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CARPUSIN: A NOVEL 2-HYDROXY-2-BENZYLCOUMARANONE FROM *PTEROCARPUS MARSUPIUM*

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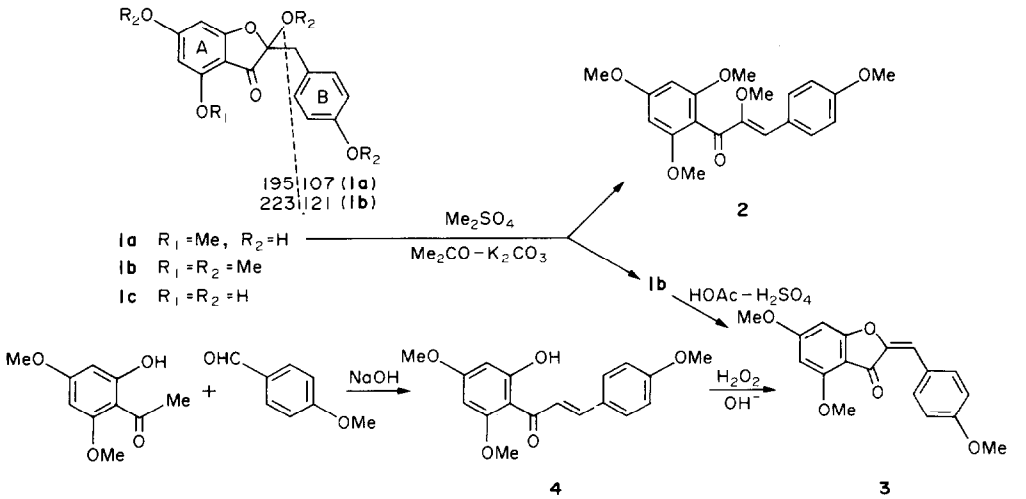
Key Word Index—*Pterocarpus marsupium*; Leguminosae; heartwood; 2-hydroxy-2-benzylcoumaranone.

Abstract—The structure of carpusin, an extractive of the heartwood of *Pterocarpus marsupium*, has been established as 2-benzyl-2, 4', 6-trihydroxy-4-methoxybenzo(b)furan-3(2H)one, on the basis of spectral evidence and its conversion to tetra-*O*-methylmaesopsin and 4,6,4'-trimethoxyaurone.

In continuation of our earlier work [1] extraction of the heartwood of *Pterocarpus marsupium* and chromatography of the ether solubles over Si gel using chloroform–ethyl acetate (3:2) as eluent, afforded a colourless crystalline compound, $C_{16}H_{14}O_6$, mp 215°, $[\alpha]_D \pm 0°$, $M^{+\cdot}$ 302, designated as carpusin (**1a**).

Compound **1a** showed phenolic properties and gave a cherry-red colour with acetic anhydride and concentrated sulphuric acid characteristic of 2-hydroxy-2-benzylcoumaranones [2]. Functional analysis of **1a** showed a carbonyl (IR ν_{max} 1675 cm^{-1}), one phenolic methoxyl and one benzylic-CH_2- (^{1}H NMR 60 MHz singlets at δ 3.9



and 3.1, respectively) and two phenolic and one alcoholic hydroxyl groups [formation of a trimethyl ether (**1b**), $M^{+\cdot}$ 344, showing additional ^{1}H NMR signals at δ 3.82, 3.85 (phenolic methoxyl) and 3.35 (alcoholic methoxyl)].

The 4,6,4′-substitution pattern of the benzene rings in **1a** was supported by the ^{1}H NMR spectrum. The protons of the A-ring appeared as a pair of *meta*-coupled doublets showing an AB pattern (J = 2.5 Hz) at δ 6.05 (H-7) and 5.95 (H-5); that of the B-ring appeared as a pair of *ortho*-coupled doublets (J = 8.5 Hz) showing an A_2B_2 pattern at δ 7.15 (H-2′, H-6′) and 6.7 (H-3′, H-5′).

The UV spectrum of **1a** showed λ_{max}^{MeOH} nm(log ε): 290 (4.41) and 324 sh comparable to that of maesopsin (**1c**) [3]. In the presence of sodium acetate the shorter wavelength band in the UV spectrum showed a bathochromic shift of 27 nm supporting the presence of a hydroxyl group at the C-6 position [4]. The methoxyl group must be at the C-4 position as shown by the negative ferric reaction and the absence of a bathochromic shift in the UV spectrum with aluminium chloride [4].

The mass spectrum of **1a** as well as that of the trimethyl ether **1b** showed prominent ions at m/z 107 and 121 (both 100%), respectively, arising from the benzylic moiety; the fragmentation being shown by the dotted line in structures **1a** and **1b**. Prominent ions at m/z 195 for **1a** and at 223 for **1b** were also observed.

In the ^{13}C NMR (90 MHz) spectrum of **1a** the signals may be tentatively assigned as follows: δ 171.91 (C-3), 168.33 (C-6), 158.80 (C-4′), 155.50 (C-4, C-7a), 130.95 (C-2′, C-6′), 123.91 (C-1′), 114.37 (C-3′, C-5′), 105.44 (C-3a), 101.32 (C-2), 92.27 (C-5), 90.43 (C-7), 55.26 (–OMe) and 40.15 (α-CH_2)

The physical data of the trimethyl ether **1b** [mp 129°, UV λ_{max}^{MeOH} nm (log ε): 292 (4.35)] are similar to that reported for the tetramethyl ether of maesopsin (**1c**) [3]. Methylation (dimethyl sulphate, acetone, potassium carbonate) of **1a** also produced α-4, 2′, 4′, 6′-pentamethoxychalcone (**2**) which was separated from **1b** by CC over Si gel. Compound **2** was reported earlier as a methylation product of maesopsin and its physical data agreed with that reported [3].

Compound **1b** on treatment with boiling acetic acid containing 5% sulphuric acid, gave 4, 6, 4′-trimethoxyaurone (**3**), mp 169–170°, UV λ_{max}^{MeOH} nm (log ε): 340 (4.21), 392 (4.45), which was found to be identical (mp, mmp and superimposable IR) with a sample prepared by the A.F.O. oxidation [5] of the required chalcone **4** obtained by the condensation [6] of 2-hydroxy-4,6-dimethoxyacetophenone and anisaldehyde. Thus structure **1a** for carpusin was confirmed.

This appears to be the first report of **1a** from natural sources and the first instance of a compound of its class from a *Pterocarpus* species.

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