[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

Cyclopropene Rearrangement in the Polymerization of Sterculic Acid

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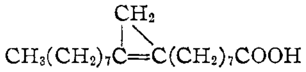
Polymerization and acetolysis of sterculic acid have been shown to proceed *via* opening of the cyclopropene ring by carboxylate to yield four isomeric products, identified by oxidative degradation.

The mixture of isomeric acids obtained by saponification of *Sterculia foetida* oil[2] was early observed to undergo polymerization,[3] the first isolation of pure sterculic acid from this mixture and demonstration of its instability being effected by Nunn[4] in 1952. The assignment by Nunn[4] of ω-(2-*n*-octylcyclopropenyl)-caprylic acid (I) as the structure of sterculic acid was subsequently corroborated,[5,6] and most recently confirmed by synthesis.[7] It represents the first naturally occurring compound of demonstrated cyclopropene structure, although both malvalic[8a] and bombacic acids[8b] probably contain cyclopropene rings and several synthetic representatives are known.[9]



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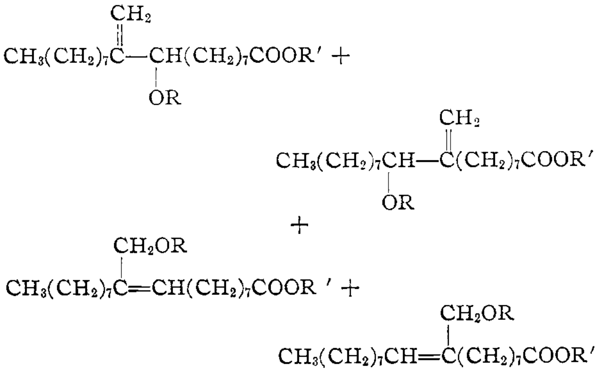
Although Faure and Smith,[5] on the basis of infrared analysis, suggested that sterculic acid polymerizes with opening of the cyclopropene ring, no structures were assigned to the products. The present investigation, previously reported in preliminary form,[10] has shown the polymerization to proceed *via* isomerization of the cyclopropene ring with carboxylic acid addition, leading to a mixture of polyesters, represented by the compounds of mixture A, shown below. The infrared spectrum of the purified polymer, essentially in agreement with that described by Faure and Smith (*cf.* below),[5] indicated the absence of cyclopropene units (no absorption at 1869 and 1010 cm.$^{-1}$).[5] Absorption at 1737 and 1169 cm.$^{-1}$ suggested the presence of ester,[11] while bands at 1648 and 901 cm.$^{-1}$ and at 1712 and 960 cm.$^{-1}$ were indicative of *unsym*-disubstituted olefin and terminal carboxyl groups, respectively.[12]

I ⟶ mixture A

(R = R′ = rearranged sterculic acid residues)

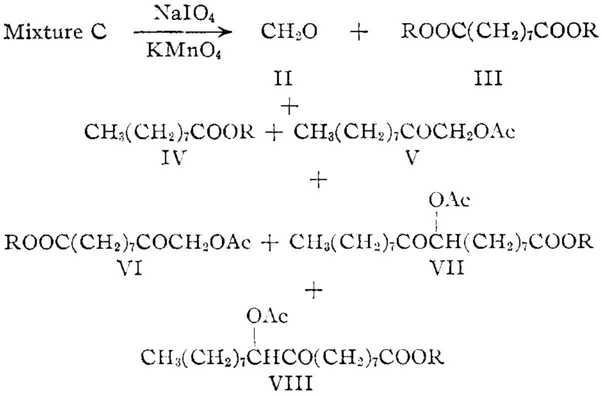


$$CH_3(CH_2)_7C(=CH_2)-CH(OR)(CH_2)_7COOR' + CH_3(CH_2)_7CH(OR)-C(=CH_2)(CH_2)_7COOR' + CH_3(CH_2)_7C(CH_2OR)=CH(CH_2)_7COOR' + CH_3(CH_2)_7CH=C(CH_2OR)(CH_2)_7COOR'$$

mixtures A, B, C

The polymer was saponified at room temperature to the corresponding unsaturated hydroxy acids (mixture B). The latter, upon acetylation, was converted to mixture C, the unsaturated acetoxy acids. Mixture C also was obtained directly from sterculic acid by heating the natural product in the presence of excess glacial acetic acid. In the latter case the product was purified by chromatography; identity of mixture C from the two sources was established by infrared spectra.

$$\text{Mixture A} \xrightarrow[2,\ H^+]{1,\ OH^-} \underset{(R = R' = H)}{\text{mixture B}} \xrightarrow{AcCl} \underset{(R = Ac,\ R' = H)}{\text{mixture C}} \xleftarrow{HOAc} \text{I}$$



$$\text{Mixture C} \xrightarrow[KMnO_4]{NaIO_4} \underset{II}{CH_2O} + \underset{III}{ROOC(CH_2)_7COOR} + \underset{IV}{CH_3(CH_2)_7COOR} + \underset{V}{CH_3(CH_2)_7COCH_2OAc} + \underset{VI}{ROOC(CH_2)_7COCH_2OAc} + \underset{VII}{CH_3(CH_2)_7COCH(OAc)(CH_2)_7COOR} + \underset{VIII}{CH_3(CH_2)_7CH(OAc)CO(CH_2)_7COOR}$$

Structural assignments for the components of mixture C were made by isolation and identification of products obtained from periodate-permanganate oxidation.[12] Among the oxidation products form-

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[1] Taken in part from the B.S. Thesis of C. L. Tarimu, June, 1958.

[2] The oil itself polymerizes at elevated temperature to a gel or gum [K. Wedemeyer, *Z. Untersuch. Nahr. u. Genussm.*, **12**, 210 (1906)] and the phenomenon spurred much of the original investigation of its components. This polymerization of the neutral glycerides, however, presumably proceeds *via* a totally different mechanism from the acidic process described in the present report, perhaps to give a polycyclopropane similar to that described (K. B. Wiberg, 131st A.C.S. Meeting, Miami, Fla., April, 1957; *cf.* Abstracts, p. 39-O) from cyclopropene itself.

