

66. *The Structure of Sterculic Acid.*

By J. R. NUNN.

Sterculic acid, the main constituent of the kernel oil of *Sterculia foetida*, has been isolated in a pure state by means of its urea complex, and evidence is presented for its being ω -(2-*n*-octylcycloprop-1-enyl)octanoic acid. Sterculyl alcohol has been prepared.

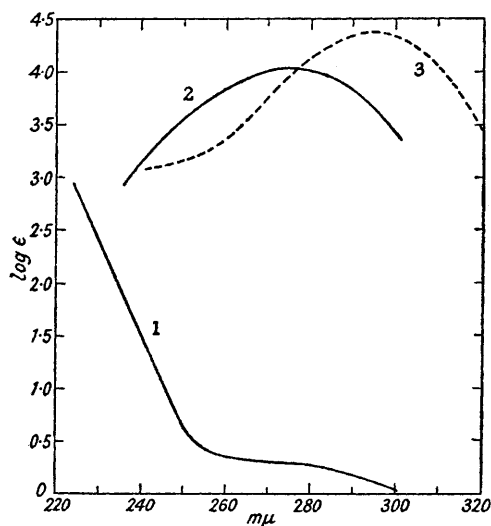
THE kernels of the seeds of *Sterculia foetida* give, on extraction with 2-methylpentane, a pale yellow oil which undergoes rapid thermal polymerization at 250° and even to some extent below this temperature. Previous attempts to isolate the acid responsible for this property failed owing to the ease with which the acid and its esters polymerize.

Steger and van Loon (*Fette u. Seifen*, 1943, **50**, 305), working on the mixed fatty acids, concluded that the acid responsible for this property was a saturated hydroxy-acid, probably C₁₈H₃₄O₃. Hilditch, Meara, and Zaky (*J. Soc. Chem. Ind.*, 1941, **60**, 198T), distilled the hydrogenated mixed methyl esters and deduced that the original mixed acids contained 72% of a doubly unsaturated acid, C₁₉H₃₄O₂. By degradative experiments on the mixed methyl esters, they concluded that it was 12-methyloctadeca-9:11-dienoic acid. However, the ultra-violet absorption spectrum of the oil gave no band characteristic of two conjugated double bonds (Braude, *Ann. Reports*, 1945, **42**, 105), so that this structure is very unlikely.

The acids were isolated by saponification of the oil in the cold and then separated by fractional crystallisation of their urea complexes from methanol (cf. Schlenk and Holman, *J. Amer. Chem. Soc.*, 1950, **72**, 500). The saturated acids appeared in the first fractions and the main acid component, for which the name sterculic acid is proposed, in the last fractions. Further purification by low-temperature crystallisation from acetone yielded pure sterculic acid of m. p. 18.2°. It had the formula $C_{19}H_{34}O_2$ and polymerized fairly rapidly at room temperature, and even slowly at 0°, the equivalent weight increasing with time. Partly polymerized material could be saponified to yield an acid having nearly the same equivalent weight as the original material, but this acid has not yet been

Solvent	Max., Å	ϵ	Concn., mole/l.
Ethanol	2750	10 500	0.0001
"	2760	15 900	0.0000114
Ethanolic NaOH	2955	22 800	0.0001

investigated. Sterculic acid does not react with pyridine-acetic anhydride and contains one active hydrogen atom per mole (lithium aluminium hydride method; Hochstein, *J. Amer. Chem. Soc.*, 1949, **71**, 305). It is optically inactive and its absorption spectrum



1, Sterculic acid. 2, 9:11-Diketnonadecanoic acid (0.0001 mole/l.) in ethanol. 3, 9:11-Diketnonadecanoic acid (0.0001 mole/l.) in ethanolic sodium hydroxide.

