good raw materials and in protection of these from any unnecessary oxidation or heat.

One may summarize some of the thermal chemical reactions of polyunsaturates. First, they are easily oxidized or conjugated. Secondly, they readily undergo Diels-Alder condensation. Thirdly, dilution would favor cyclization rather than polymerization. Fourthly, cyclic olefins are known to disproportionate to aromatic compounds. Fifthly, decarboxylation is possible under extreme conditions.

In view of the above it is interesting to examine arachidonic acid, which is widely distributed in small amounts in most animals fats. Examination of the molecular models indicates that, as shown in Figures 8 and 9, the conjugated form of this acid can readily undergo an intramolecular Diels-Alder condensation to give two fused six-numbered rings. Acids with 5 and 6 double bonds could conceivably cyclize further. Aromatization and decarboxylation of such substances would give polycyclic aromatic compounds.

Conditions in many industrial processes are favorable for the cyclization of polyunsaturated compounds. The presence of even small amounts of these cyclic isomers may markedly affect the value of the final product.

It certainly is to the advantage of every processor to examine carefully his methods and to eliminate or at least to minimize the possibility of these isomeric materials being formed.

We are grateful to Albert Milun for permission to use his hydrogenation data and to H. M. Boyd and

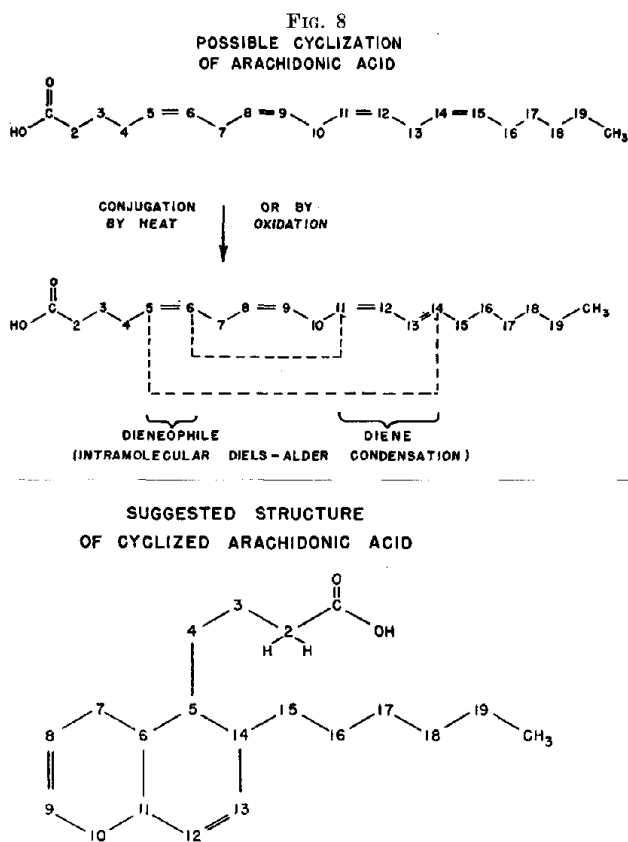


FIG. 9

W. T. Tolberg for the spectrophotometric studies they performed.

Summary

1. Methyl eleostearate has been thermally cyclized in good yields, and a concentrate of the cyclic product has been prepared.
2. Using small amounts, a technique has been devised for a) aromatization of the resultant cyclohexadiene, b) oxidation to orthophthalic acid, and c) characterization of the acid as the anhydride and the imide.
3. The significance of cyclic fatty acids in industrial processes is discussed.

Zusammenfassung

1. Ringbildung von methyleleostearat auf thermischem wege ergab gute resultate, und ein konzentrat des ring-produktes wurde prepariert.
2. Eine neue technik fuer die benutzung von kleineren mengen ermoeeglichte: a) aromatisation des entstandenem cyclohexadien, b) oxdierung zu orthophthalischer säure, und c) charakterisierung der säure als anhydrid und imid.
3. Die bedeutung von fettsäure-ringen in industriellen verfahren wird besprochen.

Resumé

1. Le méthyleleostéarate a été cyclisé thermiquement avec bon rendement et un concentré du produit cyclique a été préparé.
2. Au moyen d'une nouvelle technique, utilisant des quantités minimales de matériel, il a été possible a) d'aromatiser les cyclohexadiènes obtenus, b) d'oxyder l'acid orthophthalique, et c) d'établir la constitution de l'acide comme anhydride ou imide.
3. L'importance pour l'industrie des acides gras cycliques est discutée.

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Glycerolysis of Peanut and Mustard Oils

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COMMERCIAL monoglycerides are used in shortening to improve their cake-making properties and as emulsifiers in a variety of other products. Monoglyceride mixtures are also prepared as a first step in the manufacture of oil-modified alkyd resins and in the preparation of certain detergents. Many methods for their manufacture are known, but only two are of industrial importance. In the first method the fatty acids are esterified with excess of glycerol either alone or in the presence of mutual solvent with or without an esterifying catalyst. The second method consists of heating the fatty oils with an excess of glycerine either alone or in the presence of an ester

interchange catalyst. The second method, referred to as glycerolysis, is a special case of alcoholysis which results in the formation of a mixture of mono-, di-, and triglyceride (1).

The formation of monoglycerides depends on various factors, such as the reaction temperature and time, the amount and the nature of the catalysts used, as well as the composition and proportion of fatty acids or oils and glycerols. Tsuchya and Akiyama (2) carried out the experiments with hardened fish oil to determine the effect of time, temperature, and amount of glycerol upon the course of reaction. They showed that, at a temperature of 270-280°C. and with 25-