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TWO AURONE GLYCOSIDES FROM THE FLOWERS OF *PTEROCARPUS MARSUPIUM*

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Key Word Index—*Pterocarpus marsupium*, Leguminosae, 4,6,4′-trihydroxyaurone 6-*O*-rhamnopyranoside; 4,6,4′-trihydroxy-7-methylaurone 4-*O*-rhamnopyranoside

Abstract—Two new aurone glycosides, 4,6,4′-trihydroxyaurone 6-*O*-rhamnopyranoside and 4,6,4′-trihydroxy-7-methylaurone 4-*O*-rhamnopyranoside have been isolated and identified from the flowers of *Pterocarpus marsupium*.

INTRODUCTION

Species of *Pterocarpus* are known to be rich in isoflavonoids [1] and terpenoid [2] derivatives. A flavonoid fraction of *P marsupium* bark was found to effectively reverse the alloxan-induced changes in the blood sugar level and the beta cell population in the pancreas [3]. From the ethanolic extract of the flowers of *P. marsupium* two new aurone glycosides have been isolated and identified This is the first report of aurones from *Pterocarpus* species.

RESULTS AND DISCUSSION

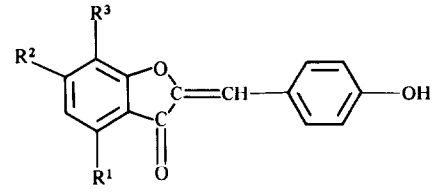
Compound **1**, the yellow pigment analysed for $C_{21}H_{20}O_9$, mp 178°. It was found to be glycosidic in nature [4]. On acid hydrolysis (7% H_2SO_4) it gave an aglycone and rhamnose, identified by co-chromatography with an authentic sample and by ^{1}H NMR spectral analysis of the glycoside (a doublet at δ1.20 corresponding to three protons of rhamnosyl –Me group, broad signal at δ3.5–3.82 for four sugar protons and a singlet at δ4.2 due to C-1″ proton of rhamnose).

The aglycone, $C_{15}H_{10}O_5$, was characterized as an aurone on the basis of colour reactions [5] and UV spectral data [6]. ^{1}H NMR studies showed six aromatic protons suggesting a trisubstituted aurone A multiplet at δ7.7–7.9 (2H) was due to C-2′ and -6′ and multiplet at δ6.8–7.0 (2H) for C-3′ and -5′ protons. Two doublets at δ6.1 and 6.3 (J = 2 Hz) were due to C-5 and C-7 protons, respectively There was a singlet at δ6.67 for benzylic proton (=CH–) [7] On acetylation it gave a triacetate, mp 62°, showing the presence of three hydroxyl groups. The positions of hydroxyls in the glycoside were confirmed by UV shifts [6]. The presence of a free –OH at C-4′ position was confirmed by a large bathochromic shift in λ_{max}^{MeOH} (*ca* 70 nm) with the addition of sodium methoxide and (68 nm) with sodium acetate. A large bathochromic shift in the λ_{max}^{MeOH} (*ca* 60 nm) with the addition of aluminium chloride confirmed the presence of a free –OH at position C-4 and the compound as 6-rhamnoside [8]

In the mass fragmentation pattern [7] two fragments at *m/z* 152 and *m/z* 118 showed that one hydroxyl group was present in the B ring and the other in A ring. Thus the structure of **1** is confirmed; this a new glycoside but the aglycone has been reported from flowers of *Limonium* [9].

