The Chemistry of Polymerized Oils.
VII. Cyclization of Methyl Beta-Eleostearate

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Recently Paschke and Wheeler (5) studied the cyclic monomer obtained on polymerization of a 10% solution of mixed methyl eleostearates in methyl laurate at 250°C. for 48 hrs.

Following our earlier work on the thermal dimer of methyl β-eleostearate (1), we examined the cyclic monomer. From our previous investigations we had concluded that it was important in thermal polymerization studies to keep the reaction conditions as mild as possible, in order to minimize secondary changes. For this reason the cyclic monomer was separated from material which had only been heated at 180° for 4½ hrs.

Experimental

Preparation of Methyl β-Eleostearate Cyclic Monomer. Methyl β-eleostearate (m.p. 12.4 to 13.6°), $E^{1\%}_{1\,cm.} = 1{,}850$ in ethanol at 268 mμ, was prepared by esterification from the acid, m.p. 71°, with p-toluenesulfonic acid as catalyst.[1] Some 115 g. of this ester were heated in a sealed evacuated ampoule for 4½ hrs. at 180°. Monomeric material (69 g.) was separated by repeated passages through a falling-film molecular still at 105°. A solution of 66.2 g. of this distillate in 50 ml. of methanol was added at 40° to a solution of 330 g. of urea in 1,500 ml. of methanol. After 24 hrs. at room temperature the precipitate (which on decomposition with water gave 37.0 g. of oil) was filtered off, and the filtrate was concentrated to 800 ml. After two days the precipitate (which on decomposition with water gave 10.5 g. of oil) was removed, and the filtrate was concentrated to 500 ml. This solution was left at 5° over-night, and the precipitate was filtered off. On treatment with water the latter afforded 0.55 g. of oil. The filtrate, after removal of urea and methanol, gave 11.2 g. of ester. On distillation in a small falling-film molecular still at 105°, this material yielded 10.0 g. of cyclic monomer, or 9% based on the original eleostearate. Its ultraviolet spectrum, which is shown in Figure 1(a), is very different from that recorded by Paschke and Wheeler (5). It had the following properties: Number of double bonds (Adams' catalyst in ethanol) = 2.00 (calc. 2.00); C = 77.42% (calc. 78.03%); H = 11.32% (calc. 11.04%).

Conversion of the Cyclic Monomer to Orthophthalic Acid. Four grams (0.0134 mole) of this cyclic monomer were refluxed with 2.45 g. of N-bromosuccinimide (0.0134 mole) in 30 ml. of carbon tetrachloride for 3 hrs. The solution was cooled, and the solid succinimide (1.27 g.) was filtered off. The filtrate was evaporated under vacuum, and the residue was heated with 5 ml. of redistilled diethylaniline at 130° under nitrogen for 1 hr. to dehydrobrominate the diene to the benzene derivative. When cooled, the mixture set semi-solid. Water and hexane were added, and the mixture was shaken. The hexane layer was separated and washed three times with dilute HCl, then four times with water. The hexane solution was dried over Na_2SO_4, and the solvent was removed to give 4.26 g. of dark oil, which was molecularly distilled at 105° to afford 2.58 g. of a straw-yellow distillate. The ultraviolet absorption curve of this material is shown in Figure 1(b).

