

first washed with 1,2-dichloroethane-ethyl acetate (9:1, 250 ml.), the washings were discarded, and the product was eluted with 1,2-dichloroethane-ethyl acetate (1:1, 200 ml.); yield 52 mg. (37%) of oil, $[\alpha]^{25D} + 84.3 \pm 0.2^\circ$ (*c* 2, chloroform), ultraviolet λ_{max} 256 $m\mu$ (ϵ 497).

Anal. Calcd. for $C_{14}H_{22}INO_7$: I, 28.63; CH_3CO , 29.13. Found: I, 27.42. Found (in another fraction): I, 31.00; CH_3CO , 26.9.

2-Amino-2,6-dideoxy-D-galactose Hydrochloride (VI).—The iodo derivative X (50 mg.) was dissolved in methanol (10 ml.) containing Raney nickel (10 mg.) and diethylamine (0.02 ml.), and was reduced under pressure for 1 hr. The reaction mixture was treated as described under the preparation of V from IV. The oil obtained upon evaporation of the ethyl acetate solution still contained 8.6% of iodine. The oil was hydrolyzed by treatment with 2 *N* hydrochloric acid (0.3 ml.) in a sealed ampule for 2.5 hr. at 110°. In the hydrolysate the major product was 2-amino-2,6-dideoxy-D-galactose hydrochloride as revealed by ninhydrin and by silver nitrate [R_{Gm} 1.81 (BEW), 1.78 (BAW)]. There appeared three additional spots, one of which had R_{Gm} 0.90 (BEW), 0.88 (BAW) and corresponded to 2-amino-2-deoxy-D-galactose hydrochloride [R_{Gm} 0.90 (BEW), 0.87 (BAW)] (probably resulting from the hydrolysis of the small amount of iodo compound left). The other two had R_{Gm} 2.67 and 3.00 (BEW), 2.44 and 2.82 (BAW). The material having R_{Gm} 1.78 (BAW) was eluted from a preparative chromatogram on Whatman No. 3 paper (BAW) by water (50 ml.) and methanol (20 ml.). Hydrochloric acid, 1 *N* (2 ml.), was added and the combined solutions were partially evaporated *in vacuo*. Addition of acetone gave rise to a crystalline product: yield 2.83 mg. (7%), dec. pt. 174–176°, $[\alpha]^{25D} + 99.4^\circ$ (5 min.) $\rightarrow + 81 \pm 1^\circ$ (final, *c* 0.24, water).

Anal. Calcd. for $C_6H_{14}ClNO_4$: N, 7.02. Found: N, 6.83.

2-Acetamido-2,6-dideoxy-D-galactose. A. From D-Fucoseamine of *C. violaceum*.—This compound was prepared according to the method of Kuhn, *et al.*⁴: m.p. 196–197° dec., $[\alpha]^{25D} + 129^\circ$ (4 min.) $\rightarrow + 92 \pm 0.1^\circ$ (final, *c* 2, water).

Anal. Calcd. for $C_8H_{15}NO_5$: C, 46.82; H, 7.37; N, 6.83. Found: C, 46.49; H, 7.40; N, 6.62.

B. From Synthetic 2-Amino-2,6-dideoxy-D-galactose Hydrochloride.—The mother solution of VI was evaporated and the residue was dissolved in a minimal amount of water. Methanol (0.5 ml.), triethylamine (0.02 ml.), and acetic anhydride (0.02 ml.) were added at room temperature and the mixture was left overnight. The whole reaction mixture was spotted on paper and chromatographed in BAW. A single spot could be detected which gave positive reaction with silver nitrate and which moved the same distance as an authentic sample of 2-acetamido-2,6-dideoxy-D-galactose A. Both compounds had an R_{Gm} of 2.68 (BAW). No material reacting with ninhydrin could be detected in the chromatograms.

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A Re-examination of the Polymerization of Sterculic Acid. II. Ozonolysis of the Sterculic Acid Polymer

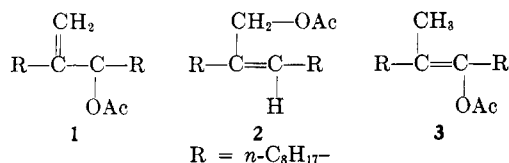
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The sterculic acid polymer was ozonized to yield formaldehyde, 2-decanone, 2-keto-1-decanol, azelaic acid, 9-ketodecanoic acid, nonanoic acid, and a mixture of 9-keto-10-hydroxy- and 9-hydroxy-10-ketostearic acids. These products are in accord with the two allyl ester structures (1a and b, and 2a and b) in the polymer as well as the enol ester structure (3a and b).

