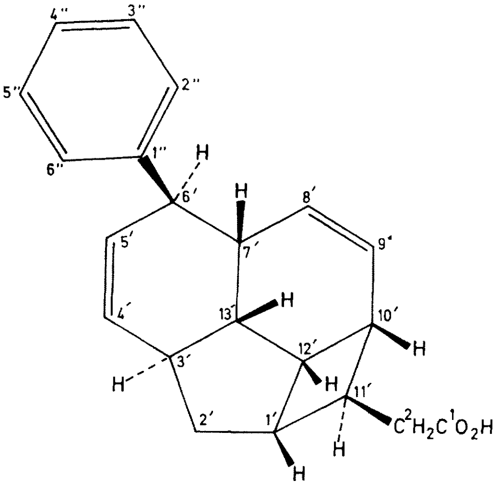
Endiandric Acid, a Novel Carboxylic Acid from *Endiandra introrsa* (Lauraceae): *X*-Ray Structure Determination

By Wickramasinghe M. Bandaranayake and James E. Banfield
(*Department of Chemistry, University of New England, Armidale, N.S.W.* 2350, *Australia*)
and David St. C. Black, Gary D. Fallon, and Bryan M. Gatehouse*
(*Department of Chemistry, Monash University, Clayton, Victoria* 3168, *Australia*)

Summary *X*-Ray crystal structure analysis shows that endiandric acid, a constituent of the Australian tree *Endiandra introrsa*, has the novel racemic structure (**1**), (1*RS*,3*RS*,6*SR*,7*SR*,10*SR*,11*RS*,12*RS*,13*RS*)-(6-phenyltetracyclo$[5.4.2.0^{3,13}0^{10,12}]$trideca-4,8-dien-11-yl]acetic acid.

Endiandra introrsa C. T. White (Lauraceae), the 'Dorrigo Plum,' is a large tree occurring in the rain forests of northern New South Wales and southern Queensland. Endiandric acid was obtained in *ca.* 0·45% yield from the dried leaves and leaf stems of a specimen† by extraction with light petroleum (b.p. 60—80 °C) and chromatography. After crystallization from aqueous methanol it had m.p. 148·5 °C and [α] 0·0° (*c*, 5% in $CHCl_3$, range 330—500 nm); the formula $C_{21}H_{22}O_2$ was established by microanalysis and high-resolution mass spectroscopy, and potentiometric titration in aqueous ethanol gave equivalent weights of 303 and 316 (required 306) and pK_a 5·1, 5·0. Endiandric acid formed a silver salt, $C_{21}H_{21}O_2Ag$, m.p. 174 °C, an *S*-benzylisothiouronium salt, $C_{29}H_{32}N_2O_2S$, m.p. 154 °C, and was converted by treatment with diazomethane into a methyl ester, $C_{22}H_{24}O_2$, m.p. 61—62 °C, which could be hydrolysed back into the original acid. The carboxy group was responsible



(1)

for i.r. absorption at 3220 and 1700 cm⁻¹. Reduction of the ester with $LiAlH_4$ afforded an alcohol, $C_{21}H_{24}O$, m.p. 79 °C, whose ¹H n.m.r. spectrum showed a triplet at δ 4·1. The presence of an unconjugated monosubstituted benzene

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† The specimen was collected by the C.S.I.R.O. phytochemical survey team, whom we thank, at Whian Whian in May 1958.

was indicated by the u.v. and ^{1}H n.m.r. spectra and the latter also showed resonances arising from four olefinic protons and a single allylic–benzylic proton at δ 3·26. The mass spectrum showed an intense M ion followed by strong ions resulting from sequential loss of benzene and acetic acid.

Hydrogenation of endiandric acid afforded a dihydro compound, $C_{21}H_{24}O_2$, m.p. 178—180 °C, a tetrahydro compound, $C_{21}H_{26}O_2$, m.p. 133—135 °C, and a decahydro compound, $C_{21}H_{32}O_2$, m.p. 128—129 °C, after uptake of 1, 2, or 5 mol. equiv. of hydrogen, respectively.