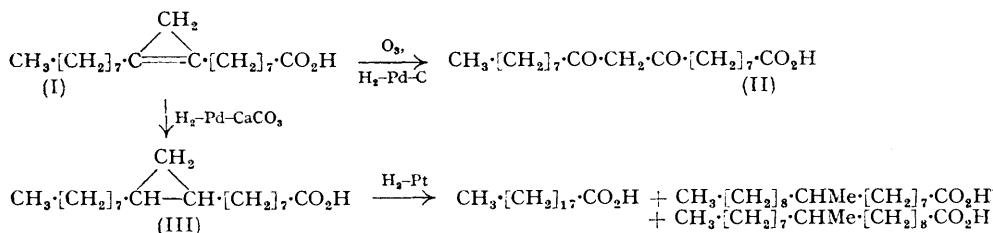
(see figure) indicates the absence of conjugated unsaturation. On hydrogenation in ethanol in the presence of palladised calcium carbonate it absorbed hydrogen equivalent to one double bond. The dihydrosterculic acid so obtained gave no colour with tetranitromethane but, in presence of Adams's platinum catalyst, absorbed a further mole of hydrogen. The fully hydrogenated product melted over a wide range (63—66.5° after one crystallisation), but elementary analysis was in very good agreement with the formula $C_{19}H_{38}O_2$. The fully hydrogenated product is probably a mixture of *n*-nonadecanoic acid (m. p. 68.6°) and two methyl-substituted octadecanoic acids.

Oxidation of sterculic acid with potassium permanganate in acetone gave, as main products, pelargonic and azelaic acids. When sterculic acid was ozonised in acetic acid and the ozonide decomposed with acetic acid-hydrogen peroxide, pelargonic and azelaic acids only were obtained, in good yield. Ozonolysis in ethyl acetate at low temperature and reduction of the ozonide with hydrogen in the presence of palladised charcoal gave a little formaldehyde (<1/5 mol.) but most of the material had been converted into an acid, $C_{19}H_{34}O_4$, m. p. 57.5—58.3°. An accurate equivalent weight determination was not possible because of fading of the end-point during titration. On oxidation with hydrogen peroxide in acetic acid, the compound $C_{19}H_{34}O_4$ gave pelargonic and azelaic acids as the only fission products, in good yields; it gave a deep red colour with ferric

chloride and its absorption spectrum was characteristic of 1 : 3-diones (cf. Bastron, Davis, and Butz, *J. Org. Chem.*, 1943, **8**, 515); the position and intensity of the maximum were dependent on the concentration and on pH (see table and figure); this behaviour is in agreement with the tautomeric nature of 1 : 3-diones and hence the substance $C_{19}H_{34}O_4$ must be 9 : 11-diketnonadecanoic acid (II).

This conclusion, together with the other evidence presented above, is consistent with the structure, ω -(2-*n*-octylcycloprop-1-enyl)octanoic acid (I), for sterculic acid.

The cyclopropene structure for sterculic acid explains the stepwise hydrogenation to give, first, (III), having a cyclopropane ring capable of being ruptured by hydrogen and yet resistant to oxidation. Hydrogenation of (III) can proceed so as to give three products which would account for the melting point range observed in the fully hydrogenated product. Hoffmann and Lucas (*J. Amer. Chem. Soc.*, 1950, **72**, 4328) have isolated a C_{19} saturated acid from *Lactobacillus arabinosus*, which is resistant to oxidation and yet is hydrogenated to give three products formulated as *n*-nonadecanoic acid and a mixture



of two methyloctadecanoic acids. They have proposed a cyclopropane structure for the acid, strong supporting evidence being given by an absorption maximum at 9.8μ (cf. Derfer, Pickett, and Boord, *J. Amer. Chem. Soc.*, 1949, **71**, 2482).*

The isolation of a trace of formaldehyde on ozonolysis is the only evidence which does not fit the structure (I) for sterculic acid easily. It seems remotely possible that, if a trace of water were present, formaldehyde may have arisen by hydrolytic fission of 9 : 11-diketnonadecanoic acid (II), but pelargonaldehyde and azelaic semialdehyde were not detected. On the other hand, it may have arisen as a result of the peculiar nature of the ozonide.