[3] A. Steger and J. van Loon, *Fette u. Seifen*, **50**, 305 (1943).

[4] J. R. Nunn, *J. Chem. Soc.*, 313 (1952).

[5] P. K. Faure and J. C. Smith, *ibid.*, 1818 (1956).

[6] K. L. Rinehart, Jr., W. A. Nilsson and H. A. Whalley, THIS JOURNAL, **80**, 503 (1958).

[7] N. T. Castellucci and C. E. Griffin, *ibid.*, **82**, 4107 (1960).

[8] (a) J. J. Macfarlane, F. S. Shenstone and J. R. Vickery, *Nature*, **179**, 830 (1957); B. Craven and G. A. Jeffrey, *ibid.*, **183**, 676 (1959). (b) G. Dijkstra and H. J. Duin, *ibid.*, **176**, 71 (1955).

[9] For a review, *cf.* E. Vogel, *Angew. Chem.*, **72**, 4 (1960).

[10] K. L. Rinehart, Jr., T. P. Culbertson and C. L. Tarimu, THIS JOURNAL, **81**, 5007 (1959).

[11] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

[12] R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701, 1710 (1955).

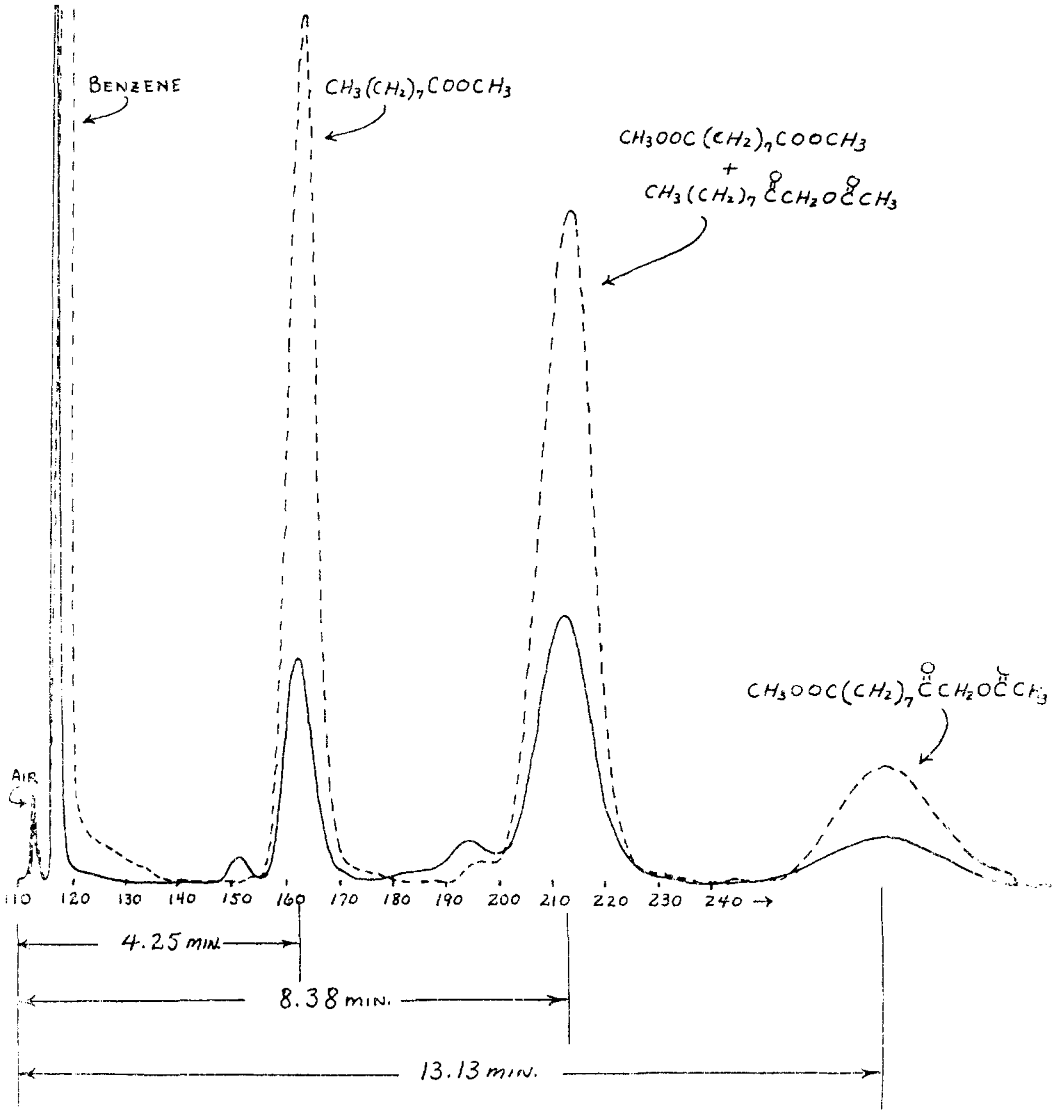

Fig. 1.—Gas chromatograms of compounds III, IV, V and VI (R = CH_3): —, from oxidation of mixture C; ----, from a prepared mixture of authentic compounds.

aldehyde[13] was determined with chromotropic acid[12] while azelaic acid (III, R = H) deposited as crystals and was identified by comparison with an authentic sample. Pelargonic acid (IV, R = H) and 1-acetoxy-2-decanone (V) were isolated from elution chromatography on silicic acid and identified by direct comparison with authentic material. The latter compound (V) was synthesized by acetolysis[14] of the diazomethyl ketone X formed from reaction of nonanoyl chloride (IX) and diazomethane.

$$\underset{\text{IX, XI}}{RCOCl} \xrightarrow{CH_2N_2} \underset{\text{X, XII}}{RCOCHN_2} \xrightarrow{HOAc} \underset{\text{V, VI}}{RCOCH_2OAc}$$