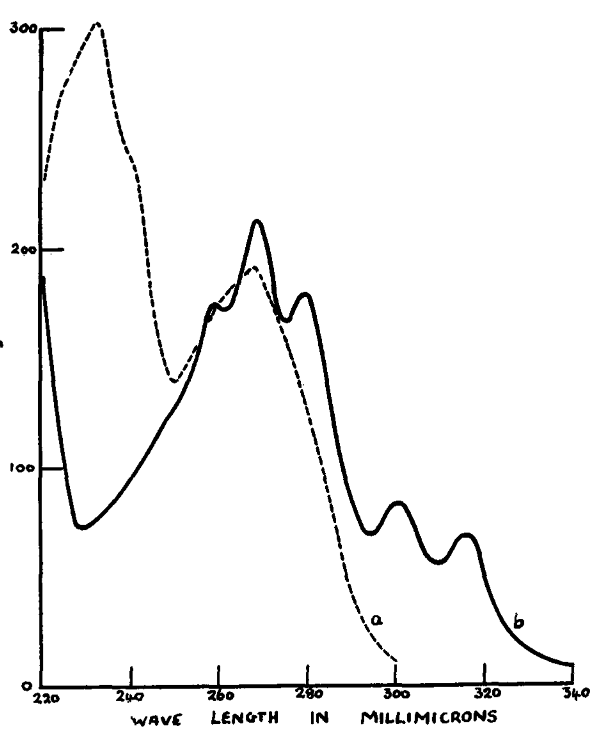

Fig. 1. Ultraviolet absorption spectra. a) Cyclic monomer. b) Material obtained by substitutive bromination and dehydrobromination of cyclic monomer.

A mixture of 0.67 g. (0.0023 mole) of the straw-yellow distillate, 0.82 g. (0.0046 mole) of N-bromosuccinimide and 12 ml. of carbon tetrachloride, was refluxed for 12 hrs. Solvent was removed under vacuum, and the residue was extracted several times with boiling hexane. After evaporation of the hexane 1.07 g. of brominated ester was obtained. This was refluxed with 2.5 g. of Na_2CO_3 in 50 ml. of water for 6 hrs. (*cf.* [5]). The solution was acidified with diluted H_2SO_4 and extracted continuously with ether for ½ hr. The ethereal extract was washed several times with water and evaporated to dryness under vacuum to give 0.72 g. of resinous material. This was dissolved in 100 ml. of acetone (previously treated with $KMnO_4$ and dried over K_2CO_3) and 2.0 g. of $KMnO_4$ added in portions, with shaking, over several hours. Fnally the solution was refluxed until the permanganate color had disappeared. The acetone was removed in vacuum, and the residue was extracted three times with 150 ml. of boiling water

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[1] Ester prepared from the acid by treatment with diazomethane in ether had $E^{1\%}_{1\,cm.} = 1{,}980$, m.p. 14.0–15.1°. Pure ester should have $E^{1\%}_{1\,cm.} = 2{,}060$ based on $E^{1\%}_{1\,cm.} = 2{,}161$ for the acid (4).

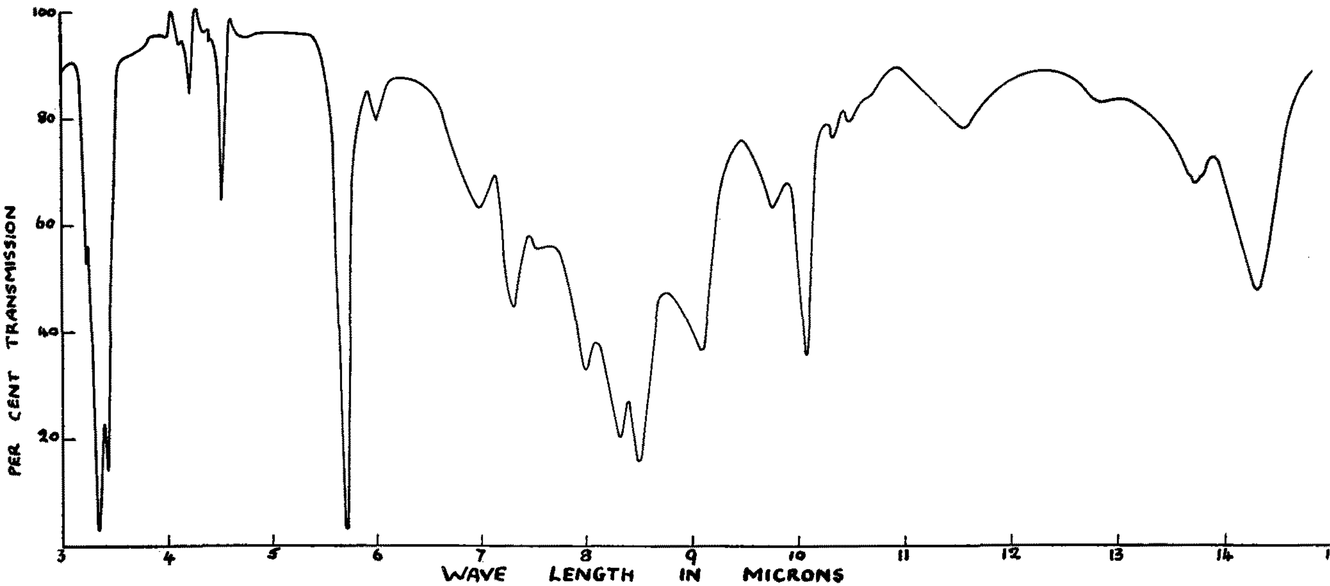


FIG. 2. Infrared absorption spectrum of cyclic monomer (2.4 g./100 g. in CS_2, cell 0.5 mm.).

