Reaction of Cyclopropenoid Fatty Acid Derivatives With Hydrogen Halides

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Abstract

The treatment of *Sterculia foetida* oil with concentrated aqueous HCl or with HBr in acetic acid results in the addition of one hydrohalogen molecule per cyclopropenoid moiety. Iodine value (I.V.) and infrared absorption measurements indicate that the mechanism parallels that of the polymerization of sterculic acid and involves the formation of four isomeric monounsaturated monohalo moieties.

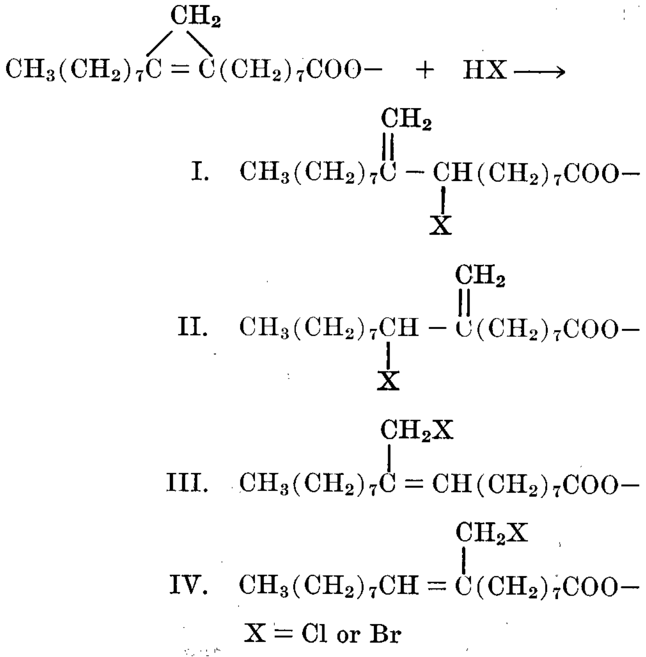
Introduction

In the course of an investigation of reactions which can be used as a basis for improved analytical methods for cyclopropenoid fatty acid derivatives, information was obtained relative to the mechanism of certain hydrohalogenation reactions. *Stercula foetida* oil was used in these experiments because of the high sterculic acid content of its fatty acids.

One of the recent methods of analysis is based upon the selective reaction of one mole of hydrogen bromide with one mole of the cyclopropenoid moiety in the titration with 0.1*N* hydrogen bromide in glacial acetic acid (1,2). We have found that the corresponding selective hydrochlorination can be accomplished by shaking the sample with an equal volume of aqueous hydrochloric acid (sp. gr. 1.18–1.19) for 1 hr. Neither of these reactions caused any appreciable reduction in the I.V. calculated on an adjusted sample-weight basis. This retention of unsaturation can be explained only by a reaction or series of reactions involving opening of the cyclopropene ring.

The infrared spectra of the hydrohalogenated oil no longer exhibited the 5.35 μ and 9.91 μ bands characteristic of the cyclopropene ring. Instead the spectra now showed a strong band at 11.05 μ and a weak band at 6.07 μ. Essentially identical infrared observations were reported by Rinehart and coworkers (3) for the polymerization and acetolysis of sterculic acid. The development of the absorption maxima at 6.07 μ and 11.05–11.12 μ was interpreted by these authors as indicative of the formation of unsymmetrically disubstituted olefins comprising about 65% of the reaction products. The remaining 35% they identified as isomeric olefins with the double bond in the principal carbon chain. The formation of all these products involves cleavage of the cyclopropene ring between the methylene carbon of the ring and either the 9- or 10-olefinic carbon.

