Phytochemistry, Vol. 23, No. 8, pp. 1814–1815, 1984.
Printed in Great Britain.

0031–9422/84 $3.00 + 0.00

PROPTEROL B, A FURTHER 1,3-DIARYLPROPAN-2-OL FROM *PTEROCARPUS MARSUPIUM*

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(*Received* 16 *September* 1983)

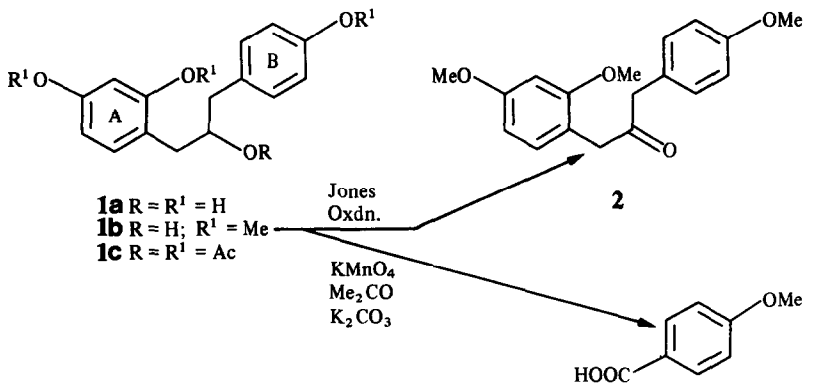
Key Word Index—*Pterocarpus marsupium*; Leguminosae; heartwood; 1,3-diarylpropan-2-ol; propterol B.

Abstract—The structure of propterol B, a heartwood extract of *Pterocarpus marsupium*, has been established as the hitherto unreported 1-(2,4-dihydroxyphenyl)-3-(4-hydroxyphenyl)propan-2-ol. The trimethyl ether of propterol B on oxidation with Jones reagent gave 1-(2,4-dimethoxyphenyl)-3-(4-methoxyphenyl)propan-2-one.

We have recently reported [1] the structure of propterol, 1,3-bis(4-hydroxyphenyl)propan-2-ol, from the heartwood of *Pterocarpus marsupium*. In this paper, the isolation and structure of a closely related compound, propterol B (**1a**), are described. The ether-soluble extracts of the above heartwood on chromatography yielded carpusin [2] and a crude product, which on rechromatography [silica gel, chloroform–methanol (49:1)] yielded colourless prisms (0.20 g, 0.002%), crystallized from chloroform–ethyl acetate, $C_{15}H_{16}O_4$, $[M]^+$ 260, mp 158°, $[\alpha]_D$ −1° (*c* 0.58; methanol), designated as propterol B (**1a**).

The UV spectrum of **1a** showed λ_{max}^{MeOH} nm (log ε) 279 (3.85), similar to that of propterol [1] and other compounds of its class, such as virolanol B [3]. The UV spectrum did not show any shift in the presence of aluminium chloride or boric acid–sodium acetate. The ^{1}H NMR spectrum (60 MHz, $CDCl_3$–DMSO-d_6) of **1a** showed multiplets at δ2.55–2.85 (4H), showing approximate doublet character, assignable to the two sets of benzylic methylene protons [4] at C-1 and C-3; and at δ3.85–4.25 (1H) corresponding to the carbinol methyne proton at C-2, the observed multiplicities suggesting the relative positions of the above groups. H-3′ appeared at δ6.29 (*d*, *J* = 2.5 Hz) and H-5′ and H-6′ in the region δ6.35–6.45 (*m*, 2H). The protons of ring B gave rise to an AA′BB′ quartet in the region δ6.97–7.16, similar to that of *p*-cresol [5], and the phenolic protons in the region δ8.55–8.58 (3H, exchanged with D_2O). The alcoholic proton signal was considered to be merged with the signal due to DMSO.