V, IX, X: R = $CH_3(CH_2)_7$–
VI, XI, XII: R = $CH_3OOC(CH_2)_7$–

The chromatogram also yielded a mixture of 9,10- and 10,9-acetoxy-ketoöctadecanoic acids (VII and VIII, R = H). Identification of these isomers was achieved by comparison of them and their derivatives with authentic materials. Compounds VII and VIII were hydrolyzed to a mixture of corresponding hydroxyketo acids (XIII and XIV) whose infrared spectrum was superimposable on that of a mixture of a synthetic 9,10- and 10,9-hydroxyketoöctadecanoic acids (XIII and XIV), prepared by permanganate oxidation of oleic acid.[15] Moreover, treatment of the mixture of XIII and XIV obtained from hydrolysis of VII and VIII with 2,4-dinitrophenylhydrazine reagent produced a dinitrophenyl-osazone identical to that obtained from synthetic XIII and XIV (from oleic acid), while oxidation of isolated XIII and XIV with chromic anhydride and sulfuric acid gave 9,10-diketostearic acid (XV), identical to authentic XV.[16] In addition, acetylation of synthetic XIII and XIV yielded a mixture of VII and VIII whose infrared

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(13) It may be noted that Nunn[4] obtained formaldehyde from the decomposition of the ozonide of sterculic acid. From the results of the present investigation it seems likely that the formaldehyde produced was due to the presence of polymer in the ozonolysis mixture.

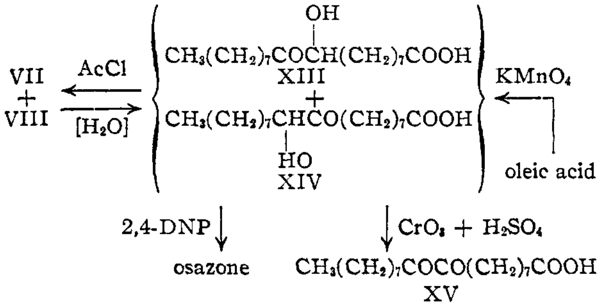
(14) A. Lardon and T. Reichstein, *Helv. Chim. Acta*, **26**, 747 (1943).

(15) G. King, *J. Chem. Soc.*, 1788 (1936).

(16) R. T. Holman, W. O. Lundberg, W. M. Lauer and G. O. Burr, THIS JOURNAL, **67**, 1285 (1945).

spectrum was superimposable upon the spectrum obtained from the mixture of VII and VIII isolated from the oxidation of mixture C.

Thus, all oxidation products expected from oxidation of mixture C were identified except compound VI; while compound VI was not found during column chromatography, its presence among the oxidation products was ascertained by gas chromatography. The oxidation products of mixture C (R = H) were first converted to their methyl esters (R = CH_3) by methanolysis and subsequent re-acetylation of the partially trans-esterified alcohol moieties. By means of fractional molecular distillation, compounds III, IV, V and VI (R = CH_3) were separated as one fraction and compounds VII and VIII (R = CH_3) as a second fraction. The mixture of methyl acetoxyketostearates (VII and VIII) obtained was shown to be identical (infrared spectrum) to the mixture of authentic isomers prepared by methyl esterification and acetylation of synthetic XIII and XIV.



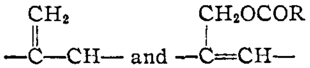
The first molecular distillation fraction gave a gas chromatogram (*cf.* Fig. 1) identical to that of a prepared mixture of authentic III, IV, V and VI (R = CH_3). Authentic compound VI employed in the gas chromatogram was synthesized by the same reaction sequence employed for IV; in this case ω-carbomethoxy-caprylyl chloride (XI) was treated with diazomethane to give XII, then with acetic acid. Although compounds III (R = CH_3) and V, which differ in molecular weight by two, appeared as one band in the gas chromatograms (Fig. 1) and could not be resolved under the conditions used; both were previously established as oxidation products (III as the acid, R = H) by silicic acid chromatography. Conversely, compound VI, which was not found as the free acid (R = H) during silicic acid chromatography, was clearly shown to be present as its methyl ester (R = CH_3) by gas chromatography. Identification of the products expected from periodate-permanganate oxidation of mixture C was thus completed.

Although, as noted above, Faure and Smith did not assign structures to the polymeric products from sterculic acid, they did call attention to an increase in absorption in the polymer's infrared spectrum, at 7.27 μ (1376 cm.$^{-1}$), attributed by them to methyl groups, thus implying the presence of groupings of the type

$$—C(CH_3)=C(OAc)—$$

No evidence for this grouping has been found in the present study. Iodoform tests on the periodate-permanganate oxidation products were negative, indicating the absence of the required methyl ketone oxidation products of that structure, while gas chromatograms of the oxidation products failed to demonstrate any major products beyond those already indicated. Moreover, the infrared spectrum of the polymer shows no band in the 1770 cm.$^{-1}$ region characteristic of vinyl esters.[11] The apparently contradictory evidence described is resolved by noting that, while a band at 1376 cm.$^{-1}$ may indicate methyl group absorption, it need not. In the present case, the band is abnormally broad for methyl absorption and, while this band (due to the presumed symmetrical bending mode)[11] is of increased intensity in the spectrum of the polymer, that near 1450 cm.$^{-1}$ (asymmetrical bending mode) remains constant. Apparently some other unidentified structural feature is the cause of the anomaly.

It was of considerable interest to estimate the relative proportions of the compounds of types



$$—\overset{\overset{\displaystyle CH_2}{\|}}{C}—\underset{\underset{\displaystyle OCOR}{|}}{CH}— \text{ and } —\overset{\overset{\displaystyle CH_2OCOR}{|}}{C}=CH—$$

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(methylene acetoxy and acetoxymethyl, respectively) in mixtures A and C. Difficulties inherent in analyzing mixture A (non-volatility, varying chain length) directed attention to mixture C, and results from mixture C in any event presumably would be applicable to mixture A.