The similarity of the changes in the infrared spectra suggests that the mechanism of these hydrohalogen reactions of the sterculic acid moiety in *Sterculia foetida* oil parallels that proposed by Rinehart et al. for polymerization and acetolysis and that the products are isomers I, II, III, and IV. The presence of isomers I and II is confirmed by the adsorption at 6.07 μ and 11.05 μ.



$$CH_3(CH_2)_7\overset{\diagup\ CH_2\ \diagdown}{C=C}(CH_2)_7COO- \quad + \quad HX \longrightarrow$$

$$\text{I.}\quad CH_3(CH_2)_7\overset{CH_2}{\overset{\|}{C}}-\underset{\underset{X}{|}}{C}H(CH_2)_7COO-$$

$$\text{II.}\quad CH_3(CH_2)_7\underset{\underset{X}{|}}{C}H-\overset{CH_2}{\overset{\|}{C}}(CH_2)_7COO-$$

$$\text{III.}\quad CH_3(CH_2)_7\overset{CH_2X}{\overset{|}{C}}=CH(CH_2)_7COO-$$

$$\text{IV.}\quad CH_3(CH_2)_7CH=\overset{CH_2X}{\overset{|}{C}}(CH_2)_7COO-$$

$$X = Cl \text{ or } Br$$

The validity of this mechanism is further supported by the retention of unsaturation and especially by the appearance of an absorption band at 8.28 μ in the infrared spectrum of the hydrobrominated product (Fig. 1). This band, which falls within the range characteristic of bromo-olefins of the form

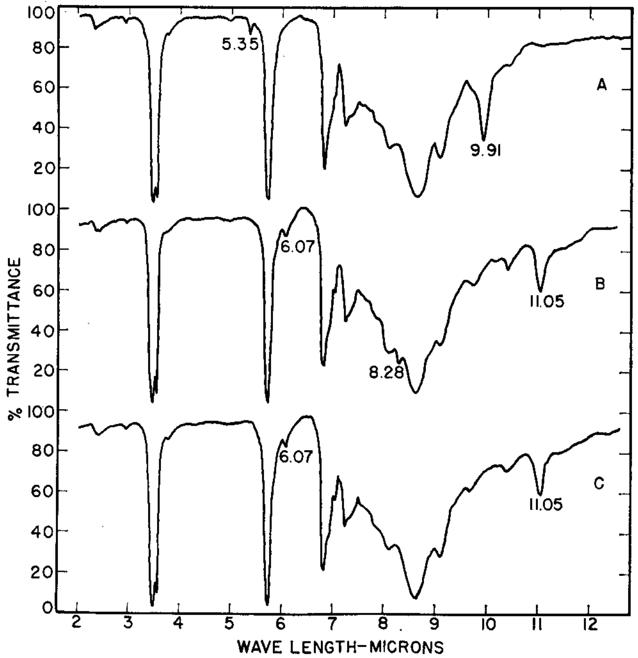


FIG. 1. Infrared absorption spectra of *Sterculia foetida* oil in carbon tetrachloride: A. Untreated; B. Hydrobrominated; C. Hydrochlorinated.

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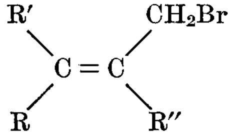
(4)

can be attributed to the presence of isomers III and IV. The presence of the characteristic band for the corresponding chloro-olefin, 7.94 μ to 8.01 μ, could not be confirmed because of an interfering triglyceride band.

The ratio of isomers I and II to isomers III and IV formed by hydrohalogenation is not known. That it is a constant for the hydrochlorination reaction, however, was shown by the reproducibility and the consistent mathematical relationship between absorptivity measurements at 11.05 μ obtained when synthetic mixtures of *Sterculia foetida* oil and corn oil were subjected to the hydrochloric acid treatment. Similar absorptivity measurements on HBr-titrated samples, on the other hand, indicated that this ratio varied from experiment to experiment.

