356. *The Structure of Sterculic Acid.*

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Infrared data support the conclusion that the sterculic acid molecule contains a *cyclo*propene ring,[1] which appears to be characterised by a strong absorption near 9·92 μ and a weak absorption near 5·35 μ. The infrared absorption band at 6·09 μ on which Verma, Nath, and Aggarwal base their formula for the acid is absent from freshly prepared specimens. The instability of the free acid appears to be due to the opening of this ring across the single bonds by interaction with the carboxyl group. Additional chemical evidence is presented for the production of 9 : 11-dioxononadeca-noic acid on ozonolysis of sterculic acid. All the evidence is consistent with the structure ω-(2-*n*-octyl*cyclo*prop-1-enyl)octanoic acid for sterculic acid.

THE structure of sterculic acid was suggested by Nunn[1] as ω-(2-*n*-octyl*cyclo*prop-1-enyl)octanoic acid (I). Infrared measurements were used to confirm the presence of a *cyclo*propane ring in dihydrosterculic acid, but the structure was deduced entirely from chemical evidence. Disregarding the latter, Verma, Nath, and Aggarwal[2] have considered structure (I) to lack supporting evidence in the fixing of the position of the double bond, which they have tried to do more exactly by means of the infrared spectrum of sterculic acid itself. They found bands at 9·96 μ and 6·09 μ, in the regions characteristic of *cyclo*-propane derivatives and of C=C double bonds, respectively, and proposed the alternative structure (II), in which the three-membered ring and double bond form a " conjugated "

$$CH_3 \cdot [CH_2]_7 \cdot C = C \cdot [CH_2]_7 \cdot CO_2H \qquad (I)$$
$$\underset{CH_2}{\diagdown}$$

$$CH_3 \cdot [CH_2]_5 \cdot CH - CH \cdot CH \colon CH \cdot [CH_2]_7 \cdot CO_2H \qquad (II)$$
$$\underset{CH_2}{\diagdown}$$

system. Dijkstra and Duin[3] argued in support of structure (I) that the difference in absorption noted between dihydrosterculic acid (9·79 μ) and sterculic acid (9·91 μ) is greater than that which would be expected from such conjugation; further, it is in the opposite direction. Such a system would not be as reactive as sterculic acid.

A sample of freshly prepared sterculic acid, obtained by the urea-complex method,[1] had m. p. 18·2—18·3°, $n_D^{24\cdot8}$ 1·4643 (Verma *et al.*[2] give m. p. 19°, n_D^{25} 1·4758). The infrared spectrum of this acid, taken within two hours of its isolation, showed a very strong band at 9·92 μ, but no band at 6·09 μ. When the acid was kept at 20—25° a band appeared at 6·07 μ; after 20 days this band was very distinct whereas the band in the 9·9 μ region had then almost completely disappeared. A specimen which had been kept for 32 days was a colourless viscous liquid, $n_D^{23\cdot8}$ 1·4801, equiv. 4780; its spectrum was identical with that of the sample kept for 20 days. The shift of wavelength from 9·92 μ to 9·80 μ found on conversion of sterculic acid into dihydrosterculic acid was accompanied by about 50% diminution in intensity. Both bands lie within the region 9·8—10·0 μ proposed by Derfer, Pickett, and Boord[4] as characteristic for *cyclo*propane groups, but Slabey,[5] from a study of 34 compounds containing this ring, found the maximum absorption at 9·79 ± 0·04 μ in all but the two cases of a monosubstituted ring, and generally at slightly lower wavelengths when two ring-hydrogens were replaced. The spectrum of dihydrosterculic acid was the same as that recorded by Hofmann *et al.*,[6] who showed conclusively that the band at 9·80 μ was due to the presence of the *cyclo*propane ring by comparison with the spectra of two synthetic long-chain acids containing such a ring.