In part I it was shown that 1,2-di-*n*-octylecyclopropene reacts with acetic acid to form the allyl esters 1 and 2 plus smaller amounts of the enol ester 3.¹



Sterculic acid (4) polymerizes in a similar fashion with opening of the cyclopropene ring and formation of a polyester.^{2–4} Permanganate-periodate oxidations of the acetylated acids from hydrolysis of the polymer showed the two allyl ester structures (1a and b and 2a and b) to be present, but no chemical or spectroscopic evidence for 3a and b could be found.⁴ The olefinic carbon atoms in 4 and its reaction products are starred (Chart I).

The ratios of the various repeating units in this structure do not correspond to those in the polymer;

the structure is illustrative only of the types of units that are present in the polymer. When a mixture of 1 and 3 was oxidized with permanganate-periodate in the presence of *t*-butyl alcohol,⁵ nonylolin acetate (from 1) and unchanged 3 were obtained.¹ Ozonolysis of the same mixture yielded the cleavage products expected from both compounds.¹ Although the permanganate-periodate reagent is able to cleave mono-,⁶ di-,^{5,6} and trisubstituted⁴ olefins, it was unable to attack the tetrasubstituted derivative 3. Ozone, on the other hand, cleaves the tetrasubstituted olefins 1,2-dimethylcyclopentene⁷ and 2,3-diphenylindene⁸ as well as 3,¹ and the presence of 3a and 3b in the sterculic acid polymer could be revealed by ozonolysis and identification of 2-decanone (from 3a) and 9-ketodecanoic acid (from 3b).

Sterculic acid was polymerized at 110° for 3 hr. and the polymer was extracted with methanol to remove low molecular weight material.⁴ Its average degree of polymerization by titration was 12.8 sterculic acid residues per chain. It was saponified (sapon. equiv.: calcd., 294.5; found, 296 and 295) to a mixture of acids

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CHART I

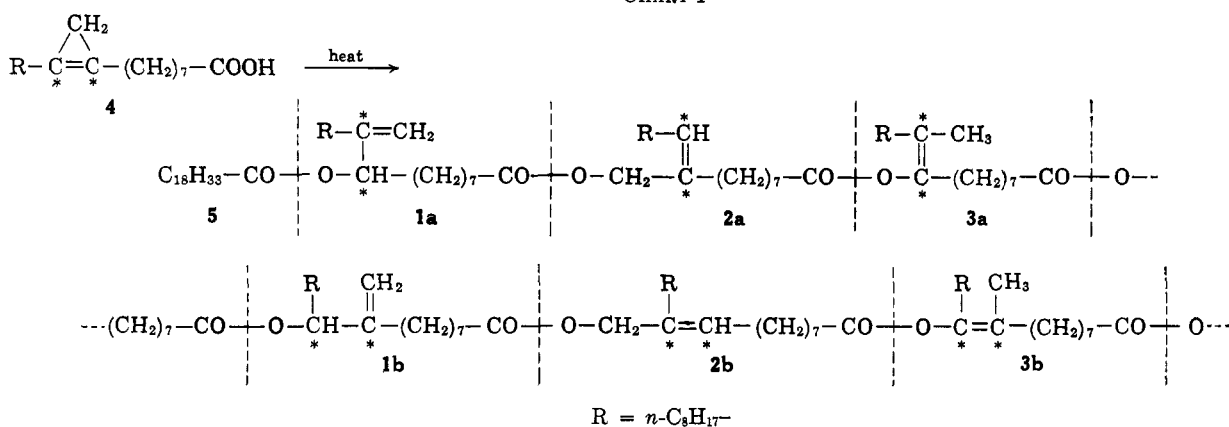
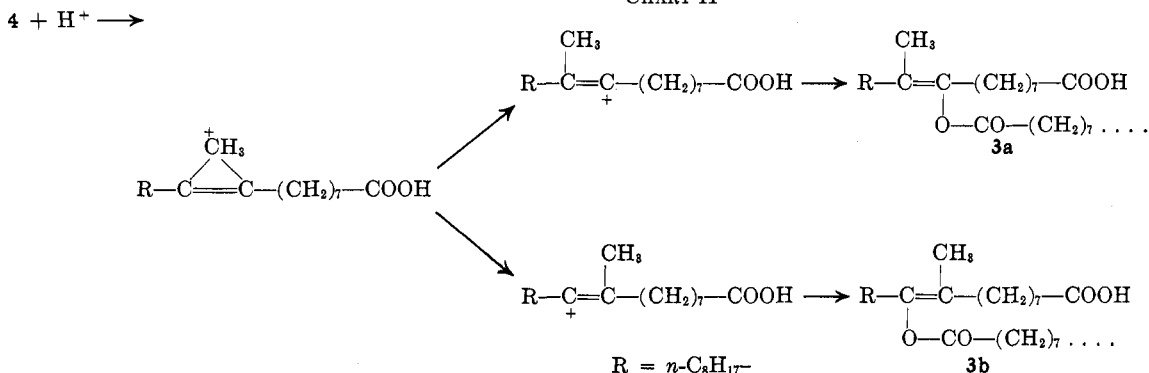


