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ISOFLAVONOIDS FROM THE HEARTWOOD OF *PTEROCARPUS MARSUPIUM*

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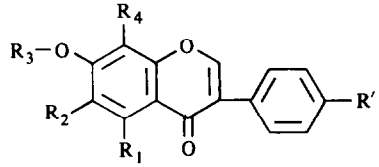
Key Word Index—*Pterocarpus marsupium*; Leguminosae; retusin 7-glucoside; irisolidone 7-rhamnoside; 5,7-dihydroxy-6-methoxyisoflavone 7-rhamnoside.

Abstract—Three new isoflavone glycosides viz retusin 7-glucoside, irisolidone 7-rhamnoside and 5,7-dihydroxy-6-methoxyisoflavone 7-rhamnoside have been isolated from the heartwood of *Pterocarpus marsupium*.

Species of *Pterocarpus* are known to be rich in isoflavonoids and terpenoids [1]. From the ethanolic extract of the heartwood of *P. marsupium* three new isoflavone glycosides (**1–3**) and the known compound 7-hydroxy-5,4′dimethoxy-8-methylisoflavone 7-rhamnoside [2] were identified.

Compound **1** was found to be glycosidic in nature and on hydrolysis it gave D-glucose (co-PC and osazone) and retusin [3] (7,8-dihydroxy-4′-methoxyisoflavone), which was identified from its colour reactions, UV and ^{1}H NMR spectral data, alkali fission and ^{1}H NMR of its acetate. The sugar moiety was found to be attached at the 7-position by comparison of the spectral shifts of the aglycone and glycoside, the glycoside giving no bathochromic shifts of band II with aluminium chloride, aluminium chloride–hydrochloric acid, sodium acetate or sodium acetate–boric acid. This was confirmed by acid hydrolysis of the methylated glycoside to give 8-*O*-methylretusin [3]. Periodate oxidation confirmed that the glucose was in the pyranose form since it consumed 2 mols of periodate per mol of the glycoside and liberated 1 mol of formic acid. The glycoside was hydrolysed by almond emulsin indicating a β-linkage. Thus, the structure of **1** was confirmed as retusin 7-*O*-β-D-glucopyranoside. This is the first report of **1** in nature.

Compound **2** was also found to be glycosidic in nature and acid hydrolysis gave an aglycone and L-rhamnose (co-PC and osazone). The aglycone was characterized as 5,7-dihydroxy-6,4′-dimethoxyisoflavone (irisolidone) [4] from its UV and ^{1}H NMR spectra and alkali fission to give iretol [5] and *p*-methoxyphenylacetic acid. Glycosidation was confirmed at position 7 by comparison of the UV spectral shifts and colour reactions of the aglycone with those of the glycoside. The glycoside gave no shift with sodium acetate but gave 13 and 12 nm bathochromic shifts (band II) with aluminium chloride and aluminium chloride–hydrochloric acid reagents, respectively showing the presence of a free hydroxyl at C-5. The structure of **2** was further confirmed by acid hydroly-



1 R_1 and R_2 = H, R_3 = Glc, R_4 = OH, R′ = OMe
2 R_4 = H, R_1 = OH, R_2 and R′ = OMe, R_3 = Rha
3 R_4 = H, R_1 = OH, R_3 = Rha, R_2 = OMe, R′ = H

sis of the methylated glycoside to give an aglycone with one free hydroxyl group at position 7 (bathochromic shift of 5 nm of band II). Periodate oxidation confirmed the pyranose form of the rhamnose and enzymic hydrolysis by takadiastase confirmed an α-linkage. Thus, **2** is characterized as irisolidone 7-*O*-α-L-rhamnopyranoside. This compound is reported for the first time.