The double bond in the cyclopropene ring would be highly reactive and it seems likely that sterculic acid polymerizes by reaction of the carboxyl group with the double bond. The polymerization of the oil obviously involves a different mechanism.

Sterculyl alcohol, made by reduction of the acid with lithium aluminium hydride, underwent the same stepwise hydrogenation as sterculic acid itself, showing that the cyclopropene ring was intact.

EXPERIMENTAL

M. p.s are corrected.

Extraction and Saponification of the Oil.—On the advice of the Department of Botany and Plant Pathology, Pretoria, seeds for this investigation were obtained from the Bosbouwpræfstation, Department van Landbouw, Buitenzorg, Indonesië, Java, and from the Bureau of Forestry, Manila, Philippine Islands. The hard shells of the seeds were removed and the kernels (ca. 48% of the seed) pulverized to a fine meal. Extraction (Soxhlet) with 2-methylpentane yielded a pale yellow oil (51%). However, since a yield of 45% of oil was obtained by stirring the crushed kernels with four changes of warm 2-methylpentane, this procedure was adopted for large-scale preparations.

Saponification was effected by dissolving the oil in a cold concentrated solution of alcoholic potassium hydroxide and leaving the whole overnight. The acids (90% of the oil) were liberated with sulphuric acid and isolated in ether. After the ether had been evaporated from the dried (Na_2SO_4) extract, the acids were dried in a vacuum at room temperature.

* *Added in Proof.*—Dihydrosterculic acid shows an absorption maximum at 9.85μ .

Fractionation of the Acids.—The initial urea complex was formed by adding the mixed acids (121 g.) to a solution of urea (121 g.) in methanol (363 c.c.) at the b. p. Complex no. 1 separated on cooling. All subsequent complexes were formed by adding the requisite amount of finely divided urea to the filtrate from the preceding complex. The mixture was warmed to dissolve the urea and then cooled again to allow the new crop of complex to crystallise. The complexes were decomposed by shaking them with water-ether, a little sulphuric acid being added to prevent emulsion formation. The progress of fractionation is shown in the table.

Urea added,		Complex,		Urea added,		Complex,	
g.		g.	no.	g.		g.	no.
121		101	1	60		82	4
60		77	2	80		53	5
30		21	3				

The filtrate from complex no. 5, when concentrated to one-third of its volume, deposited complex no. 6 (47 g.). The filtrate therefrom, concentrated to half its volume, deposited complex no. 7 (24 g.).

Recovery from complex No. 1 gave mainly a mixture (29 g.) of saturated acids. Complex No. 2 gave a mixture (20 g.) of saturated and unsaturated acids. Complex No. 3 gave a mixture of unsaturated acids (5.5 g.). The acids (total, 50 g.) obtained on decomposition of complexes 4—7 and the final filtrate were crystallised separately from acetone at -50° , and the pure materials dried at 1 mm., with a nitrogen bubbler, at room temperature. The acids obtained from these fractions were all *sterculic acid*, m. p. 18.2° (Found : C, 77.5, 77.6; H, 11.9, 11.9%; active H, 1.03 atoms. $C_{19}H_{34}O_2$ requires C, 77.5; H, 11.6%; active H, 1.0 atom). The acid gave a yellow colour with tetranitromethane in chloroform.

Sterculic acid polymerized too rapidly, even at room temperature, for its equivalent weight to be determined by titration: 2 hours after its preparation a sample gave the value 308 ($C_{19}H_{34}O_2$ requires equiv., 294.5). The rate of polymerization at 96° in a nitrogen atmosphere was determined by titrating samples at intervals :

Time (min.)	0	10	20	40	60	80	170	230
Equiv.	(294)	373	414	526	700	814	1220	1460

The solubility in ethanol decreased with increasing molecular weight, but the material was soluble in benzene.

Partly polymerized material could be saponified to yield an acid of lower equivalent weight. Thus material of equivalent weight 424 by direct titration gave an equivalent weight of 300 by saponification. The resulting acid could not be induced to crystallise.