With dimethyl sulphate–acetone–potassium carbonate, **1a** gave a trimethyl ether (**1b**), oil, $C_{18}H_{22}O_4$, $[M]^+$ 302. The ^{1}H NMR spectrum of **1b** showed signals, in addition to those of **1a**, at δ3.80 (*s*, 6H) and 3.85 (*s*, 3H) for three methoxyl groups. Thus the presence of three phenolic groups in **1a** was confirmed. The IR spectrum of **1b** showed $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600–3400 (broad) corresponding to an alcoholic hydroxyl. With pyridine–acetic anhydride, **1a** gave a tetraacetate (**1c**), $C_{23}H_{24}O_8$, which resisted all attempts at crystallization, and showed $[M - MeCOOH]^+$ at *m/z* 368 in the mass spectrum, IR ν_{CO} at 1750 and 1775 cm^{-1}, ^{1}H NMR signals at δ1.85 (*s*, 3H, one alcoholic –OAc) and δ2.15, 2.05 (*s*, 6H and *s*, 3H, respectively, three phenolic –OAc). Thus the presence of three phenolic groups and one alcoholic hydroxyl group in **1a** was established. The secondary nature of the alcoholic hydroxyl group was supported by the appear-



Scheme 1.

ance of H-2 in the region δ4.95–5.25 (*m*, 1H) in the ^{1}H NMR spectrum of **1c**, having shifted downfield ($\Delta\delta$1.05) upon acetylation [4]. The shift observed in the case of the aromatic protons of ring A was in agreement with the assigned substitution pattern [6].

The mass spectrum (EIMS, probe, 70 eV) of **1a** showed a $[M-H_2O]^+$ ion at *m/z* 242 (5%), and prominent ions at *m/z* 123 (100%), 137 (20%), 153 (70%) and 107 (98%), the fragmentation pattern being completely compatible with the proposed structure.

The ^{13}C (^{1}H) NMR spectrum (90 MHz, DMSO-d_6) of **1a** showed 12 signals assignable to the 15 carbon atoms. The multiplicities observed in the off-resonance spectrum were also in agreement with the assignments. The signals due to the carbon atoms of ring A, approximately comparable to those of the 2,4-dimethoxybenzylic moiety [7], appeared at δ114.43 (*s*, C-1'), 155.71 (*s*, C-2'), 102.29 (*d*, C-3'), 156.15 (*s*, C-4'), 105.71 (*d*, C-5') and 129.76 (*d*, C-6'); those of ring B comparable to those of *p*-cresol [8] at δ131.17 (*s*, C-1''), 129.55 (*d*, C-2'', 6''), 115.89 (*d*, C-3'', 5'') and 154.96 (*s*, C-4''). The signals assigned to C-2', C-4' and C-4'' as well as those of C-6', C-2'' and C-6'' might be interchanged. The benzyl carbons at C-1 and C-3 appeared at δ41.88 (cf. ethylbenzene [8]), and C-2, holding a secondary alcoholic hydroxyl group [8], at δ71.68. Nevertheless, in the off-resonance spectrum the signal due to C-1 and C-3 merged with that due to DMSO-d_6, and that due to C-2 appeared as a broad signal.

Compound **1b**, on oxidation with Jones reagent [9], yielded a compound, $C_{18}H_{20}O_4$, mp 82°, $[M]^+$ 300, IR ν_{CO} 1725 cm^{-1}, which was characterized as 1-(2,4-dimethoxyphenyl)-3-(4-methoxyphenyl)propan-2-one (**2**). Compound **1b** on oxidation with potassium permanganate–acetone–potassium carbonate, gave several products which on fractional crystallization from water yielded only anisic acid.

The CD spectrum of propterol B showed a negative Cotton effect; $\Delta\varepsilon_{287} -6.5\times10^{-4}$ (*c* 0.117; methanol); however, its absolute configuration could not be determined as no comparable data were available.

Acknowledgements—We thank Prof. C. V. Ratnam, Head, Department of Chemistry, Osmania University, for providing facilities, and Prof. G. Srimannarayana of this Department for helpful discussions.

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