Compound **2**, analysed for $C_{22}H_{22}O_9$, mp 168°, was found to be glycosidic in nature [4] and on hydrolysis it gave rhamnose (co-PC) and an aglycone which was shown to be an aurone by its colour reactions [5] and UV spectrum [6] ^{1}H NMR spectrum of the glycoside showed a doublet at δ1.20 corresponding to three protons of rhamnosyl –Me group

^{1}H NMR studies of the aglycone showed five aromatic protons suggesting a tetrasubstituted nuclei. The multiplet at δ7.8–7.9 (2H) was attributed to C-2′ and -6′ and a multiplet at δ6.88–7.10 (2H) to C-3′ and -5′ protons. A singlet at δ6 25 (1H) was due to C-5 proton. The aglycone $C_{16}H_{12}O_5$, analysed for three hydroxyls (triacetate, IR 3374 cm^{-1}) and a ^{1}H NMR signal at δ1.45 corresponding to 3H of the methyl group The two free –OH groups in the glycoside were shown to be at positions-4′ and -6′ by UV spectral shifts (bathochromic shift of 45 and 46 nm of band I with sodium methoxide and sodium acetate, respectively) [6]. No change in the λ_{max}^{MeOH} with the addition of aluminium chloride confirmed that this compound was a 4-rhamnoside [8]. C-7 position of –Me group was confirmed by ^{1}H NMR studies.



1 R³ = H, R¹ = OH, R² = *O*-rha
2 R³ = Me, R² = OH, R¹ = *O*-rha

Mass spectral data showed a molecular ion peak at 430 Two fragments at *m/z* 166 and 118 showed that one –OH was present in the B ring and a –OH and –Me were present in the A ring Thus **2** is a new compound, namely, 4,6,4′-trihydroxy-7-methylaurone 4-*O*-rhamnopyranoside The aglycones of **1** and **2** were further confirmed by synthesis. Aglycone of **1** was sythesized by condensing 4,6-dihydroxycoumaranone with *p*-hydroxybenzaldehyde [10] The aglycone of **2** was prepared from 4,6-dihydroxy-7-methylcoumaranone and *p*-hydroxybenzaldehyde.

EXPERIMENTAL

The flowers of *Pterocarpus marsupium* were identified by the botanical survey of India. The air-dried and crushed flowers were extracted with boiling EtOH The concd extract (150 ml) fractionated into petrol and C_6H_6 The remaining mother liquor was concd and chromatographed over a silica gel column. Compound **1** was extracted from $CHCl_3$–EtOAc fractions and compound **2** from EtOAc fraction The compounds were crystallized from MeOH Purity of the compounds was checked by PC and TLC