Hydrogenation of Sterculic Acid.—Sterculic acid (9.41 mg.) in ethanol in the presence of palladised calcium carbonate absorbed 0.784 c.c. of hydrogen (N.T.P.) ($C_{19}H_{34}O_2$ requires 0.715 c.c. for one double bond). After hydrogenation of 1 g. of acid, the product was isolated by evaporation of the ethanol in a vacuum and then recrystallised from acetone at -10° ; it had m. p., 38.8 — 39.8° (Found : C, 77.1; H, 12.2%; equiv., 298. $C_{19}H_{36}O_2$ requires C, 77.0; H, 12.2%; equiv., 296.5). It gave no colour with tetranitromethane in chloroform and was not oxidised by potassium permanganate in boiling acetone. In glacial acetic acid and in the presence of Adams's platinum catalyst, *dihydrosterculic acid* (24.11 mg.) absorbed 1.65 c.c. (0.95 mol.) of hydrogen (N.T.P.).

Sterculic acid [(a) 23.13 mg.; (b) 22.19 mg.] in glacial acetic acid in the presence of Adams's platinum catalyst absorbed (a) 3.38 c.c. (1.92 mol.), (b) 3.22 c.c. (1.91 mol.) of hydrogen (N.T.P.). Whereas the hydrogenation with palladised calcium carbonate was complete in a few minutes, hydrogenation with Adams's platinum catalyst required several hours. The product from a large-scale hydrogenation was isolated in ether after dilution of the acetic acid solution with water. Evaporation of the ether left a solid residue, which was crystallised several times from ethanol at 0° as colourless plates, m. p. 65.2 — 66.8° (Found : C, 76.6; H, 12.8%; equiv., 298, 296. Calc. for $C_{19}H_{38}O_2$: C, 76.45; H, 12.8%; equiv., 298.5). The m. p. was 63 — 66.5° after one recrystallisation.

Oxidation of Sterculic Acid with Potassium Permanganate.—Sterculic acid (5.0 g.) in pure dry boiling acetone (70 c.c.) was treated with finely powdered potassium permanganate (14 g.) in small quantities during 1.5 hours. The acetone was then distilled off on a water-bath. The distillate was clear when diluted with water and was discarded. The residue was diluted with

water, and sulphur dioxide was passed in to dissolve the manganese dioxide, after which the mixture was steam-distilled, 750 c.c. of distillate being collected. The distillate, neutralised with sodium carbonate, was extracted with ether. Evaporation of the dried (Na_2SO_4) ethereal extract left an oil (0.3 g.), which gave no ketone reactions. The alkaline solution, remaining after the ether-extraction, was concentrated to about 100 c.c., acidified with sulphuric acid, and extracted with ether. Evaporation of the dried (Na_2SO_4) ethereal extract left an oil (0.94 g.), which was distilled to yield a colourless acid (0.56 g.) as the main fraction, b. p. 230—235°/655 mm. The remainder of the material, a high-boiling tar, decomposed on further heating. The *p*-bromophenacyl ester of the above acid crystallised in colourless plates (from ethanol), m. p. 62—63.3° alone or mixed with *p*-bromophenacyl pelargonate (Found : C, 57.4; H, 6.6. Calc. for $\text{C}_{17}\text{H}_{23}\text{O}_3\text{Br}$: C, 57.5; H, 6.5%).

The residue from the steam-distillation was extracted with ether and this solution in turn was extracted with sodium carbonate solution. Evaporation of the dried (Na_2SO_4) neutral ethereal extract left an oil (20 mg.) which was discarded. The sodium carbonate extract was acidified and the precipitate isolated in ether. Evaporation of the ether from the dried (Na_2SO_4) extract gave a semi-solid acid (2.83 g.). The methyl ester, made by treatment with diazomethane in ether, was distilled, yielding, as main fraction, a pale yellow oil (0.8 g.), b. p. 85—89°/0.1 mm. The remainder of the material distilled at 177—200°/0.1 mm., with much decomposition, giving a viscous red oil (1.2 g.). The first fraction was hydrolysed and the acid (0.62 g.) crystallised from water in large colourless leaflets, m. p. 106—108° alone or mixed with azelaic acid (Found : C, 57.5; H, 8.6%; equiv., 93.8, 94.4. Calc. for $\text{C}_9\text{H}_{16}\text{O}_4$: C, 57.4; H, 8.6%; equiv., 94.1). Hydrolysis of the second fraction yielded a liquid acid which proved to be mainly polymerized sterculic acid.