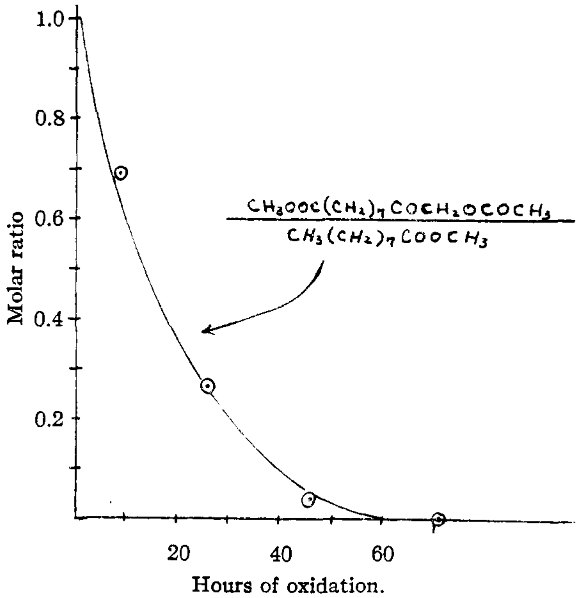


Fig. 2.—Molar ratio of VI (R = CH_3) to IV (R = CH_3), determined by gas chromatographic analysis after periodate–permanganate oxidation of mixture C. No trace of VI could be detected after the 71-hour oxidation.

As a first approach, quantitative analysis of the gas chromatograms of oxidation products was investigated. One difficulty in this method already has been noted: lack of resolution of compounds III and V. This problem is not, however, insurmountable since compounds III and V should be formed in equal amounts since they arise mole for mole from oxidation of the same olefin; the same is

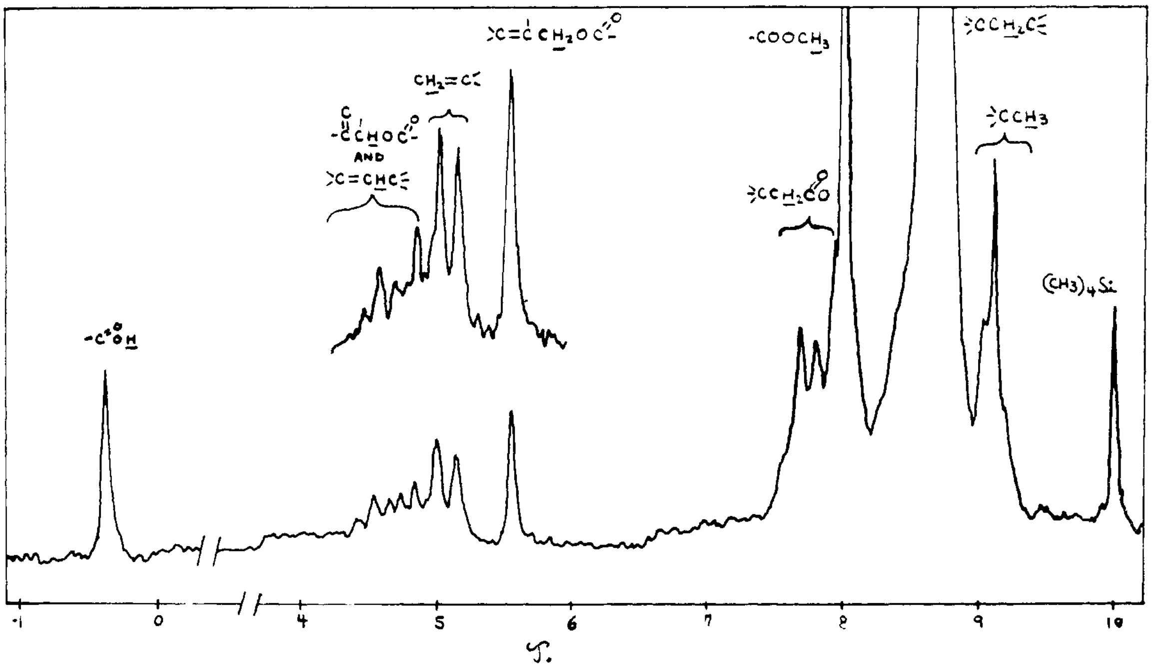


Fig. 3.—Nuclear magnetic resonance spectrum of mixture C.

true for compounds IV and VI. Moreover, since the cyclopropene unit in sterculic acid is essentially symmetrically substituted, the two isomeric methylene acetoxy acids, *a priori*, should be formed in equal amounts; thus, equal amounts of compounds III, IV, V and VI should be present. A greater difficulty in this analytical method was the slow emergence of compounds VII and VIII as a very broad, ill-defined band from columns amenable to analysis of compounds III-VI, rendering comparative analyses difficult. A still greater, intolerable, difficulty was provided by the observation that the compounds to be analyzed were unstable under the oxidation conditions. This is already apparent from Fig. 1, where it is noted that the prediction that equal quantities of compounds IV and VI should be obtained is obviously incorrect. This would be explained most simply if further oxidation of the α-acetoxyketones (V, VI, VII and VIII) were occurring, since this would give additional methyl pelargonate (IV) and azelate (III) as oxidation products, and cause preponderance of IV over VI (and of III over V, though that is less apparent due to their unresolved peak). This hypothesis was confirmed when the periodate-permanganate oxidations were conducted for varying lengths of time. Extrapolation of the ratio of VI to IV to zero oxidation time indicated that equal quantities of the two indeed were formed initially, but that the ratio steadily decreased with prolonged oxidation (*cf.* Fig. 2). The overoxidation was further demonstrated by oxidation of 1-acetoxy-2-decanone (V) to pelargonic acid by sodium periodate.

The approximate molar proportion of methylene acetoxy acids to acetoxymethyl acids was finally established by the n.m.r. spectrum of the acetolysis mixture. This spectrum (Fig. 3) is complex and broad in most regions, and it is difficult to assign bands to protons of the individual isomers. However, a singlet peak at τ[17] = 5.62 may be assigned to the —COOCH$_2$C=C protons of the acetoxymethyl group.[18] Comparison of the area of this peak to that of the carboxyl proton, common to all isomers, hence of unit area, assigned 0.70 proton to the peak. The molar proportion of the acetoxymethyl isomers was then 0.35 and the methylene-acetoxy isomers constituted 65% of the mixture. This value is in rough accord with the quantitative determination of formaldehyde (from methylene acetoxy isomers) which gave 0.43 mole of formaldehyde. Since the closest analog studied previously, allyl acetate,[12] gave only 0.50 mole of formaldehyde, the 0.43 mole found in the present study indicates the predominant formation of methylene acetoxy isomer.