containing 1 g. of NaOH. The combined extracts were acidified with HCl, boiled down to 100 ml., and extracted continuously with ether for 5 hrs. The material left after removal of the ether was sublimed at 180° under 1-mm. pressure to afford 0.16 g. of sublimate. (Under these conditions authentic *o*-phthalic acid was found to sublime quantitatively as the unchanged acid.) This material contained 0.102 g. of *o*-phthalic acid as determined spectrophotometrically by means of its absorption maximum at 281 mμ ($\epsilon = 1{,}440$). This amount of *o*-phthalic acid corresponds to a 17% yield based on the cyclic monomer; Paschke and Wheeler (5) record a 20% yield. Tests with mixtures of *o*-phthtalic, oxalic, and succinic acids showed that the amount of *o*-phthalic acid in such mixtures could be determined in this manner with an accuracy of about 2%.

The sublimate was crystallized from 1.5 ml. of water to give 35 mg. of *o*-phthalic acid, m.p., and mixed m.p. with an authentic specimen 202° (dec.). On sublimation at atmospheric pressure this was converted to the anhydride, m.p. 130°, mixed m.p. with an authentic specimen 130–132°. For further identification the anhydride was converted to *o*-phthalimide, m.p., and mixed m.p. with authentic *o*-phthalimide 233.5–234.5°.

Discussion

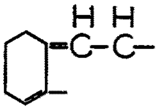
Our results on the structure of the cyclic monomer are similar to those of Paschke and Wheeler (5) in that a) dehydrogenation followed by oxidation gave *o*-phthalic acid in similar yield to theirs (17% against 20%); b) it is agreed that the postulated dialkylcyclohexadiene type of structure is present. We have however considered the mixture of isomers which constitutes the cyclic monomer in more detail and discuss this below.

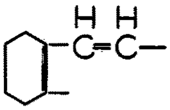
The possible conjugated diene structures consist of the following types:

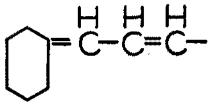

I

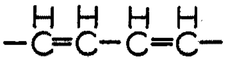

II


III


IV


V


VI


$$\overset{H}{-C}=\overset{H}{C}-\overset{H}{C}=\overset{H}{C}-$$
VII

Of these it is likely that I, II, and III will absorb maximally near 270 mμ whereas IV, V, and VI will absorb near 240 mμ (2, 3). Only VII absorbs near 230 mμ. From Figure 1(a) it will be seen that bands occur at 232 mμ and 268 mμ with a faint shoulder at 240 mμ. The 268 mμ band is not due to conjugated triene since the characteristic associated peaks at 258 mμ and 279 mμ are absent. It is therefore possible that dienes of all seven types are present. Types I and/or II and III account for about 60%, assuming $\epsilon = 10{,}000$ (2, 3). It is difficult to calculate the amounts of types IV, V, and VI because they are present in small amounts and only give rise to a shoulder in the absorption curve. Type VII accounts for about 40%, assuming $\epsilon = 20{,}000$, but this percentage includes types IV, V, and VI owing to the contribution of the shoulder at 240 mμ to the total intensity at 232 mμ.

The strong band at 10.13 μ in the infrared spectrum (Figure 2) of the cyclic monomer is characteristic for conjugated *trans-trans* diene (structure VII). The small bands at 10.3 and 10.5 μ are possibly due to structures V and VI (3). The strong band at 14.3 μ is probably due to a substituted cyclohexadiene (structures I–III). The infrared results thus support those obtained from the ultraviolet spectra.