CHART II



(neut. equiv.: calcd., 313; found, 312.5 and 314) that gave a spot for a keto acid on thin layer chromatography (t.l.c.) indicative of the enol ester structures 3a and b.

The infrared spectrum of the polymer had the bands at 5.77 and 8.55 (ester), 5.83 and 10.35 (carboxyl) and 6.08 and 11.1 (unsymmetrical disubstituted olefin) previously described,⁴ plus a band at 8.8 μ attributed to an enol ester.¹ The ultraviolet spectrum of the mixture of acids from the saponification of the polymer showed a maximum at 232 m μ (ϵ 1350, ethanol). The same band (ϵ 21,000) was given by rearranged methyl sterculate collected from the exit of the gas chromatograph and by sterculene rearranged by alumina.⁹ On this basis, the polymer was calculated to have 6.5% rearranged unreacted sterculic acid residues as end groups (5) corresponding to an average degree of polymerization of 15.

The polymer was ozonized at low temperature and the ozonide decomposed under reducing conditions. Formaldehyde (from 1a and b), 2-decanone (from 3a), and 2-keto-1-decanol (from 2b) were identified in the neutral fraction. The acid fraction was esterified and distilled, and the fractions from the distillation were saponified. In this way pelargonic acid (from 2a and 3b), azelaic acid (from 2b and 3a), 9-ketodecanoic acid (from 3b), and a mixture of 9-hydroxy-10-keto- and 9-keto-10-hydroxystearic acids (from 1a and 1b) were obtained and identified.

The presence of a keto acid in the products from the saponification of the polymer together with the isolation of 2-decanone and 9-ketodecanoic acid from the ozonolysis is good evidence for the presence of the enol

ester group in the polymer formed from sterculic acid at 110°. The rearrangement of 1,2-di-*n*-octylcyclopropene⁹ gave only 2-3% of conjugated diene structures which could give rise to the two ketone derivatives above; therefore, the relatively large amounts (about 10% of the polymer ozonized) of the two ketones isolated show that they arise from the enol acetate structures (3a and b) rather than from the rearranged sterculic acid residues (5) at the end of the polymer chain. Protonation of the methylene carbon atom in 4 followed by ring opening and addition of the carboxyl ion is a mechanism for the formation of the enol ester structures (see Chart II).

Experimental

Materials and Methods.—G.l.c. and t.l.c. were done as described in part I.¹ The spray used for t.l.c. was 0.2 g. of 2,4-dinitrophenylhydrazine in 5 ml. of concentrated sulfuric acid diluted to 25 ml. with water. Aldehydes and ketones gave immediate yellow or orange spots; other compounds gave brown spots when the plates were charred in the oven at 120°. Sterculic acid was prepared from methyl sterculate as described previously.¹⁰

Polymerization.—Sterculic acid (108 g.) was placed in a 1-l., round-bottom flask equipped with a nitrogen bubbler and heated for 3 hr. on an oil bath at 110°. After this time the Halphen test¹¹ was negative and the cyclopropene bands at 5.38 and 9.92 μ ⁸ were absent in the infrared spectrum. The polymer was extracted three times with 900 ml. of methanol to leave 95.4 g. of material soluble in ether, chloroform, carbon tetrachloride, and *t*-butyl alcohol and insoluble in ethanol, acetic acid, and acetone. Titration of a sample (2.236 g.) in *t*-butyl alcohol with 0.1 *N* sodium hydroxide gave an equivalent weight of 2493 corresponding to an average degree of polymerization (D.P.) of 12.8. Evaporation of the methanol extracts left 11.2 g. of polymer of D.P. 2.7 that was discarded.