Although the *cyclo*propane ring appears an improbable structure from the viewpoint

[1] Nunn, *J.*, 1952, 313.
[2] Verma, Nath, and Aggarwal, *Nature*, 1955, **175**, 84.
[3] Dijkstra and Duin, *ibid.*, 1955, **176**, 71.
[4] Derfer, Pickett, and Boord, *J. Amer. Chem. Soc.*, 1949, **71**, 2482.
[5] Slabey, *ibid.*, 1954, **76**, 3604.
[6] Hofmann, Jucker, Miller, Young, and Tausig, *ibid.*, p. 1799.

of bent bonds, Walsh [7] has predicted theoretically that such a structure is possible and stable. In this ring, because of its smallness, the two double-bonded carbon atoms are virtually linked by a third bond through the intermediate carbon atom, and one would expect from general considerations that the strain on the C=C link and its bonding force would be intermediate between those of the normal ethylenic and of the acetylenic linkages. Dunitz, Feldman, and Schomaker [8] have measured this interatomic distance in *cyclo*propene by an electron-diffraction method as $1.28_6 \pm 0.04$ Å, which lies between the normal bond lengths of 1·35 Å for C=C in ethylene and 1·20 Å for C≡C in acetylene.[9] It seems reasonable, therefore, to suppose that the stretching-vibration frequency of the C=C bond in a *cyclo*propene group will be intermediate between that of an ethylenic and of an acetylenic bond, and that the presence of such a ring will result in a band somewhere between 6·1 μ and 4·6 μ where these respective absorptions usually occur.[10, 11] The actual position of the *cyclo*propene vibration will, of course, depend to some extent on the nature of the substituent groups. Such a band was found in the spectrum of fresh sterculic acid at 5·35 μ, in a spectral region which is usually very empty. The band was quite distinct, though not very intense (about 7% absorption for an approximately 1·9% w/v solution in carbon disulphide in a 0·5 mm. cell). However, a strong band would not be expected here because of the symmetrical placing of the ring in the molecule.[12] This band cannot result from conjugation of a *cyclo*propane ring with a C=C double bond, since aliphatic conjugation usually shifts the absorption to slightly longer wavelengths and enhances the intensity.[13]

Although the *cyclo*propene group is a possible stable structure, it would be expected to be fairly reactive. That the rapid polymerisation of sterculic acid is associated with the presence of this ring and involves its destruction is readily seen from the infrared spectrum of the polymerised material, in which the band at 5·35 μ has completely disappeared and only a very weak absorption still remains near 9·9 μ. The carboxyl group also takes part in this reaction. This is borne out by the high equivalent weight of the polymerised material, and by the infrared spectrum, in which the very broad absorption between 3 and 4 μ, the broad, strong band at 10·7 μ, and the band at 7·78 μ, all of which are characteristic of fatty acid spectra and are associated with the presence of the carboxylic acid group,[14] have disappeared. From the spectrum it seems that an ester has been formed, for the C=C stretching absorption has shifted from 5·86 μ in the acid to 5·76 μ in the polymerised material, and a strong, new band has appeared at 8·58 μ. Both these bands, and the shift in C=O absorption, are characteristic of esters and lactones.[15] Nunn [1] has suggested that sterculic acid polymerises by reaction of the carboxyl group with the double bond, but the appearance of a double-bond absorption band at 6·07 μ in the spectrum of the polymerised material which is not present in the fresh sterculic acid spectrum, together with an increase in the methyl-group absorption [16] at 7·27 μ, indicates that the reaction occurs by splitting of the C–C linkages and opening of the ring. It seems most unlikely that the three-membered ring in the conjugated structure (II) would be opened by reaction with the carboxyl group at room temperature, when even fully conjugated acids such as octadeca-9 : 11-dienoic acid are fairly stable.

The key compound in Nunn's chemical evidence [1] for structure (I) was the dioxo-acid obtained by hydrogenation of the ozonide formed from sterculic acid, and deduced to be 9 : 11-dioxononadecanoic acid (III). This compound would not be produced on ozonolysis of structure (II). Its identification as (III) depended on its ultraviolet absorption spectrum,

[7] Walsh, *Trans. Faraday Soc.*, 1949, **45**, 179.