The formation of conjugated triene (peaks at 259, 268.5, and 279.5 mμ) and traces of tetraene (peaks at 300 and 316 mμ) (Figure 1[b]) on substitutive bromination and dehydrobromination may be noted. The former is probably formed from the conjugated diene VII. The latter could be the final product of disubstitutive bromination and loss of hydrobromic acid from several of the possible structures or could arise from minute amounts of residual eleostearate.

All our evidence goes to show that a cyclohexadiene of type I is the probable primary product of cyclization. Under the influence of heat some double bonds migrate, giving rise to structures II–VI. Structure VII is probably the final result of the double bond migration. It is surmised that VII also contains a ring because the cyclic monomer does not form a urea complex.

Summary

Evidence is presented for the presence of various structural types in the cyclic product obtained by thermal polymerization of methyl β-eleostearate under mild conditions. Of these types a 1,2-dialkyl-3,5-cyclohexadiene is probably the primary product.

Acknowledgment

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Seed Germination as an Index of Potential Free Fatty Acid Content of Sesame Oil[1]

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Introduction of the new indehiscent (non-shattering) varieties, Rio (1) and Palmetto (5), of sesame may make possible economic production of this ancient crop as a domestic source of edible oil and protein supplement. In the harvest of normal dehiscent or shattering type of sesame, hand labor is required to prevent excessive loss of seed. While the new indehiscent varieties may be machine-harvested, very careful adjustment of the combine used for threshing is required to prevent excessive damage to the seed. The seed capsules of indehiscent sesame require considerable force for threshing, and the seeds are tender and easily damaged. Even microscopic cracks in the seed coat cause the seed to lose viability. Free fatty acid content of oil in dead seeds apparently increases much more rapidly than in live seeds. Hoffpauir, Petty, and Guthrie (4) reported that free fatty acid content of oil from dead cottonseed greatly exceeded that of viable seed. Beroza and Kinman (3) found little change in free fatty acid in seed which had been hand-threshed to prevent damage to the seed after storage at 100°F. for five to 11 months.

This report presents the results of experiments designed to estimate the relationship between viability of seed at harvest time and the free fatty acid in oil from seed which had been stored for various periods after threshing.

Experimental Materials and Methods

Twenty-three samples of seed of the variety Rio were obtained from a machine-harvesting experiment designed to obtain information on requirements for maximum threshing efficiency and minimum seed damage. These samples were combined from the windrow during the period from October 14 through October 20, 1954. Rainfall on the windrows, totaling 2.61 in. between September 27 and October 7, 1954, caused only slight damage, as indicated by practically the same viability in seed combined before and after the rains. Seed samples were cleaned immediately after threshing and stored in paper envelopes at room temperature. On October 23 germination tests of these samples were started. Two lots of 100 seed were taken from each sample, treated with Spergon to prevent mold, placed between sheets of moist filter paper in Petri dishes and incubated at 28°C. for eight days. In counting the seed, any portion of over one-half seed was considered as a whole seed. Seeds which showed any indication of germination were considered viable. Non-viability shown in these tests was used as a measure of threshing damage.

Free fatty acid content of the oil (hereinafter referred to as FFA) was determined by a method derived from methods of the A.O.A.C. (2) and A.O.C.S. (6). A 10-g. sample of seed was ground in petroleum ether with a Sargent centrifugal wet mill. The extracted oil was filtered with suction into a tared flask, the ether evaporated, and the oil weighed. Oil content of these samples was approximately 49%. FFA was determined and reported as percentage of oleic acid in the oil.

A random sample of plants taken from the same field were hand-threshed on December 10 to avoid seed damage. The hand-threshed seed lots were used as check samples in all later runs for FFA and viability.

Experimental Results

Hand-threshed seed (a total of 180 samples representing two replications of each of 90 indehiscent sesame strains grown in yield tests in 1954) averaged 98.3% germination while machine-threshed seed from the same plots averaged 67.1% germination. Loss of viability was apparently almost entirely caused by damage in threshing.

Germination of seed of 10 varieties produced in 1953 ranged from 98.7 to 17.3% three months after harvest; FFA ranged from 0.22 to 3.18% five months after harvest.[2] The correlation coefficient computed between the data for viability and FFA was —.926

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[1] Presented at annual meeting, American Oil Chemists' Society, Houston, Tex., April 23–25, 1956.