(9) T. Shimadate, H. W. Kircher, J. W. Berry, and A. J. Deutschman, Jr., *J. Org. Chem.*, **29**, 485 (1964).

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The infrared spectrum of the polymer showed the bands previously reported.⁴ A band at 8.8 μ suggested the presence of an enol ester.¹

Saponification.—Two samples (6.706 and 8.214 g.) of the polymer were saponified with 1 *N* potassium hydroxide in ethanol (50 ml.) and excess base was titrated with 0.5 *N* hydrochloric acid to give a saponification equivalent of 296 and 295 (theoretical 294.5). The acids from the saponifications were isolated, they had a neutral equivalent of 312.5 and 314 (theoretical 313).

The ultraviolet spectrum of the acids (19.7 mg. at 100 ml., 95% ethanol) showed a maximum at 232 $m\mu$ with an absorbance of 0.83. Rearranged methyl sterculate collected from the exit of the gas chromatograph had the identical absorption with ϵ 21,000. On this basis the sterculic acid polymer contained 6.5% of rearranged sterculic acid residues as end groups.

T.l.c. of the acids and of their methyl esters showed two major spots of low R_f corresponding to hydroxy acids, a spot that developed with 2,4-DNP spray indicative of a ketone and two minor spots of high R_f corresponding to the rearranged sterculic acid residues. The methyl esters could be distilled without decomposition, b.p. 115–150° at 0.05 mm. G.l.c. of the esters showed a peak having a retention time very similar to that of methyl 9-ketostearate.

Ozonolysis.—The polymer (78 g.) in methylene chloride (750 ml.) was cooled to –35° and ozone (0.06 mole/hr.) was passed through the solution for 5 hr. Excess ozone was flushed out with nitrogen and the solution was added to 65 g. of zinc dust in 600 ml. of 50% acetic acid with vigorous stirring, after which the solution was placed on a boiling water bath for 1 hr. The aqueous portion that had steam distilled with the methylene chloride was treated with methone (10 g.) in ethanol (60 ml.) to yield 6.12 g. of the methone derivative of formaldehyde, m.p. and m.m.p. 189–190°, lit.¹² 189°, after two crystallizations from ethanol.

The residue in the flask was taken up in ether, washed with water, evaporated, and hydrolyzed with 10% potassium hydroxide in methanol (600 ml.). After addition of water, the alkaline solution was extracted with ether to yield the neutral components (12.2 g.); it was then acidified and extracted with ether to give the acid components (61 g.).

Neutral Components.—The neutral fraction was acetylated at room temperature overnight with pyridine and acetic anhydride (15 ml. each) and distilled. The first fractions (6.10 g., b.p. 103–111° at 30 mm.) contained primarily 2-decanone (4.44 g. estimated by g.l.c.); fractions 5 and 6 (1.40 g., b.p. 51–100° at 0.06 mm.) contained 2-ketodecyl acetate; and fractions 7–9 (1.97 g., b.p. 103–180° at 0.06 mm.) contained a large mixture of com-

pounds by t.l.c. 2-Decanone was converted to its 2,4-dinitrophenylhydrazone, m.p. and m.m.p. 74–75°, lit.¹³ 73–74°. 2-Ketodecyl acetate was recrystallized from methanol, m.p. 55.5–56.5°, lit.⁴ 55.5–55.8°.

Acid Components.—The acids were converted to their methyl esters with 7% boron trifluoride in methanol (500 ml.) to yield 56 g. of product which was distilled. Fractions 1–3 (5.87 g., b.p. 109–110° at 30 mm.) and fraction 4 (2.20 g., b.p. 35–38° at 0.08 mm.) contained mostly methyl pelargonate (7.63 g. estimated by g.l.c.). They were hydrolyzed to pelargonic acid which was converted to its *p*-toluidide, m.p. and m.m.p. 82–83.5°, lit.¹⁴ 84°.