[8] Dunitz, Feldman, and Schomaker, *J. Chem. Phys.*, 1952, **20**, 1708.

[9] Herzberg, " Infrared and Raman Spectra," van Nostrand Co. Inc., New York, 1945, pp. 398, 439.

[10] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954, pp. 31, 49.

[11] Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397; Randall, Fowler, Fuson, and Dangl, " Infrared Determination of Organic Substances," van Nostrand Co. Inc., New York, 1949.
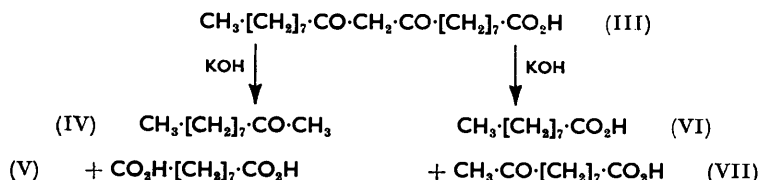
[12] Ref. 10, p. 34.

[13] Ref. 10, p. 35.

[14] Sinclair, McKay, and Jones, *J. Amer. Chem. Soc.*, 1952, **74**, 2570.

[15] Ref. 10, p. 153.

[16] Rasmussen, Tunnicliff, and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1068.

its reaction with ferric chloride, and on its oxidative degradation to the expected fragments. Additional chemical evidence of the correctness of this structure has now been obtained. The infrared spectrum of a new sample showed a very broad, strong band at 6·24 μ, which is characteristic of β-diketones in the enolised form.[16] The dioxo-acid and its ethyl ester gave an intense red colour with alcoholic ferric chloride, and the ester yielded a light-blue copper derivative, m. p. 90—92°, crystallising easily from methanol and very soluble in cold benzene. Alkaline hydrolysis of the dioxo-acid (III) should yield four products :

$$CH_3 \cdot [CH_2]_7 \cdot CO \cdot CH_2 \cdot CO \cdot [CH_2]_7 \cdot CO_2H \quad (III)$$

(IV) $CH_3 \cdot [CH_2]_7 \cdot CO \cdot CH_3$ $CH_3 \cdot [CH_2]_7 \cdot CO_2H$ (VI)

(V) $+ CO_2H \cdot [CH_2]_7 \cdot CO_2H$ $+ CH_3 \cdot CO \cdot [CH_2]_7 \cdot CO_2H$ (VII)

Of these, methyl *n*-octyl ketone (IV), azelaic acid (V), and 9-oxodecanoic acid (VII) have now been isolated and identified.

All the spectral and chemical evidence which exists with regard to sterculic acid supports the originally proposed structure (I).

EXPERIMENTAL

M. p.s are corrected.

Isolation of Sterculic Acid.—*Sterculia foetida* seeds were obtained from the Forest Research Institute, Bogor, Indonesia. The pulverised kernels (*ca.* 58% of total seed) yielded a yellow oil (48%) when stirred with five portions of warm *iso*hexane (*ca.* 40°). The oil was saponified, and the acids liberated with concentrated hydrochloric acid were converted into their urea complexes, from which the sterculic acid was eventually isolated.[1] The acid, crystallised from acetone, had m. p. 18·2—18·3°, $n_D^{24·8}$ 1·4643. It polymerised rapidly to a colourless, syrupy liquid : a sample left at room temperature (20—25°) for 32 days had $n_D^{23·8}$ 1·4801, equiv., 4780.

Preparation of 9 : 11-Dioxononadecanoic Acid.—Sterculic acid was ozonised in cold ethyl acetate, the ozonide then hydrogenated in the presence of 30% palladised charcoal, and from this mixture 9 : 11-dioxononadecanoic acid (III) was isolated *via* the sodium salt.[1] The acid crystallised from hexane in plates, m. p. 59·6—59·9° (Found : C, 69·9; H, 10·5. Calc. for $C_{19}H_{34}O_4$: C, 69·9; H, 10·5%). Nunn[1] reported long needles, m. p. 57·5—58·3°. It gave an intense red colour with alcoholic ferric chloride.

