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A HOMOISOFLAVANONE FROM *PTEROCARPUS MARSUPIUM**

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Key Word Index—*Pterocarpus marsupium*; Leguminoseae; homoisoflavonoid.

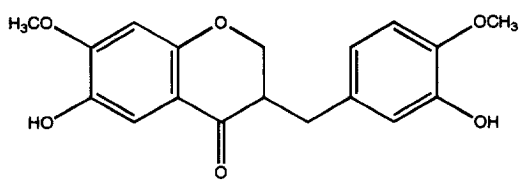
Abstract—A novel 6,7,3′,4′-tetraoxygenated homoisoflavonoid, characterized as 6-hydroxy-7-*O*-methyl-3-(3-hydroxy-4-*O*-methyl benzyl)chroman-4-one, has been isolated from the ether-soluble portion of the heartwood of *Pterocarpus marsupium*. This is the first report of the isolation of a homoisoflavonoid from a *Pterocarpus* species. Copyright © 1997 Published by Elsevier Science Ltd

INTRODUCTION

Pterocarpus marsupium Roxb is well known for its commercial importance and is used as a substitute for teak. It is commonly known as Vengisa of bijasal and possesses medicinal properties [1–4] which made it useful in the Ayurvedic and Unani systems of medicine. A phytochemical investigation of the heartwood of *P. marsupium* has led to the isolation of a new homoisoflavonoid, pteromarsupone (**1**), besides several known compounds such as *trans*-pterostilbene [5, 6], liquiritigenin [7], isoliquiritigenin [7], 1,3-bis[4-hydroxyphenyl]-propan-2-ol [8], 1-(2,4-dihydroxyphenyl)propan-2-ol [9] and 8-hydroxy-4′-methoxy isoflavanone-7-*O*-glucopyranoside [10]. Compound **1** belongs to a small class of natural products (homoisoflavonoids) some of which are known for their antimutagenic [11] and antiinflammatory [12] properties and are of chemotaxonomic interest [13].

RESULTS AND DISCUSSION

Compound **1** gave a molecular ion peak $[M]^+$ at *m/z* 330. Its IR spectrum showed characteristic absorptions of carbonyl and hydroxyl groups at 1640 and 3400 cm^{-1}, respectively. The ^1H NMR spectrum showed the presence of two methoxyl groups and contained characteristic peaks at δ 4.14 (*dd*, 1H) and 4.39 (*dd*, 1H) for C-2 protons, at δ 2.83 (*m*, 1H) for a C-3 proton, and at δ 2.60 (*dd*, 1H) and 3.15 (*dd*, 1H) for C-9 benzylic protons, indicating that **1** possessed a homoisoflavonoid skeleton. This was supported by a benzylic carbon peak at δ 31.88 in its ^{13}C NMR spectrum. On acetylation, **1** gave a diacetate, showing the presence of two hydroxyl groups. Thus **1** was a tetraoxygenated 3-benzyl-4-chromanone. The substitution pattern in ring A and B was deduced by coupling the mass fragmentation pattern with the UV and ^1H NMR data. The base peak at *m/z* 137 was due to the hydroxymethoxy tropylium ion from ring B. The ^1H NMR spectrum showed signals at δ 6.75 (*d*, J_{meta} = 1.8 Hz), 6.85 (*d*, J_{ortho} = 7.93 Hz) and 6.71 (*dd*, J_{meta} = 1.8 and J_{ortho} = 7.93 Hz) for C-2′, C-5′ and C-6′ protons, respectively, indicating a 3′,4′-dioxygenation pattern. The hydroxyl group was placed at C-3′ and the methoxyl group at C-4′ on the basis of the UV data and the NOE effects. Irradiation of the methoxyl signals at δ 3.81 caused a NOE enhancement of H-5′ and H-8, thereby suggesting them to be at C-4′ and C-7 positions. Again a peak at *m/z* 193 supported the presence of another set of hydroxyl and methoxyl groups in ring A. Since compound **1** did not



give a positive $FeCl_3$ test and its UV spectrum in methanol showed no bathochromic shift on treatment with either aluminium chloride or sodium acetate, it was inferred that it contained a free-OH at C-6 rather than at C-5. This was supported further by peaks at δ 6.50 (*s*, 1H) and 7.25 (*s*, 1H) for H-8 and H-5, respectively. Based on the above spectral characteristics, the new homoisoflavonoid, pteromarsupone, has been assigned the structure 6-hydroxy-7-*O*-methyl-3-(3-hydroxy-4-*O*-methyl benzyl) chroman-4-one. This