To test whether the mixture of products found was the result of allylic isomerization of a different initial product mixture, tiglyl acetate was heated for one hour at reflux in glacial acetic acid, conditions somewhat more vigorous than those employed in the acetolysis of sterculic acid. No rearrangement was observed, in essential agreement with the reports that α- and γ-methallyl alcohols are esterified without rearrangement in acetic acid[19a,b,c] and that α- and γ-methylallyl acetates are hydrolyzed in aqueous sulfuric acid to the respective unrearranged alcohols.[19a,c,20]

The formation of allylic acetates from rearrangement of the cyclopropene group is not unexpected in light of the quantitative formation of allyl acetate from solvolysis of cyclopropyl tosylate.[21]

(17) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

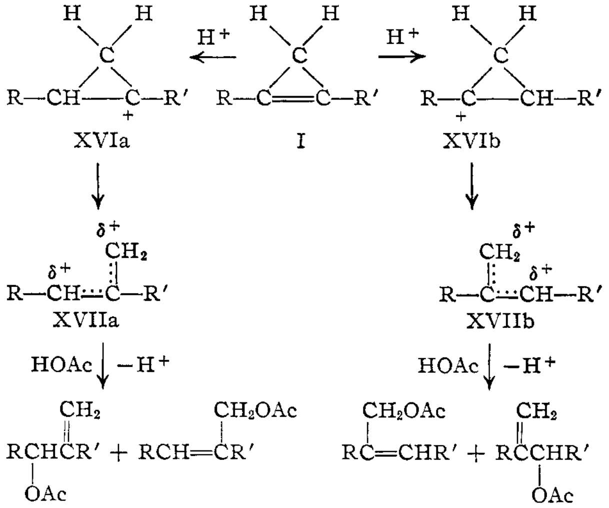
(18) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, 1959.

(19) (a) R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 753 (1956); (b) L. W. J. Newman and H. N. Rydon, *J. Chem. Soc.*, 261 (1936); (c) C. Prevost, *Ann. chim.*, [10] **10**, 147 (1928).

(20) E. H. Ingold and C. K. Ingold, *J. Chem. Soc.*, 756 (1932).

(21) J. D. Roberts and V. C. Chambers, **This Journal**, **73**, 5034 (1951).

The mechanism of the present rearrangement has not yet been studied in detail, but presumably proceeds by initial protonation of the double bond of the cyclopropene ring to give a cyclopropyl carbonium ion, similar to that formed in tosylate solvolysis.[21] In the most straightforward path two isomeric cyclopropyl carbonium ions (XVIa and XVIb) are formed, which then collapse to their respective allylic carbonium ions (XVIIa and XVIIb), which in turn react with acetate to give the observed products. Equilibration of the acetates, once formed, appears to be precluded by the results described above for the stabilities of tiglyl and methallyl acetates.



mixture C, R = $CH_3(CH_2)_7$–; R′ = $-(CH_2)_7COOH$

Experimental[22]

Polysterculic Acid (Mixture A).—*Sterculia foetida* oil[4] (100 g.), obtained by pentane extraction of *S. foetida* seeds which had been ground to a fine meal in a Waring blendor, was treated with 1000 ml. of 2.5 *N* ethanolic potassium hydroxide during 24 hr. at room temperature. The mixture was diluted with 3000 ml. of water, acidified to *p*H 4 with aqueous hydrochloric acid, and extracted with ether. The ether extract was washed with cold water, then dried over anhydrous sodium sulfate at 10°. Ether evaporation—*in vacuo* and without external heating—yielded 81 g. of semisolid material which gave a positive Halphen test (red color)[23,24] and an infrared spectrum (carbon tetrachloride) with bands (at 1869 and 1010 cm.$^{-1}$) indicative of the presence of sterculic acid.[5]

A.[25a]—When a mixture of the *Sterculia foetida* acids was fractionated as its urea adducts[4,25b] one of the acid fractions containing nearly pure sterculic acid polymerized on standing several days at room temperature. The viscous oily polymer (mixture A) was extracted with methanol and dried in vacuum. It was soluble in ether and contained infrared bands at 1738 and 1168 (ester),[11] at 1712 and 960 (terminal carboxyl),[11] and at 1650 and 905 (terminal methylene)[11] but none at 1869 or 1010 cm.$^{-1}$.

Anal. Calcd. for $(C_{19}H_{34}O_2)_n$: C, 77.49; H, 11.64; sapn. equiv., 294. Found: C, 77.63; H, 11.62; sapn. equiv., 248.

B.—In a large run, to avoid the tedious urea fractionation technique, the total mixture of *S. foetida* acids was heated under varying conditions to effect polymerization. The product was incompletely polymerized (appreciable solubility in methanol) after it was heated for 30 min. at 100°, but was finally found to be completely polymerized (insoluble in methanol) after it had been heated at 150° during 2 hr. Extraction of the crude polymer with hot methanol, followed by several washings with water and subsequent drying, yielded 56 g. of residual polysterculic acid (mixture A) as a viscous oil. This material gave no color with the Halphen reagent and its infrared spectrum was identical to that of the polymer obtained in A above.

Unsaturated Hydroxy Acids (Mixture B).—Mixture A (56 g.) was saponified on standing with 500 ml. of ethanolic potassium hydroxide at room temperature for 18 hr. After acidification, ether extraction and evaporation of the ether, 52 g. of unsaturated hydroxy acids (mixture B) was obtained. The crude acids were dissolved in 160 ml. of methanol and treated with urea, as shown in the following table, to remove adductable material.[26] Each adduct was decomposed with water and the acids recovered were isolated by extraction into hexane.