Fractions 5–7 (8.46 g., b.p. 76–78° at 0.08 mm.) contained dimethyl azelate (5 g.) and an unknown ester (3.3 g.) of slightly longer retention time on g.l.c. The mixture was hydrolyzed to the acids and crystallized from 30 ml. of benzene. The crystals (2.62 g., m.p. 99–104°) were recrystallized from hot water and identified as azelaic acid, m.p. 104–106°, m.m.p. 105–107°, lit.¹⁴ 106°. The benzene filtrate was evaporated to a syrup that crystallized on standing. It was recrystallized from chloroform and then from petroleum ether (b.p. 30–40°) to yield 9-ketodecanoic acid, m.p. 47–48°, lit.¹⁵ 47.5–48.5°. The acid gave a single spot on t.l.c. (2,4-DNP spray), a positive iodoform test,¹⁴ a neutral equivalent of 180 (calcd. 186), and a semicarbazone derivative of m.p. 126–127°, lit.¹⁶ 127°, which, after recrystallization from methanol and drying *in vacuo*, melted 130–130.5°. The ethyl ester of the semicarbazone was prepared with ethanol and sulfuric acid at room temperature, m.p. 98–99°, lit.^{15,16} 97–98°. The same derivative was obtained from the ethyl ester of the acid and semicarbazine hydrochloride, m.p. 97–98°.

Fractions 8 and 9 from the distillation (21.9 g., b.p. 135–200° at 0.08 mm.) were hydrolyzed and the derived acids were crystallized from methanol three times to yield a mixture of 9-hydroxy-10-keto- and 9-keto-10-hydroxystearic acid, m.p. 62.5–66°, lit.¹⁷ 64.5–65.5°, neut. equiv. 316 (calcd. 314). A 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol-benzene, m.p. 146.5–147°, lit.¹⁶ 146.5. The mixture of acids (1.24 g.) in acetic acid (10 ml.) was treated with chromic anhydride (0.25 g.) in acetic acid–water (2 ml.) on an ice bath. Water was added and the ether extract was crystallized from acetone and ethanol to yield pale yellow plates of 9,10-diketostearic acid, m.p. 84–84.5°, lit.¹⁷ 85.5°.

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Rearrangement of the Vinylog of Benzpinacol¹⁻³

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The *trans* vinylog of benzpinacol in boiling acetic acid undergoes 1,2-phenyl group migration to give the β,γ -unsaturated ketone. The *cis* isomer is first cyclodehydrated to the 2,5-dihydrofuran but is rearranged to the same ketone under more drastic acid catalysis. Rigorous proof of structure of the ketone includes degradations, reactions connecting it with a known compound, and n.m.r. spectrum of its carbinol. Lithium aluminum hydride reduction of tetraphenyl acetylene dicarbinol gives the *trans* ethylene dicarbinol and tetraphenylbutadiene, the latter seemingly by two successive conjugate ("1,4") reductions.

This investigation was suggested by the 1,2-phenyl group migration in the facile, pinacol-like rearrange-

ment of the cyclopropylog of benzpinacol, 1,2-di(di-phenylhydroxymethyl)cyclopropane.³ In an inconclusive study of the *cis* and *trans* vinylogs of pinacol (I) it had been suggested⁵ that 1,4-methyl group migration might occur and give a true vinylog of pinacolone, the

(1) (a) Supported in part by a contract with the office of Ordnance Research, U. S. Army, 1957–1958. (b) Received some support from a National Science Foundation grant, summer, 1963. (c) An important part of this work was completed by D. W. Boykin, Jr., under a University Philip Francis du Pont Fellowship, 1963–1964.

(2) (a) The larger part of this work was done in 1957 and is described in a Ph.D. Dissertation (R. G. Bass), University of Virginia, May 1961. (b) Reported in part by R. G. Bass and R. E. Lutz, Southeast Regional Meeting of the American Chemical Society, Richmond, Va., Nov., 1959; "The Bulletin" (Va. sect.), Vol. 36, 1959, abstracts, p. 197. (c) Specific mention of this work is made in ref. 4a and b.

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(4) Cf. (a) R. E. Lutz, J. I. Dale, and D. W. Boykin, Jr., *J. Am. Chem. Soc.*, **85**, 2340 (1963); (b) D. W. Boykin, Jr., and R. E. Lutz, *ibid.*, **86**, 5046 (1964).

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