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[Received September 28, 1962—Accepted November 13, 1962]

A Method for the Structural Analysis[1] of Triglycerides and Lecithins

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Abstract

The structural analysis of lecithins and triglycerides is described. The procedure is carried out on 2–5 mg of sample by a combination of reductive ozonolysis and thin-layer chromatography (TLC). The ozonides as well as the aldehyde "cores" derived from reduction of the ozonides are separated by TLC and analyzed quantitatively by densitometry. The constituent saturated fatty acids of the separated aldehyde "cores" are methylated and analyzed by gas-liquid chromatography (GLC). The scope of the method is demonstrated by the analysis of several synthetic and natural triglycerides and several lecithins isolated from natural sources.

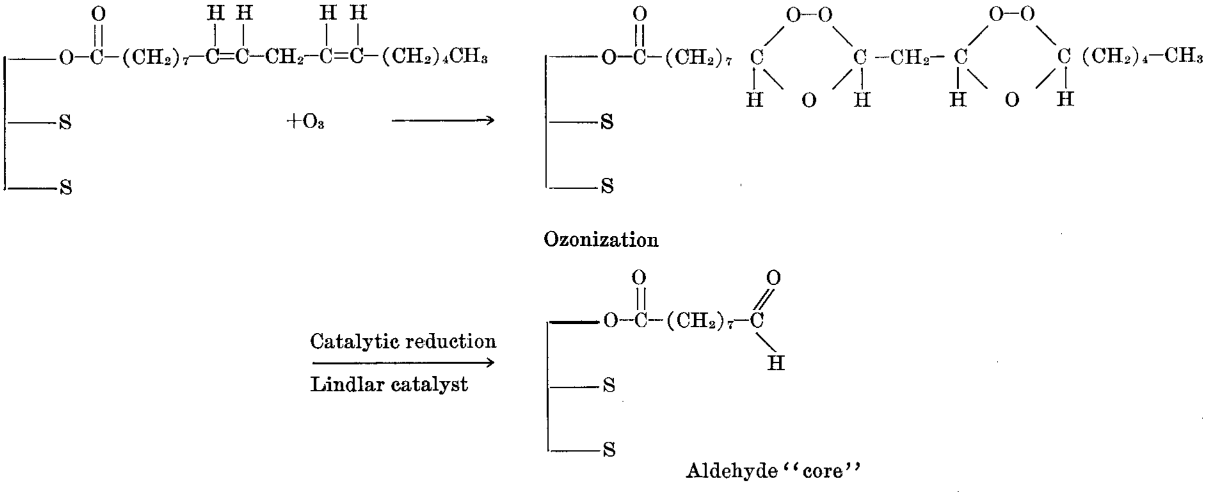
Introduction

Generally, the component triglycerides of fats and oils are determined on the basis of the fatty acid composition of simple fractions. In some methods, the fractionation is carried out directly on the fats or oils (9,37,41,44,45,46), in others after oxidation of the unsaturated fatty acid constituents (20, 22,25,48). Pancreatic lipase hydrolysis, together with fatty acid analysis, has also been used to obtain information on triglyceride structure (1,6,31,32,42,43).

The position of the fatty acids in lecithin has been studied mainly by methods based on the specific action of lecithinase A (12,13,15,26,30,22,40). It was generally believed that lecithinase A was specific for the hydrolysis of the fatty acids in the α-position. However, recent evidence (16,47) indicates that the attack by this enzyme is directed to the fatty acids on the β-position. Although enzymatic methods provide information on the position of the fatty acids in both lecithin and triglycerides, they do not permit a direct determination of the positional arrangement of the fatty acids in the parent molecules.

Present methods for the structural analysis of triglycerides are laborious or time consuming, and require gram-wise amounts of material which limits their application with regard to both the number of analyses that may be performed and to samples which are available in relatively large amounts. These drawbacks have been largely eliminated in the analysis of triglycerides by a method described recently by the authors (34). Presented here are further developments in this method for triglyceride analysis and its application to the analysis of the positional arrangement of the fatty acids in lecithin.

The two basic reactions of the method are demonstrated on glyceryl-1-linoleate-2,3-distearate as follows:



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[1] Supported in part by the U. S. Public Health Service, National Institutes of Health Research Grant H-5735 (C1).