The molecular structure and stereochemistry of endiandric acid [(**1**) and Figure] were determined by X-ray crystallographic analysis using a crystal from a sample obtained by slow evaporation of a benzene solution.

Crystal data: endiandric acid, $C_{21}H_{22}O_2$, $M = 306{\cdot}4$, triclinic, $a = 13{\cdot}858(5)$, $b = 11{\cdot}066(4)$, $c = 5{\cdot}619(2)$ Å, $\alpha = 93{\cdot}52(7)$, $\beta = 96{\cdot}58(7)$, $\gamma = 106{\cdot}17(8)°$; $D_m = 1{\cdot}23(3)$, $D_c = 1{\cdot}24$ g cm^{-3}, $Z = 2$, space group $P\bar{1}$, $F(000) = 328$.

Single crystal X-ray diffraction data, between the limits $6° < 2\theta < 130°$, were measured with a Philips PW 1100 X-ray diffractometer using a $\theta/2\theta$ scan technique with graphite monochromated Cu-K_α radiation. 1587 unique data [$I \geqslant 3\sigma(I)$] were obtained. The structure was solved by direct methods using the program MULTAN[1]; all atomic parameters (hydrogen co-ordinates were calculated) were refined by full-matrix least-squares techniques[2] with anisotropic thermal parameters for non-hydrogen atoms (isotropic for hydrogen). At convergence the R-factor for the 1587 unique data was 0·054.‡

This appears to be the first report of a constituent of any of the 80 species of the genus *Endiandra*, of which 25 are endemic to Australia.[3] The structure (**1**) is unusual in that it contains a new tetracyclic framework, which, although compact, incorporates one *trans* ring junction.

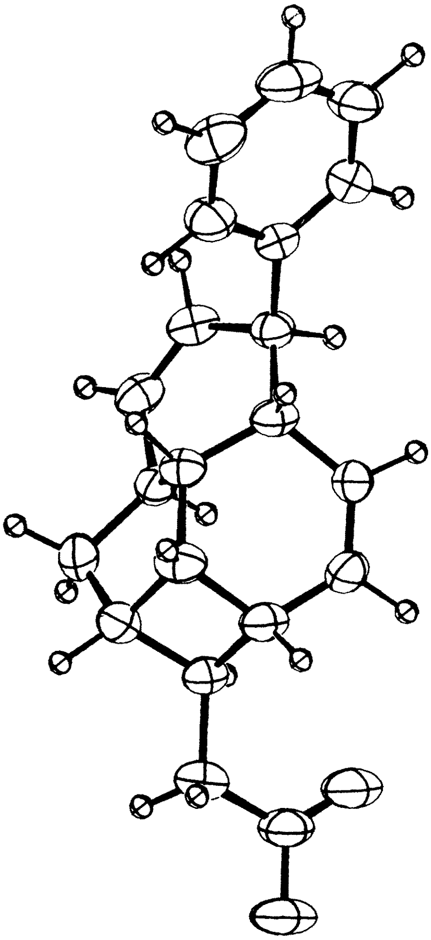

FIGURE. Molecular structure of endiandric acid (**1**). Hydrogen thermal ellipsoids have been reduced for clarity. The crystallographic numbering, corresponding to the deposited material, is given in structure (**1**).

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, A**27**, 368.

[2] G. M. Sheldrick, 1976, 'SHELX,' Program for Crystal Structure Determination, University Chemical Laboratory, Cambridge.

[3] H. K. Airy Shaw, 'A Dictionary of the Flowering Plants and Ferns,' 8th edn., Cambridge University Press, Cambridge, 1973; N. T. Burbidge, 'Dictionary of Australian Plant Genera,' Angus and Robertson, Sydney, 1963.