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compound has not been reported from any other natural source. This is the first report of the isolation of a homoisoflavonoid from *Pterocarpus* species and the oxygenation pattern that **1** contains is also rare occurring among earlier known homoisoflavonoids.

EXPERIMENTAL

Mps: uncorr; IR: KBr; UV: MeOH; ^{1}H NMR: 250 MHz; ^{13}C NMR: 62.9 MHz; EIMS technique was used for MS analysis. CC: silica gel (60–80 mesh); TLC; silica gel G.

Plant material. The heartwood of *Pterocarpus marsupium* was collected locally and identified by Professor C. R. Babu, Department of Botany, University of Delhi, Delhi (India).

Extraction and isolation. The dried heartwood of *P. marsupium* (1.0 kg) was crushed and extracted with different solvents of increasing polarity for several hours in a soxhlet. The Et_2O-soluble fraction of the solvent free EtOAc extract was concentrated *in vacuo* and the residue subjected to CC on silica gel. The column was initially eluted with C_6H_6 and then with C_6H_6–EtOAc with an increasing concentration of EtOAc. Elution with C_6H_6–EtOAc (7:3) gave fractions that mainly contained compound **1** along with some minor components. The separation and purification of **1** was achieved by prep. TLC using C_6H_6–EtOAc (7:3) as the developing solvent.

6-*Hydroxy*-7-*O*-*methyl*-3-(3-*hydroxy*-4-*O*-*methyl benzyl*)-*chroman*-4-*one* (**1**). Recrystallized from $CHCl_3$–MeOH as needles (8 mg), mp. 187°, $R_f = 0.66$ and 0.74 in C_6H_6-EtOAc (7:3) and CH_2Cl_2–CH_3OH (9:1), respectively, $[\alpha]-71°$ (MeOH, $c = 0.2$). UV λ_{max}^{MeOH} nm: 276. IR ν_{max}^{KBr} cm^{-1}: 3400, 1640; ^{1}H NMR $(CD_3)_2CO$: δ 2.60 (1H, *dd*, H-9), 2.83 (1H, *m*, H-3), 3.15 (1H, *dd*, H-9), 3.81 (6H, *s*, 2 × -OCH_3), 4.14 (1H, *dd*, H-2), 4.39 (1H, *dd*, H-2), 6.50 (1H, *s*, H-8), 6.71 (1H, *dd*, $J = 1.8$ and 7.93 Hz, H-6′), 6.75 (1H, *d*, $J_m = 1.8$ Hz, H-2′), 6.85 (1H, *d*, $J_o = 7.93$ Hz, H-5′), 7.25 (1H, *s*, H-5); ^{13}C NMR $(CD_3)_2CO$: δ 31.88 (C-9), 47.45 (C-3), 55.76 and 55.93 (2 × -OCH_3), 70.30 (C-2), 100.06 (C-4a), 110.60 (C-8), 112.03 (C-5′), 116.01 (C-2′), 116.10 (C-5), 120.25 (C-6′), 132.06 (C-1′), 146.40 (C-3′, C-4′ and C-6), 152.26 (C-8a), 157,26 (C-7), 191.82 (C-4); EIMS (probe) 70 eV, *m/z* (rel. int.): 330 $[M]^+$ (68), 313 (5), 194 (10), 193 (19), 167 (24), 149 (9), 138 (12), 137 (100), 122 (6), 94 (4), 72 (4), 55 (4), 28 (3), 18 (30). Acetate (pyridine–Ac_2O, 24 hr at room temp) mp: 174°.

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