Fraction	Urea added, g.	Precipitate, g.	Adducted acids obtained, g.
1	52	55	12
2	52	61	4
3	100	94	0
4	200	181	0

The residual methanolic solution of unadducted acids was concentrated *in vacuo*, taken up into water, and extracted with ether. The ether extracts yielded 32 g. of unadductable, isomeric unsaturated hydroxy acids (purified mixture B) as a viscous oil which possessed infrared absorption at 3615 and 1231 cm.$^{-1}$ (hydroxyl),[11] 1707 and 935 cm.$^{-1}$, and 1645 and 900 cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{36}O_3$: C, 73.02; H, 11.60; neut. equiv., 313. Found: C, 73.57; H, 11.57; neut. equiv., 318.

Unsaturated Acetoxy Acids (Mixture C). A. From Mixture B.—Acetylation of 15 g. of mixture B was carried out at room temperature in an excess of acetyl chloride. The process yielded 12.5 g. of the isomeric unsaturated acetoxy acids (mixture C) whose infrared spectrum was consistent with that expected: bands at 1735 and 1239 cm.$^{-1}$ (acetate),[11] and no hydroxyl absorption.

Anal. Calcd. for $C_{21}H_{38}O_4$: C, 71.14; H, 10.80; neut. equiv., 355. Found: C, 71.32; H, 11.02; neut. equiv., 367.

B. From Acetolysis of Sterculic Acid.—Acetolysis of sterculic acid was carried out with 102 g. of saponified *S. foetida* oil in refluxing glacial acid during 30 min. to give the crude mixture C. Initial experiments under milder conditions (lower temperatures and shorter reaction times) gave rise to products which still contained some unreacted cyclopropenyl (positive Halphen test and absorption at 1010 cm.$^{-1}$). Adductable material was separated by means of several treatments with urea in methanol solution. Isolation

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[22] All temperature measurements reported are uncorrected. Infrared spectra were determined (in carbon tetrachloride solution unless otherwise indicated) with a Perkin-Elmer recording spectrophotometer model 21B with sodium chloride optics by Mr. P. McMahon, Mrs. M. D. Verkade, Mr. D. W. Vittum, Jr., Mr. W. O. Dalton and Mr. D. H. Johnson. The n.m.r. spectra were determined by Mr. O. W. Norton with a Varian high resolution spectrometer (model V-4300B, equipped with super stabilizer) at 60 Mc. in carbon tetrachloride using tetramethylsilane as an internal standard.[17] Peak areas of the n.m.r. spectra and of the gas chromatograms were measured with a planimeter. Microanalyses were by Mr. J. Nemeth, Mrs. A. S. Bay and Miss J. Liu.

[23] G. Dijkstra and H. J. Duin, *Nature*, **176**, 71 (1955).

[24] P. K. Faure, *ibid.*, **178**, 372 (1956).

[25] (a) Isolated by W. A. Nilsson. (b) K. L. Rinehart, Jr., C. L. Tarimu, H. A. Whaley and W. A. Nilsson, paper in preparation.

[26] The small amount of material adducted by urea is presumably stearic and other acids present in *S. foetida* oil,[3] which had been incorporated (carboxyl function) into the polymer and which presumably furnished end groups for it. The constituent acids of *S. foetida* are remarkably homogeneous, reportedly consisting of 70% of sterculic acid [T. P. Hilditch, "The Chemical Constitution of Natural Fats," 3rd ed., rev., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 244]. It is of interest to note that sterculic acid does, reluctantly, form a urea adduct,[4,26] while the component acids of mixture B do not. This is reasonable in view of the enhanced bulk of the $-\overset{\overset{\large CH_2}{\|}}{C}\underset{\underset{\large OAc}{|}}{CH}-$ and $-\overset{\overset{\large CH_2OAc}{|}}{C}{=}CH-$ groups over that of the $-\overset{CH_2}{\overbrace{C{=}C}}-$ group.

of the unadducted residue gave 65 g. of unsaturated acetoxy acids (mixture C). A portion (2.8 g.) was chromatographed over a silicic acid column employing a mixture of Skelly B, methyl Cellosolve and water (100:9:1, by volume) as eluting solvent. Although 27 50-ml. fractions were taken, most of the eluted material was present in fractions 5–13. Fractions 8 and 9, a major peak, yielded a slightly yellow-colored oil which was decolorized with activated charcoal and dried; wt. 0.54 g. Its infrared spectrum was identical (superimposable) to that of the mixture C of unsaturated acetoxy acids prepared by saponification and subsequent acetylation of polysterculic acid (mixture A).

Anal. Calcd. for $C_{21}H_{38}O_4$: C, 71.14; H, 10.80; neut. equiv., 355. Found: C, 71.09; H, 10.91; neut. equiv., 354.

Oxidation of Mixture C by Periodate–Permanganate.[12]—All oxidations of mixture C by this process were carried out in aqueous solutions at room temperature employing 8 mmol. of sodium metaperiodate, 0.13 mmol. of potassium permanganate, 3 mmol. of potassium carbonate and 400 ml. of water per millimole of mixture C. The reaction mixtures were worked up by acidification with 10% sulfuric acid, followed by extraction of oxidation products into ether. The ethereal solutions were washed with water, dried and finally evaporated to yield the oxidation products.

Determination of Formaldehyde.—Oxidation, as described above, was carried out on a sample of mixture C (330 mg., 0.93 mmol.) during 24 hr. The presence of formaldehyde was shown by appearance of the violet color in an aliquot of the reaction mixture upon treatment with chromotropic acid.[12] A control solution gave no color.

In order to determine quantitatively the formaldehyde present, a series of solutions of known amounts of formaldehyde (from similar oxidations of erythritol) were prepared and treated with chromotropic acid in a like manner. These established a working curve of formaldehyde concentration *vs.* absorbance at 570 mμ[12] of the chromotropic acid–formaldehyde adduct.

By this means, the formaldehyde concentration was determined to be 1.60×10^{-6} mmol./ml. in the oxidation mixture, a 43% yield since mixture C represented 3.72×10^{-6} mmol./ml.

Column Chromatography of Oxidation Products.—Products obtained from periodate–permanganate oxidations of mixture C were chromatographed on a silicic acid column (120 g. per gram of oxidation product) with Skelly B-methyl Cellosolve–water 100:9:1 (by volume) as eluting solvent. Fractions (50 ml.) were collected automatically, evaporated and weighed. From plots of concentration *vs.* fraction number, major peaks of the distribution were selected for further investigation.