In order to ensure that no other dibasic acid was present, all the aqueous solutions above were extracted continuously with ether for several hours. Traces of azelaic acid only were recovered.

Ozonolysis of Sterculic Acid.—(i) *In acetic acid.* Into a solution of sterculic acid (3.3 g.) in acetic acid (70 c.c.) was passed ozonised oxygen at 300 c.c./min. (ca. 0.0093 g. of ozone/min.) for 30 minutes. The solution was cooled in ice-water when the temperature tended to rise. At the end of the reaction, hydrogen peroxide (2 c.c.; 140-vol.) was added and the mixture heated on a water-bath. After 1 hour more hydrogen peroxide (4 c.c.) was added and again after 2 hours (2 c.c.). Heating was stopped after 4 hours and the solution left overnight; it was then refluxed for 1 hour and steam-distilled, 600 c.c. of distillate being collected.

The distillate, made alkaline with sodium hydroxide, was extracted with ether. Evaporation of the dried (Na_2SO_4) ethereal solution yielded an oil (10 mg.) which was discarded. The aqueous layer was acidified and extracted with ether. Evaporation of the solvent afforded an oil which, on distillation, gave some acetic acid and pelargonic acid (0.5 g.), b. p. 238—140°/655 mm., only (Found : C, 68.1; H, 11.4%; equiv., 156. Calc. for $\text{C}_9\text{H}_{18}\text{O}_2$: C, 68.3; H, 11.5%; equiv., 158.2). The *p*-bromophenacyl ester crystallised in plates (from ethanol), m. p. 63—63.8° alone or mixed with *p*-bromophenacyl pelargonate (Found : C, 57.6; H, 6.6; Br, 22.0. Calc. for $\text{C}_{17}\text{H}_{23}\text{O}_3\text{Br}$: C, 57.5; H, 6.5; Br, 22.5%). The amide crystallised in leaflets (from aqueous methanol), m. p. 98.5—99.5° alone or mixed with pelargonamide.

The residue from the steam-distillation was extracted with ether and this solution in turn was extracted with sodium hydrogen carbonate solution. Evaporation of the dried (K_2CO_3) ethereal solution left an oil (0.15 g.) which gave no ketone reactions and was discarded. The sodium hydrogen carbonate solution was boiled until free from ether and acidified. The solid acid (1 g.) was filtered off, dried, and esterified with diazomethane in ether. Evaporation of the ether and distillation of the ester gave a colourless oil, b. p. 152—153°/20 mm., together with a small quantity of tar. The ester was hydrolysed and the acid crystallised from water in large colourless plates, m. p. 106—108° alone or mixed with azelaic acid. No other dibasic acid could be detected in any of the aqueous solutions.

(ii) *In ethyl acetate.* Ozonised oxygen was passed into sterculic acid (1.41 g.) in anhydrous ethyl acetate (35 c.c.) at -25° (rate as above) for 30 minutes, care being taken to avoid an excess of ozone by testing the effluent gas at regular intervals. At the end of the reaction 30% palladised charcoal was added to the solution which was cooled in ice-water and hydrogenated. Hydrogenation was complete in 5 hours, 89.5 c.c. of hydrogen (N.T.P.) (87% of theory) being absorbed. The catalyst was filtered off and the solvent distilled. The distillate was refluxed with 2 : 4-dinitrophenylhydrazine (0.5 g.) in ethanol (50 c.c.) and hydrochloric acid (0.5 c.c.) for 2.5 hours, and then evaporated to a small volume (5 c.c.). To this were added ethanol (50 c.c.) and hydrochloric acid (0.5 c.c.). After storage overnight in the ice-box, the

