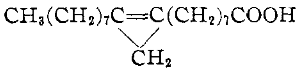
COMMUNICATIONS TO THE EDITOR

SYNTHESIS OF STERCULIC ACID

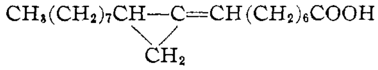
Sir:

Sterculic acid[1] (I) has been assigned the definitive formulation 2-*n*-octyl-1-cyclopropenecaprylic acid on the basis of ozonolysis to 9,11-diketononadecanoic acid,[1,2] hydrogenation to *cis*-9,10-methyleneoctadecanoic acid (dihydrosterculic acid),[1,3,4] and nuclear magnetic resonance spectra.[5] These studies conclusively eliminate alternative structures such as II and III.



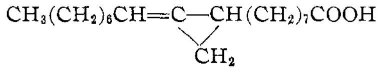
$$CH_3(CH_2)_7\underset{CH_2}{C{=}C}(CH_2)_7COOH$$

I



$$CH_3(CH_2)_7\underset{CH_2}{CH{-}C}{=}CH(CH_2)_6COOH$$

II



$$CH_3(CH_2)_6CH{=}\underset{CH_2}{C{-}CH}(CH_2)_7COOH$$

III

We now report the further confirmation of formulation I by synthesis of sterculic acid from the acetylenic precursor, stearolic acid, by the general method of Simmons and Smith.[6]

Stearolic acid and methylene iodide reacted in the presence of a zinc–copper couple[7] for nine hours[8] in refluxing ether; products were isolated from the ethereal solution by the procedure of Nunn.[1] Fractional crystallization of the urea adducts led to the isolation of I (4%), m.p. 18.9–19.6° [lit. m.p. 19.3–19.9°,[5] 18.2°,[1,2] 19°[4]]. The acid [*Anal.* Found: C, 77.58; H, 11.79] gave a red color with the Halphen reagent[9]; its infrared spectrum (CCl_4) was identical (superimposable) with that of an authentic sample of I, showing bands at 2882, 1698, 1253, 1086 and 1007 cm.$^{-1}$. Hydrogenation of the acid (palladium–charcoal catalyst) gave dihydrosterculic acid, m.p. 38.4–39.5° [lit. m.p. 38.6–39.6°,[10] 39.0–40.2°[3]]; the infrared spectrum was identical with that published for the authentic acid, showing characteristic absorption at 1020 cm.$^{-1}$ (cyclopropane).[3] The dihydro acid readily was converted to dihydrosterculamide, m.p. 86.3–87.5° [lit. m.p. 86.4–87.6°[10]].

In addition to sterculic acid, the fractionated urea adducts yielded unchanged stearolic acid and a third acidic fraction, m.p. 21.4–24.6°; this fraction was shown to consist of two acids isomeric with sterculic acid [*Anal.* Found: C, 77.51; H, 11.82; neut. eq., 293; R_f 0.68 and 0.72[11]; V_R' 1950 and 2070 ml.[11]]. The mixture showed infrared absorption bands (CCl_4) at 1020–1028 cm.$^{-1}$ (cyclopropane),[12] 1714 and 957 cm.$^{-1}$ (end group carboxyl)[12] and a broad band at 1730–1767 cm.$^{-1}$ (olefin).[13] Attempted chromatographic separation of the acids on cellulose powder on a larger scale led to incomplete resolution. Hydrogenation of the mixture (palladium–charcoal catalyst) gave, in quantitative yield, dihydrosterculic acid, m.p. 38.4–39.5 (identified by mixture melting point and infrared spectrum). These data are consistent with the formulation of the acidic fraction as a mixture of the acids II and III.

The unsaturated acid mixture was oxidized by the periodate–permanganate method[14] to the products expected from structures II and III. Suberic acid, m.p. 138–139.5° (from II), hendecanoic acid, m.p. 27.8–29.0° (from II) and caprylic acid, m.p. 14.3–15.5° (from III) were identified by comparison with authentic samples. Nonane-1,9-dicarboxylic acid, m.p. 107–109° [lit. m.p. 109°][15] (from III) was converted to the diamide, m.p. 172–173° [lit. m.p. 173°].[16] Two remaining potential oxidation products, α-methylcapric acid (from II) and nonane-1,8-dicarboxylic acid (from III) have not been detected in the chromatographed products.

No formaldehyde or formic acid was detected in the oxidation products, indicating the absence of $C{=}CH_2$ groupings.

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

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

[3] K. Hofmann, O. Jucker, W. R. Miller, A. C. Young, Jr., and F. Tausig, THIS JOURNAL, **76**, 1799 (1954).

[4] J. P. Verma, S. Das Gupta, B. Nath and J. S. Aggarwal, *J. Indian Chem. Soc.*, **33**, 111 (1956).

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

[6] H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

[7] R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

[8] The yield of sterculic acid diminished with reaction time (12 hours, 2.5% ; 24 and 48 hours, (trace amounts) presumably through polymerization of the acid, *cf.* K. L. Rinehart, Jr., C. L. Tarimu and T. P. Culbertson, THIS JOURNAL **81**, 5007 (1959).

[9] G. Dijkstra and H. J. Duin, *Nature*, **176**, 71 (1955); P. K. Faure, *ibid.*, **178**, 372 (1956).

[10] K. Hofmann and C. W. Yoho, THIS JOURNAL, **81**, 3356 (1959).

[11] Paper chromatography was carried out on silicone impregnated Whatman No. 1 with 85% acetic acid as solvent according to the method of H. K. Mangold, B. G. Lamp and H. Schlenk, *ibid.*, **77**, 6070 (1955). Gas chromatographic separation employed the technique of C. H. Orr and J. E. Callen, *ibid.*, **80**, 249 (1958). V_R' values are calculated for a flow rate of 65 ml./min. (He).

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

[13] Double bonds *exo* to cyclopropane rings have been shown to absorb at frequencies higher than normal, *e.g.*, methylene cyclopropane absorbs at 1724–1786 cm.$^{-1}$ *cf.* J. T. Gragson, K. W. Greenlee, J. M. Derfer and C. E. Boord, THIS JOURNAL, **75**, 3344 (1953).

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

[15] J. v. Braun and E. Danziger, *Ber.*, **45**, 1970 (1912).

[16] C. R. Barnicoat, *J. Chem. Soc.*, 2926 (1927).

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