Pelargonic acid (IV, R = H), mainly distributed over three fractions, was obtained as a slightly colored oil. Successive low temperature (−40°) crystallizations from acetone gave the pure acid, m.p. 8–11°, undepressed (m.p. 8.5–11.2°) in admixture with authentic pelargonic acid, infrared spectrum superimposable upon that of pelargonic acid.

1-Acetoxy-2-decanone (V) was found distributed over several fractions. The combined, crude, crystalline material was recrystallized repeatedly from methanol at −70°. Pure V had m.p. 54–55°, undepressed in admixture (m.p., 54.5–55°) with authentic 1-acetoxy-2-decanone (*cf.* below) infrared spectrum identical with authentic compound.

Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 67.25; H, 10.23.

The mixture of isomeric 9,10- and 10,9-acetoxy-ketostearic acids (VII and VIII, R = H) emerged in the latter part of elution over a large number of fractions. The material was decolorized with activated charcoal and dried thoroughly. An infrared spectrum obtained from the purified material was found to be superimposable upon that prepared from an authentic sample of the mixture of isomeric acetoxyketo acids (*cf.* below).

Anal. Calcd. for $C_{20}H_{36}O_5$: C, 67.38; H, 10.18; neut. equiv., 357. Found: C, 67.42; H, 10.42; neut. equiv., 352.

A portion of the mixture of VII and VIII (R = H), obtained from chromatography, was hydrolyzed in 2.5 *N* alcoholic potassium hydroxide to the corresponding hydroxyketo acids XIII and XIV. The product was converted[27] to the 2,4-dinitrophenylosazone, m.p. 147–147.5°, undepressed (m.p. 148–148.5°) in admixture with the osazone[15] from the authentic isomeric hydroxyketo acid mixture (m.p. 148.5–149.5°, *cf.* below).

A second sample of XIII and XIV (R = H) from the chromatogram was oxidized to XV with chromic acid. The diketo acid XV obtained had m.p. 82–83°. Authentic XV[28,29] melted 83–84° (lit.[29] 85–86°).

During preparation of the periodate-permanganate oxidation products of mixture C for chromatography, azelaic acid (III, R = H) crystallized from solution. The crude acid was collected and recrystallized from aqueous ethanol; m.p. 105–107°, undepressed in admixture (m.p. 104.5–107°) with authentic azelaic acid.

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.43; H, 8.57; neut. equiv., 94. Found: C, 57.64; H, 8.55; neut. equiv., 97.

Preparation of Oxidation Products for Gas Chromatography.—For analysis of the products obtained from periodate–permanganate oxidations of mixture C by gas chromatography, it was desirable[30] to convert the carboxylic acid products to their corresponding methyl esters. In these experiments, samples (709 mg., 2 mmol.) of mixture C were submitted to oxidation for varying periods of time (9, 26, 46 and 71 hr.). Oxidation products obtained from each run were dissolved in 40–50 ml. of methanol containing 0.5 ml. of concd. sulfuric acid and heated under reflux during 18 hr. Isolation and infrared analysis of the reaction products showed the presence of methyl esters (1737 cm.$^{-1}$), but also showed the loss of acetate ester by appearance of a band at 3465 cm.$^{-1}$ (hydroxyl) and disappearance of the acetate band at 1230 cm.$^{-1}$. Reacetylation of the free hydroxyl functions was carried out by heating the esterification products with acetyl chloride in a sealed tube at 60–65° during 7 hr.

Products from the acetylation reaction were molecularly distilled. Compounds III, IV, V and VI (R = CH_3) distilled 70–125° (0.04 mm.) (air-bath), while compounds VII and VIII (R = CH_3) distilled 130–140° (0.04 mm.) (air-bath). The mixture collected at the lower temperature range was analyzed by gas chromatography (*cf.* text), and the mixture of isomeric acetoxyketostearates, collected at the higher temperature, was compared (infrared spectra) to authentic, synthetic VII and VIII (R = CH_3).

Anal. Calcd. for $C_{21}H_{38}O_5$: C, 68.07; H, 10.34. Found: C, 68.51; H, 10.29.

Gas Chromatography of Oxidation Products.—The instrument used in this work was an F and M Linear Programmed Temperature Gas Chromatograph, model 202–B, with helium as the carrier gas. A 3/8-in. (o.d.) × 4-ft. stainless steel tube, fitted with an individual heater and packed with fire brick (60–80 mesh) containing 25% (by weight) of Dow Corning high vacuum Silicone grease, was employed for chromatography of the oxidation products. The following operating conditions are representative: helium pressure, 20 p.s.i.; helium flow rate, 80–100 ml./min.; block temperature, 250°; injection port temperature, 240°. The column temperature rise was programmed at 9°/min., starting at 110° upon sample injection and ending at 240°.

Identification of the oxidation products of mixture C was made by comparison of chromatograms obtained from a prepared mixture of authentic products with those obtained from the oxidations. Since peak area measurements cannot be directly related to the number of moles of a given component,[31] correction factors were determined by measurement of peak areas obtained from chromatograms of the prepared mixture containing known amounts of authentic compounds.

Syntheses of Stearic Acid Derivatives.—A mixture of 9,-10- and 10,9-hydroxyketostearic acids (XIII and XIV[32]; 590 mg., 1.88 mmol.) dissolved in 50 ml. of methanol containing

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(27) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

(28) Prepared by D. A. Davenport.

(29) R. T. Holman, W. O. Lundberg, W. M. Lauer and G. O. Burr, This Journal, **67**, 1285 (1945).

(30) J. Cason, J. S. Fessenden and C. L. Agre, *Tetrahedron*, **7**, 289 (1959).

(31) A. I. M. Keulemans, "Gas Chromatography," Reinhold Publishing Corp., New York, N. Y., 1959, p. 35.