orange crystals (0.18 g.) were filtered off, dried, and then chromatographed in benzene on alumina. Concentration of the eluate gave flattened orange needles which, recrystallised from ethanol, had m. p. 164—167° alone or mixed with formaldehyde 2 : 4-dinitrophenylhydrazone (Found : C, 40.4; H, 3.0. Calc. for $C_7H_6O_4N_4$: C, 40.0; H, 2.9%). The solid residue remaining after removal of the ethyl acetate was dissolved in ether (150 c.c.) and extracted with sodium hydrogen carbonate solution. An insoluble sodium salt, which was precipitated, was filtered off. The neutral ethereal solution was evaporated, leaving an oil (0.22 g.), which had no ketonic reactivity and distilled with decomposition at 150—300°/650 mm. It was discarded. The sodium hydrogen carbonate extract and the insoluble sodium salt were combined and acidified, the liberated acid being isolated in ether. Evaporation of the ether left 9 : 11-diketnonadecanoic acid as a solid (1.1 g.) which crystallised from 2-methylpentane in long colourless needles, m. p. 57.5—58.3° (Found : C, 69.8; H, 10.5. $C_{19}H_{34}O_4$ requires C, 69.9; H, 10.5%). This substance gave a deep red colour with ferric chloride in ethanol. It could not be titrated with sodium hydroxide to a definite end-point to phenolphthalein, and values varying from 250 and 285 were obtained for the equivalent weight. It did not form a semicarbazone.

Oxidation of 9 : 11-Diketnonadecanoic Acid (II)—The substance was oxidised rapidly by potassium permanganate in acetone solution, but the product was an ether-insoluble polymer.

A mixture of 9 : 11-diketnonadecanoic acid (0.5 g.), acetic acid (10 c.c.), and hydrogen peroxide (1 c.c.; 140-vol.) was heated on a water-bath for 1 hour. Hydrogen peroxide (1.5 c.c.) was then added and the solution refluxed for a further hour. Steam-distillation afforded a volatile acid and no volatile neutral material. Distillation of the acid gave an oil (0.2 g.), b. p. 240°/650 mm. The *p*-bromophenacyl ester had m. p. 61.5—62.5° alone or mixed with *p*-bromophenacyl pelargonate. The residue from the steam-distillation contained no neutral material; it was extracted with ether and this solution treated with an ethereal solution of diazomethane. The residue (0.37 g.) obtained after evaporation of the ether was distilled (b. p. 150—153°/20 mm.). Hydrolysis of the distillate and crystallisation of the acid from water gave azelaic acid, m. p. and mixed m. p. 105—108°.

Sterculyl Alcohol.—Sterculic acid (7.3 g.) was reduced with lithium aluminium hydride (2.7 g.) in ether (150 c.c.) in the usual manner. The *alcohol*, recrystallised from acetone at —35° and dried at room temperature in a high vacuum, had m. p. 10.6°, n_D^{20} 1.4617 [Found : C, 80.9; H, 12.9%; active H (by $LiAlH_4$ method, Hochstein, *loc. cit.*) 1.02 atoms. $C_{19}H_{36}O$ requires C, 81.3; H, 12.9%; active H, 1.0 atom]. With palladised calcium carbonate, the alcohol (30.66 mg.) absorbed 2.50 c.c. of hydrogen (N.T.P.) ($C_{19}H_{36}O$ requires 2.45 c.c.), and with Adams's platinum catalyst it (15.66 mg.) absorbed 2.77 c.c. (N.T.P.) ($C_{19}H_{36}O$ requires 2.50 c.c.). An attempt to distil the alcohol resulted in extensive decomposition with the formation of a viscous, liquid distillate, b. p. 143—155°/0.4 mm., which was not investigated.

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