Compound **3** was also found to be glycosidic in nature and hydrolysis with 7% H_2SO_4 gave rhamnose (Co-PC and osazone) and an aglycone which was shown to be an isoflavone by its colour reactions and UV and ^{1}H NMR spectra. The aglycone analysed for two hydroxyl (diacetate IR 3358 cm^{-1}) and one methoxyl group (Ziesel, IR 2864 and 1183 cm^{-1} and a ^{1}H NMR signal at δ3.8 corresponding to the 3H of the methoxyl group). The two free hydroxyl groups were shown to be at the 5 and 7 positions by colour tests [6] and UV spectral shifts (bathochromic shifts of 12 and 11 nm of band II with aluminium chloride and aluminium chloride–HCl, respectively and a bathochromic shift of 10 nm (band II) with sodium acetate). The position of the methoxyl group was assigned by alkali fission, which gave, iretol, mp 184° (lit. 186°) [5] and phenylacetic acid, mp 75° (lit. 76°). The formation of iretol suggested the presence of a methoxyl group at the 6 position. Potassium permanganate oxidation gave benzoic acid, mp 120° (lit. 122°) which further proved that there was no B-ring substitution. Finally the structure was confirmed by its ^{1}H NMR spectrum as 5,7-dihydroxy-6-methoxyisoflavone, which has not been reported previously from any other plant source. The rhamnose was found to be attached at position 7 by a comparative study of the colour reactions of UV spectral shifts of the aglycone and the glycoside. The glycoside gave 11 and 13 nm bathochromic shifts with aluminium chloride and aluminium chloride–hydrochloric acid, respectively, but gave no shift with sodium acetate. The structure of **3** was confirmed when acid hydrolysis of the methylated glycoside gave an aglycone which was found to contain only one hydroxyl group at position 7 (10 nm bathochromic shift of band II with sodium acetate). Periodate oxidation and enzymic hydrolysis by takadiastase, respectively, confirmed the pyranose form and α-linkage of the rhamnose. Thus, the structure of **3** was confirmed as 5,7-dihydroxy-6-methoxy-7-*O*-α-L-rhamnopyranoside. This is a novel compound not reported earlier from any other plant sources.

EXPERIMENTAL

Isolation. The heartwood of *P. marsupium* was identified by the botanical survey of India. The heartwood was extracted with boiling EtOH and the concd extract (150 ml) fractionated into petrol, C_6H_6 was EtOAc soluble portions. The remaining mother liquor was concd and macerated with Me_2CO. Compounds **1** and **2** were extracted from the Et_2O fraction by prep. TLC. Compound **3** was pptd by petrol from the Me_2CO fraction using fractional pptn to remove impurities. Purity of the compounds was checked by PC and TLC.

Compound **1**. Mp 190°, $C_{22}H_{22}O_{10}$. (Found: C, 58.40, H, 5.05. Calc. for $C_{22}H_{22}O_{10}$: C, 59.19; H, 4.93%.) UV λ_{max}^{MeOH} nm: 254, 310 (sh); + $AlCl_3$ 255, 311 (sh); + $AlCl_3$–HCl 254, 310 (sh); + NaOAc 254, 310; + NaOAc–H_3BO_3 253, 310 (sh). ^{1}H NMR (90 MHz, $CDCl_3$): δ4.00 (3H, *s*, OMe), 5.20 (1H, *br*, H-1″ glucosyl) 3.82 (*br*, sugar protons), 7.94 (1H, *s*, C-2), 6.95 (*d*, *J* = 8.5 Hz, 2H, C-3′, C-5′), 7.46 (2H, *d*, *J* = 8.5 Hz, C-2′, C-6′), 7.28 (1H, *d*, *J* = 9.00 Hz, C-6), 8.23 (1H, *d*, *J* = 9.0 Hz, C-5).

Aglycone of **1**. Mp 249° (lit. 249°), $C_{16}H_{12}O_5$. (Found: C, 67.8; H, 4.29. Calc. for $C_{16}H_{12}O_5$: C, 67.5; H, 4.22%.) UV λ_{max}^{MeOH} nm: 261, 308 (sh); + $AlCl_3$ 281, 322 (sh); + $AlCl_3$–HCl 261, 308 (sh); + NaOAc 277, 314 (sh); + NaOAc–H_3BO_3 269, 310 (sh). Acetate (pyridine–Ac_2O, 24 hr at room temp.) mp 166°. (Found: C, 65.01; H, 4.34, acetyl 23.39. Requires C, 65.2; H, 4.38; acetyl, 23.29%.) ^{1}H NMR (aglycone diacetate) (90 MHz, $CDCl_3$): δ7.94 (1H, *s*, C-2), 4.00 (3H, *s*, OMe), 6.96 (2H, *d*, *J* = 9.0 Hz, C-3′, C-5′), 7.47 (2H, *d*, *J* = 9.0 Hz, C-2′, C-6′), 7.25 (1H, *d*, *J* = 9.0 Hz, C-6) 8.20 (1H, *d*, *J* = 9.0 Hz, C-5).

