

IDENTITY OF DANIELLIC ACID WITH ILLURINIC ACID

JOHN S. MILLS

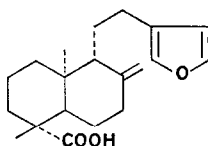
The National Gallery, Trafalgar Square, London WC2N 5DN

(Received 16 March 1973. Accepted 1 May 1973)

Key Word Index—*Daniellia oliveri*; Leguminosae; African copaiba; illurinbalsam; diterpenes.

Abstract—African copaiba balsam is the product of *Daniellia oliveri* (Rolfe) Hutch. and Dalz. Daniellic acid is identical with illurinic acid.

THE DITERPENE daniellic acid (I) was isolated^{1,2} from the oleoresin of *Daniellia oliveri* (Rolfe) Hutch. and Dalz. (Leguminosae; Caesalpinioideae, syn. *Paradaniellia oliveri* Rolfe; *Daniellia thurifera* Oliver non Bennet).³ I wish to show that the same compound was in fact isolated from the same source, and rather fully characterized, over 60 yr previously, but, partly owing to nomenclatural confusion, this was later overlooked.



(I)

Umney⁴ examined a commercial consignment from Nigeria of 'African copaiba Balsam', otherwise known as 'wood oil' or 'Illorin (or Illurin) balsam' (Illorin is a town in W. Nigeria). He speculated that the botanical source was '*Hardwickia Copaifera?*) *mannii*' and he isolated a crystalline acid, m.p. 124°. This same acid was reisolated by Tschirch and Keto⁵ from similar commercial material as well as from a South American copaiba (*Copaifera* sp.), and called illurinic acid. They report it as C₂₀H₂₈O₃ m.p. 128–129°, [α]_D –55° (reported for (I)² m.p. 129–130.5°, [α]_D –58°, and for its enantiomer, lambertianic acid,⁶ m.p. 126.5–127.5°, [α]_D +55°). They followed Umney in attributing it to '*Oxystigma* (*Hardwickia* ? *Copaifera* ?) *mannii* Harms'. and this error unfortunately persisted into Tschirch and

¹ CRIQUI, A. (1956) Thesis, Strasbourg.

² HAEUSER, J., LOMBARD, R., LEDERER, F. and OURISSON, G. (1961) *Tetrahedron* **12**, 205.

³ HUTCHINSON, J. and DALZIEL, J. M., revised KEAY, R. W. J. (1954) *The Flora of West Tropical Africa*, Vol. 1, p. 463, Crown Agents, London.

⁴ UMNEY, J. C. (1891) *Pharm. J.* **22**, 449; (1893) *ibid.* **24**, 215.

⁵ TSCHIRCH, A. and KETO, E. (1901) *Arch. Pharm.* 548.

⁶ DAUBEN, W. G. and GERMAN, V. F. (1966) *Tetrahedron* **22**, 679.

Stock's book,⁷ although the source was given as *Daniellia oliveri* (or synonymously) by many authorities at least from 1908 onward.⁸⁻¹⁵

I have been able to examine Umney's original African copaiba, three samples of which are preserved in the Museum of the Pharmaceutical Society of Great Britain, now at the University of Bradford. These had closely similar gas chromatograms (after methylation with diazomethane) with only one major ester component, corresponding to methyl daniellate. The free acid was readily isolated by crystallization of the KOHq soluble acid fraction and proved identical by the usual criteria with daniellic acid isolated from three samples of dried *Daniellia oliveri* resin from the Kew collection (W. H. Johnson, 54.1912, Onitsa, S. Nigeria; C. Barter, Nupe, Niger Expedition, 1859; M. Poisson, 37.1901, Dahomey). The last two were originally wrongly attributed to *Daniellia thurifera* Benn.).

Since African copaiba has sometimes been said to come from *Daniellia thurifera* Benn.¹⁶ three samples were examined of the resin ('Bungo'; 'African frankincense') of this species from Kew, including Daniell's own of which he published a meticulous account.¹⁷ (The others are C. E. Lane Poole, 15.1912, Freetown, Sierra Leone, and C. Barter, Sierra Leone, ca. 1859.) There is no ambiguity as to the origin of Daniell's sample since Bennett based his description¹⁸ of genus and species on Daniell's materials. GLC showed the three samples to be similar, with several (unidentified) ester peaks but only traces of methyl daniellate.

There thus remains no doubt that the oleoresin of *Daniellia oliveri* examined by Haeuser *et al.*² is that formerly available in commerce as African copaiba, and that daniellic acid is identical with illurinic acid.

Acknowledgements—I thank the Director, Royal Botanic Gardens, Kew, and Dr. W. E. Court, University of Bradford for resin samples, and Miss R. Angel, Museums Department, Kew, for her help in matters of nomenclature.

⁷ TSCHIRCH, A. and STOCK, E. (1933-36) *Die Harze*, p. 1408, Borntraeger, Berlin.

⁸ ANON (1908) *Bull. Imp. Inst.* **6**, 250; (1915) *ibid.* **13**, 44.

⁹ THOMPSON, H. N. (1910) *Colonial Repts.—Misc.* **66**, 88.

¹⁰ HOLLAND, J. H. (1911) *Kew Bull. Additional Series*, IX, Part 2, 268.

¹¹ DUDGEON, G. C. (1922) *The Agricultural and Forest Products of British West Africa*, 2nd Edn, p. 147, Imperial Institute Handbook, London.

¹² LELY, H. V. (1925) *The Useful Trees of Northern Nigeria*, p. 88, Crown Agents, London.

¹³ DALZIEL, J. M. (1937) *The Useful Plants of West Tropical Africa*, p. 186, Crown Agents, London.

¹⁴ *The British Pharmaceutical Codex* (1949 Edn) p. 271.

¹⁵ IRVINE, F. R. (1961) *The Woody Plants of Ghana*, p. 295, Oxford University Press, London.

¹⁶ *Dispensatory of the USA* (1950 Edn) p. 327.

¹⁷ DANIELL, W. F. (1855) *Pharm. J.* **14**, 400.

¹⁸ BENNETT, J. (1855) *Pharm. J.* **14**, 251.