(32) Prepared by D. A. Teets according the procedure of G. King.[15]

1 ml. of concd. sulfuric acid was heated under reflux during 5 hr. Excess methanol was removed from the reaction mixture *in vacuo*, and the residue was taken up in 10 ml. of water. The methyl esters (254 mg.) obtained from ether extracts were treated with acetyl chloride in a sealed tube during 1 hr. at 60–65°, and at room temperature overnight. The mixture was worked up, and crude isomeric methyl acetoxyketostearates (252 mg.; VII and VIII, R = CH_3), were purified by means of molecular distillation, b.p. 133–143° (0.04 mm.) (air-bath).

Anal. Calcd. for $C_{21}H_{38}O_5$: C, 68.05; H, 10.34. Found: C, 67.98; H, 10.25.

A mixture of VII and VIII (R = H) was prepared by direct acetylation of synthetic XIII and XIV.

Anal. Calcd. for $C_{20}H_{36}O_5$: C, 67.38; H, 10.18. Found: C, 66.95; H, 10.08.

A 2,4-dinitrophenylosazone was also prepared from synthetic XIII and XIV in the usual way. The product, after recrystallization from ethanol, melted 148.5–149.5° (*cf.* above).

9,10-Diketostearic acid (XV)[28] was obtained by chromic acid oxidation of 9,10-dihydroxystearic acid,[33] according to the method of Nicolet and Jurist,[34] m.p. 83–84° (lit.[34] m.p. 86°).

Methyl 10-Acetoxy-9-ketodecanoate (VI, R = CH_3).—ω-Carbomethoxycaprylyl chloride [prepared from methyl hydrogen azelate (10.0 g., 0.049 mmol.) and thionyl chloride (11.9 g., 0.10 mmol.) at 60°], in 15 ml. of ether solution at −10°, was added slowly to diazomethane[35] (*ca.* 8.4 g., 0.20 mmol.) in 300 ml. of ether at −10°. A mild exothermic reaction was observed during addition. The reaction mixture was stirred and maintained between −10 and −5° during 2 hr., then stirred at room temperature overnight. Excess diazomethane was removed by careful distillation of ether until the yellow color of the reaction mixture disappeared. While heating was continued at 40–50°, dry glacial acetic acid[36] (1.25 g., 25 mmol.) was added, and reflux was continued during 1 hr. Ether and excess acetic acid were removed *in vacuo* to yield an amber-colored semi-solid. A portion of this residue (5.83 g.) was fractionally distilled. Fraction I (0.584 g., b.p. 83–102° (0.06 mm.)) was methyl azelate (identified by comparison of infrared spectrum to an authentic sample); fraction II (2.290 g., b.p. 108–119° (0.06 mm.)) crystallized upon cooling (m.p. 50.5–51.0°) and proved to be methyl 10-chloro-9-ketodecanoate.

Anal. Calcd. for $C_{11}H_{19}ClO_3$: C, 56.29; H, 8.16; Cl, 15.11. Found: C, 56.67; H, 8.06; Cl, 15.27.

The third fraction [b.p. 128–133° (0.04 mm.), 1.075 g.] was the desired methyl 10-acetoxy-9-ketodecanoate (VI, R = CH_3), m.p. 47.5–48.0° (ether–hexane).

Anal. Calcd. for $C_{13}H_{22}O_5$: C, 60.44; H, 8.59. Found: C, 59.98; H, 8.67.

The compound was allowed to react with 2,4-dinitrophenylhydrazine in the usual way. The derivative, isolated and recrystallized from ethanol, m.p. 149.0–149.5°, was a 2,4-dinitrophenylhydrazone of the ketone portion of the parent molecule as well as a 2,4-dinitrophenylhydrazide of the carbomethoxy grouping; infrared absorption at 1736 and 1225 cm.$^{-1}$ showed the acetate function to be intact.

Anal. Calcd. for $C_{24}H_{28}N_8O_{11}$: C, 47.67; H, 4.67; N, 18.54. Found: C, 47.88; H, 4.73; N, 18.59.

1-Acetoxy-2-decanone (V).[37]—Pelargonyl chloride (10 g., 0.057 mol.) was allowed to react with excess diazomethane as described above. Acetolysis with dry acetic acid gave the crude crystalline acetoxy ketone, m.p. 45–53°. After repeated recrystallizations from cold ether, the pure compound amounted to 7.20 g., m.p. 55.0–55.8°.

Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 67.25; H, 10.35.

No indication of the presence of chloromethyl ketone was obtained as in the previous case.

A sample of V (107 mg., 0.5 mmol.) was dissolved in 40 ml. of methanol to which was added 40 ml. of 0.1 *M* sodium metaperiodate solution. The mixture remained at room temperature, in darkness, and the progress of oxidation was followed by periodate analysis of aliquots.[38] One equivalent of periodate (0.497 mol.) was consumed during 24 hr., and the oxidation products were extracted into ether from the acidified mixture. The material obtained was heated in methanolic sulfuric acid for 18 hr. The presence of methyl pelargonate was indicated by gas chromatography (retention time identical to that of authentic methyl pelargonate).

Attempted Isomerization of Tiglyl Acetate.—Equal volumes (1 ml.) of glacial acetic acid and tiglyl acetate,[39] prepared by acetylation of tiglyl alcohol (the latter obtained *via* lithium aluminum hydride reduction of tiglic acid[40]), were mixed. A sample of the mixture was analyzed by gas chromatography immediately after mixing. The mixture was heated under reflux during 1 hr., and a sample again was analyzed by gas chromatography. The two samples gave superimposable chromatograms.

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The Proton Magnetic Resonance Spectra of Olefins. I. Propene, Butene-1 and Hexene-1

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The high-resolution proton magnetic resonance spectra of propene, butene-1 and hexene-1 have been obtained on "neat" samples and on samples in dilute carbon tetrachloride solution. The spectra have been analyzed in terms of chemical shifts and spin–spin coupling constants. Some possible explanations of the chemical shifts are discussed. The spin–spin coupling constants observed in butene-1 may indicate that the three rotational conformers are equally abundant in the liquid.

In this paper are presented observations on the high resolution proton magnetic resonance spectra of propene, butene-1 and hexene-1, representing the first part of a general investigation into the spectra of olefins. Two facets of such an investigation which currently appear to us to be of interest include: (1) a determination of the effects of *gem*, *cis* and *trans* substitution on the chemical shift of ole-