Compound **2**. Mp 198°, $C_{23}H_{24}O_{10}$ (Found: C, 59.15; H, 5.50. Calc. for $C_{23}H_{24}O_{10}$: C, 60.00; H, 5.21%.) UV λ_{max}^{MeOH} nm: 255, 316 (sh); + $AlCl_3$ 268, 318 (sh); + $AlCl_3$–HCl 267, 327 (sh); + NaOAc 256, 315 (sh). ^{1}H NMR (90 MHz, DMSO-d_6): δ8.3 (1H, *s*, C-2), 3.92–4.00 (6H, *s*, OMe-6, OMe-4′), 7.2 (2H, *d*, *J* = 8.5 Hz, C-2′, C-6′), 6.7 (2H, *d*, *J* = 8.3 Hz, C-3′, C-5′), 6.6 (1H, *s*, C-8), 4.95 (H-1 Rha, *s*) 3–3.85 (*m*, five sugar protons) 0.95 (3H, *s*, Me-Rha).

Aglycone of **2**. Mp 194° (lit. 195°). $C_{17}H_{14}O_6$ (Found: C, 68.61; H, 5.05. Calc. for $C_{17}H_{14}O_6$: C, 64.90; H, 4.45%.) UV λ_{max}^{MeOH} nm: 264, 334 (sh); + $AlCl_3$ 275, 337 (sh); + $AlCl_3$–HCl 276, 336 (sh); + NaOAc 272, 337 (sh). Acetate (pyridine–Ac_2O, 24 hr at room temp.) mp 163°. (Found: C, 63.45; H, 4.65, acetyl 20.85. Requires C, 63.31; H, 4.32; acetyl, 21.61%.) ^{1}H NMR (90 MHz, DMSO-d_6): δ8.4 (1H, *s*, C-2) 3.73–3.8 (6H, *s*, OMe-6, OMe-4′), 7.4 (2H, *d*, *J* = 8.5 Hz, C-2′, C-6′), 6.8 (2H, *d*, *J* = 8.3 Hz, C-3′, C-5′), 6.4 (1H, *s*, C-8).

Aglycone from methylated **2**. UV λ_{max}^{MeOH} nm: 250, 301 (sh); + $AlCl_3$ 248, 300 (sh); + $AlCl_3$–HCl 250, 298; + NaOAc 255, 302 (sh).

Compound **3**. Mp 194° (d), $C_{22}H_{22}O_9$. (Found: C, 61.12; H, 5.71. Calc. for $C_{22}H_{22}O_9$: C, 61.39; H, 5.11%.) UV λ_{max}^{MeOH} nm: 245, 309 + NaOAc 244, 310 (sh); + $AlCl_3$ 256, 317 (sh); + $AlCl_3$–HCl 258, 316 (sh). ^{1}H NMR (90 MHz, DMSO-d_6): δ8.3 (1H, *s*, C-2), 3.6 (3H, *s*, OMe-6), 6.7 (1H, *s*, C-8), 6.9–7.1 (5H, *m*, C-2′, C-6′, C-4′, C-3′, C-5′), 0.94 (3H, *br*, Me-Rha), 5.10 (H-1″ Rha, *s*), 3.0–4.0 (*m*, sugar protons).

Aglycone of **3**. Mp 208°, $C_{16}H_{12}O_5$. (Found: C, 67.12; H, 5.10. Calc. for $C_{16}H_{12}O_5$: C, 67.6; H, 4.22%.) UV λ_{max}^{MeOH} nm: 255, 310 (sh); + NaOAc 265, 312 (sh); + $AlCl_3$ 267, 318; + $AlCl_3$–HCl 266, 318 (sh). Acetate (pyridine–Ac_2O, 24 hr at room temp.) mp 190°. (Found: C, 64.98; H, 5.01, acetyl, 23.12. Requires C, 65.21; H, 4.34; acetyl 23.36%.) ^{1}H NMR (90 MHz, DMSO-d_6) δ8.4 (1H, *s*, C-2), 3.8 (*s*, 3H, OMe-6), 6.5 (1H, *s*, C-8), 6.8–6.9 (*m*, 5H, C-2′, C-6′, C-4′, C-3′, C-5′).

Aglycone from methylated **3**. UV λ_{max}^{MeOH} nm: 238, 300 (sh); + NaOAc 248, 298 (sh); + $AlCl_3$ 238, 300 (sh); + $AlCl_3$–HCl 237, 300 (sh).

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