Ethyl ester. In one preparation of the dioxo-acid the solution in ethyl acetate had to be left for 2 days, and it was decided to complete the esterification. Ethanol and a drop of concentrated sulphuric acid were added and the mixture left for 4 days. The resulting neutral product melted at 18° and gave an intense red colour with alcoholic ferric chloride. Reaction with copper acetate in methanol produced a grey-green precipitate which, crystallised from methanol (green solution), gave a light-blue solid, m. p. 90—92° (Found : Cu, 8·3. $C_{42}H_{74}O_8Cu$ requires Cu, 8·2%). This *copper derivative* was very soluble in cold benzene, but not soluble in chloroform, with which it appeared to react when warmed; hydrochloric acid regenerated the ester, m. p. 19°.

Alkaline Hydrolysis of 9 : 11-Dioxononadecanoic Acid (III).—The sodium salt (1·4 g.) was heated under reflux with potassium hydroxide (1·0 g.) in 50% ethanol (10 ml.); during 30 min. water (11 ml.) was added, and the mixture was left simmering overnight. The sweet-smelling layer, isolated by extraction with pentane, was an oil of m. p. 2° (0·21 g.). Rupe and Willi[17] gave 2·5° as the m. p. of methyl *n*-octyl ketone (IV). Our ketone (0·21 g.) was heated with *p*-nitrophenylhydrazine (0·165 g.) in ethyl alcohol (2 ml.) near the b. p., and 1 drop of acetic acid added. The orange precipitate, recrystallised from hexane–ethyl acetate, gave bright yellow crystals, m. p. 94·5—96° (Found : C, 66·5; H, 8·6. $C_{16}H_{25}O_2N_3$ requires C, 66·0; H, 8·6%). A specimen of methyl *n*-octyl ketone prepared according to Rupe and Willi's method,[17] melted at 2·3° and gave a p-*nitrophenylhydrazone*, m. p. 96—97·5°. A mixture of the two samples melted at 94·5—96·5°.

The alkaline solution (above) which had been extracted with pentane was acidified and the

[17] Rupe and Willi, *Helv. Chim. Acta*, 1932, **15**, 842.

liberated acids were extracted with ether; the ethereal extract was shaken for 17 hr. with a saturated solution of sodium hydrogen sulphite and set aside for 2 days. From the precipitated crystals of the bisulphite addition compound, a keto-acid (0·4 g.), m. p. 20°, was obtained. The semicarbazone behaved similarly to that of 9-oxodecanoic acid as described by Barger, Robinson, and Smith : [18] it first melted over a range 110—130° (from ethyl acetate) but, when heated to 80° for 4 hr. in a vacuum, it lost 13·8% of its weight and then melted at 129—130°. Barger, Robinson, and Smith [18] recorded m. p. 127° (Found : C, 54·2; H, 8·5; N, 17·3%; equiv., 245·4. Calc. for $C_{11}H_{21}O_3N_3$: C, 54·3; H, 8·7; N, 17·3%; equiv., 243·3).

The ethereal layer of the filtrate from the bisulphite addition compound was separated, washed with water, dried, and evaporated : a soft mass of crystals remained. After being washed with pentane and then with warm water, the residue was crystallised from hot water, yielding plates, m. p. 105—106° alone or when mixed with an authentic specimen of azelaic acid (Found : C, 57·6; H, 8·6%; equiv., 94·7. Calc. for $C_9H_{16}O_4$: C, 57·4; H, 8·6%; equiv., 94·1).

Infrared Spectra.—These were recorded on a Perkin-Elmer Model 21 double-beam spectro-photometer with sodium chloride optics. The spectra of all the substances were taken in both carbon disulphide and tetrachloroethylene solutions (about 1·5—2% w/w in a 0·5 mm. cell) in order to cover the complete range from 2 to 15 μ.

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[18] Barger, Robinson, and Smith, *J.*, 1937, 718.