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

A. V. SUBBA RAO, JAMES MATHEW and A. V. B. SANKARAM*

Department of Chemistry, Osmania University, Hyderabad, India; *Regional Research Laboratory, Hyderabad, India

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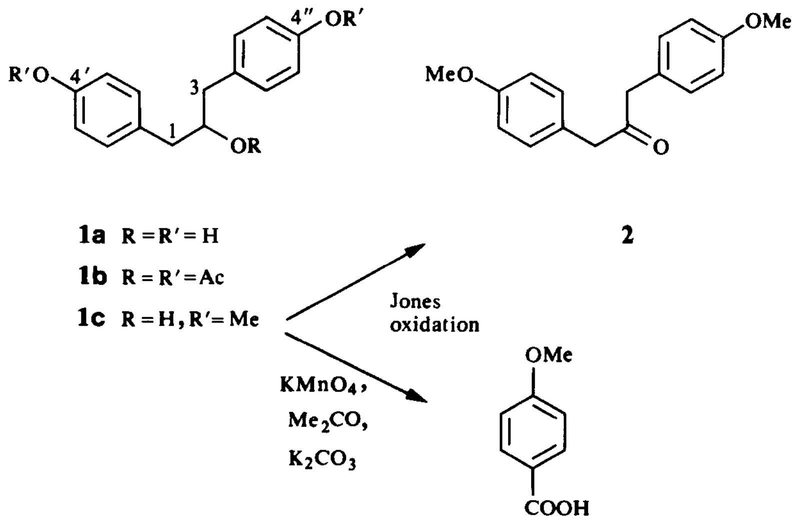
Key Word Index—*Pterocarpus marsupium*; Leguminosae; heartwood; 1,3-diarylpropan-2-ol; propterol; ^{13}C NMR; ^{1}H NMR; acetylation shifts; mass spectra.

Abstract—The structure of propterol, an extractive of the heartwood of *Pterocarpus marsupium*, has been established to be 1,3-*bis* (4-hydroxyphenyl)propan-2-ol, on the basis of its spectral data and Jones oxidation of its dimethyl ether to known 1,3-*bis*(4-methoxyphenyl)propan-2-one. Propterol appears to be among the simplest of highly reduced flavonoids encountered in nature.

Excepting an isolated instance in the Myristicaceae [1, 2] there has been no report of 1,3-diarylpropan-2-ols. This paper reports the isolation of a new 1,3-diarylpropan-2-ol, propterol (**1a**), from the heartwood of *Pterocarpus marsupium*. Recently, the structure of carpusin, 2,6,4′-trihydroxy-4-methoxy-2-benzylcoumaranone, isolated from the above wood was reported [3] from our laboratories. The ether extract of the above wood on CC [silica gel, eluent chloroform–ethyl acetate (7:3)], has now afforded a new compound, propterol (0.8 g, 0.008 %), colourless prisms, mp 173°, $C_{15}H_{16}O_3$, $[M]^{+\cdot}$ 244, the structure of which has been established to be 1,3-bis(4-hydroxyphenyl)propan-2-ol (**1a**).

The UV spectrum of compound **1a** showed $\lambda_{\max}^{\text{MeOH}}$ nm (log ε) 279 (3.80), comparable to that of *p*-*C*-alkylated phenol [4]. Resonances at δ 3.30 (1H) and 8.47 (2H) (broad, both exchangeable with D_2O) in the ^{1}H NMR spectrum [90 MHz, $(CD_3)_2CO$], and absorptions at $\nu_{\max}^{\text{KBr}}$ 3600–3200 cm^{-1} (*br*) in the IR spectrum of compound **1a** suggested the presence of one alcoholic and two phenolic hydroxyl groups. Its ^{1}H NMR spectrum showed AA′BB′ quartet at δ 6.80–7.20, accounting for four pairs of aromatic protons, comparable to that of *p*-cresol [5]; signals at δ 2.75 (*d*, J = 6 Hz, 4H) assignable to two sets of benzylic protons at the positions 1 and 3, and δ 3.40 (*m*, 1H, H-2) assignable to the methyne proton of a secondary alcohol.

On acetylation (pyridine–acetic anhydride) compound **1a** gave a triacetate (**1b**), homogeneous on TLC, which resisted all attempts for crystallization, $C_{21}H_{22}O_6$, $[M]^{+\cdot}$ 370. In the ^{1}H NMR spectrum of the triacetate **1b**, the methyne proton appeared at δ 5.27 (*m*, 1H), showing the expected acetylation shift (Δδ 1.87).



1a R = R′ = H
1b R = R′ = Ac
1c R = H, R′ = Me

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*The multiplicities and coupling constants are from the coupled spectrum.

The ^{13}C NMR [90 MHz, $(CD_3)_2CO$] spectrum of compound **1a** showed only five resonances at δ 156.74, 131.55, 116.16, 75.04 and 43.61 for the fifteen carbon atoms of its molecular formula, which are assignable to two *p*-hydroxybenzyl moieties attached to a secondary carbon carrying a hydroxyl group. Due to the close similarity in environments, the signals due to the carbons C-2′, C-2″, C-6′, C-6″ (δ 131.55, *ddt**, $^1J = 156.25$, $^3J = 4.88$ and 7.30 Hz), C-3′, C-3″, C-5′, C-5″ (δ 116.16, *dd*, $^1J = 157.47$, $^3J = 4.88$ Hz) and C-4′, C-4″ (δ 156.74, *t*, $^3J = 8.55$) overlapped into three signals and are closely comparable to the corresponding carbons of *p*-cresol [6]. The signals at δ 43.61 (*t*, $^1J = 125.73$ Hz) and 75.04 (*dt*, $^1J = 143.82$, $^2J = 4.88$ Hz) are assignable to C-1 and C-3 (benzylic carbon [7]) and $>\underline{C}HOH$ [8] respectively. The signal assignable to C-1′, C-1″ was hidden in the signal at δ 131.55 but got separated in the off-resonance and coupled spectra, and appeared in the coupled spectrum at δ 131.39 (*dt*, $^3J = 7.32$ and 3.66 Hz). The multiplicities and coupling constants of these signals observed in the coupled spectrum fully support the structure of compound **1a**.

In the mass spectrum (EIMS, probe, 70 eV) of propterol, the prominent ions at *m/z* 107 (100%) and 137 (50%) formulated respectively as $CH_2{=}C_6H_4{=}\overset{+}{O}H$ and $Ar{-}CH_2{-}CH{=}\overset{+}{O}H$ were observed as anticipated.

On methylation (dimethyl sulphate, acetone, potassium carbonate) propterol gave the anticipated dimethyl ether (**1c**), oil, $C_{17}H_{20}O_3$, $[M]^{+\cdot}$ 272. The ^1H NMR spectrum of the compound **1c** showed an additional signal at δ 3.75 (*s*, 6H) corresponding to two methoxyl groups. Compound **1c** on Jones oxidation [9] afforded a compound, $C_{17}H_{18}O_3$, mp 86°, IR ν_{CO}^{KBr} cm^{-1}: 1710, characterized as 1,3-bis(4-methoxyphenyl)propan-2-one (**2**) (lit. [10] mp 86–86.2°). Compound **1c** on oxidation with potassium permanganate, in the presence of acetone and potassium carbonate, gave *p*-anisic acid, mp 183° [11]; the anticipated homoanisic acid could not be isolated from the oxidation products.

1,3-Diarylpropan-2-ols, though represented [1, 2], belong to a rare class of flavonoids. Propterol is unique in possessing a symmetrical substitution pattern in the aromatic rings, and it appears to be among the simplest of flavonoids encountered in nature.

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