Compound **1**, mp 178°, $C_{21}H_{20}O_9$ (Found C, 60 62, H 4 68 Calc. for $C_{21}H_{20}O_9$ C 60 57, H 4.80%) UV λ_{max}^{MeOH} nm 225, 245 (sh), 345 (sh), 392, + $AlCl_3$ 225, 245 (sh), 348 (sh), 452, + NaOMe 227, 247 (sh), 346 (sh), 462, + NaOAc 227, 248 (sh), 350, 460 IR ν_{max}^{KBr} cm^{-1} 3368 (–OH), 1632 (>C=O), 730, 680 ^1H NMR (60 MHz, $CDCl_3$) δ 1 2 (3H, *d*, rhamnose –Me), 4.2 (1H, *s*, H-1″), 3 55–3 8 (4H, *br*, sugar protons), 7.7–7 9 (2H, *m*, H-2′ and -6′), 6 1 (1H, *d*, $J = 2$ Hz, H-5), 6 3 (1H, *d*, $J = 2$ Hz, H-7), 6 74 (1H, *s*, =CH–), 6.8–7 0 (2H, *m*, H-3′ and -5′) MS (70 eV) *m/z* 416 (M^+), 270 (100), 269, 253, 242, 152, 124, 118. Acid hydrolysis (7% H_2SO_4) of **1** yielded an aglycone (R_f 0 75, solvent *n*-BuOH–HOAc–H_2O, 4 1 5, spray I_2 vapours) and rhamnose Aglycone of **1**, mp 208°, $C_{15}H_{10}O_5$ (Found C, 67 1, H 3 5, Calc C, 66 67, H 3 7%) ^1H NMR (60 MHz, $CDCl_3$) δ: 6 15 (1H, *d*, H-5), 6 36 (1H, *d*, H-7), 6.75 (1H, *s*, =CH–), 7 7–7 9 (2H, *m*, H-2′ and -6′), 6 8–7 0 (2H, *m*, H-3′ and -5′) Acetate (pyridine–Ac_2O, 24 hr at room temp.) mp 62° (Found C, 63 58, H 4 09, acetyl 32 59 Requires C, 63 63, H 4.04, acetyl 32 57%) Compound **2**, mp 168°, $C_{22}H_{22}O_9$ (Found C, 60.92, H 5 20 Calc for $C_{22}H_{22}O_9$ C 61 39, H 5 11%) UV λ_{max}^{MeOH} nm 220, 260, 350 (sh), 395, + NaOMe 225, 262 (sh), 360 (sh), 440, + NaOAc 222 (sh), 265 (sh), 359 (sh), 441, + $AlCl_3$ 222, 260, 352 (sh), 395. IR ν_{max}^{KBr} cm^{-1} 3374 (–OH), 1638 (>C=O), 722, 668 ^1H NMR (60 MHz, $CDCl_3$) δ 1 2 (3H, *d*, rhamnose –Me), 4 3 (1H, *s*, H-1″), 3.4–3.6 (4H, *br*, sugar protons), 7 8–7 9 (2H, *m*, H-2′ and -6′), 6.88–7 1 (2H, *m*, H-3′ and -5′), 6 25 (1H, *s*, H-5), 1 45 (3H, *s*, –Me), 6 65 (1H, *s*, =CH–) MS (70 eV) *m/z* 430 (M^+), 280 (100), 166, 138, 118 Acid hydrolysis of **2** with 7% H_2SO_4 gave an aglycone (R_f 0 71, solvent *n*-BuOH–HOAc–H_2O 4 1 5) and rhamnose Aglycone of **2**, mp 160°, $C_{16}H_{12}O_5$ (Found C, 68 2, H 4 10, Calc for $C_{16}H_{12}O_5$ C, 67 6, H 4 2%) Acetate (pyridine–Ac_2O, 24 hr at room temp) mp 92° (Found C, 64 31, H 4 42, acetyl 31 48, Calc C 64 39, acetyl 31 46%)

Synthesis of 4,6-4′-*trihydroxy-7-methylaurone* 2,4,6-*trihydroxytoluene*. To phloroglucinaldehyde [11] (1g) in HOAc (100 cm^3) Pd/C (5%, 1 5 g) was added and the mixture shaken in an atmosphere of pure H_2 Solution was filtered and catalyst washed with HOAc From the extract HOAc was removed under red pres H_2O was added and the product was extracted in Et_2O The Et_2O extract was washed with $NaHCO_3$ and then extracted with Na_2CO_3 soln Acidification of the carbonate solution gave crystalline needles, mp 52°

4,6-*dihydroxy-7-methyl coumaranone* Dry HCl gas was passed for 3 5 hr into a stirred mixture of trihydroxytoluene (80 g), 50 g chloroacetonitrile, 20 g powdered dry $ZnCl_2$ and 500 ml of dry Et_2O A second phase oily at first and later solid, separated The mix was left overnight, the solid separated and washed with fresh Et_2O. The yellow solid was dissolved in 400 ml ice H_2O and the solution heated under reflux for 1 hr The solid which separated on cooling was boiled for 5 hr in a solution of 100 g KOAc in 20 ml of water The hot solution was treated with decolorizing carbon and filtered The product was charged over a silica gel column From the ethyl acetate fraction yellow coloured needles were obtained, mp 140–145° (dec)

Synthesis of aurone Equimolecular amounts (100 mg) of 4,6-dihydroxy-7-methylcoumaranone and *p*-hydroxybenzaldehyde were dissolved in 5 ml HOAc and 0 2 ml conc HCl added [10] After 4 hr at room temp, the solution was poured into water and the product collected and recrystallized from aqueous EtOH, mp 160°

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