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TWO ANTHOCHLOR PIGMENTS FROM HEARTWOOD OF *PTEROCARPUS MARSUPIUM*

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Key Word Index—*Pterocarpus marsupium*; Leguminosae; 6,4′-dihydroxy-7-methylaurone 6-*O*-rhamnopyranoside; aureusidin 6-*O*-rhamnopyranoside.

Abstract—Two new aurone glycosides, 6,4′-dihydroxy-7-methylaurone 6-*O*-rhamnopyranoside and 4,6,3′,4′-tetrahydroxy aurone 6-*O*-rhamnopyranoside have been isolated and identified from the heartwood of *Pterocarpus marsupium.*

From the aqueous extract of the heartwood of *P. marsupium*, two novel aurone glycosides have been isolated and identified. Compound **1**, the yellow pigment analysed for $C_{22}H_{22}O_8$, mp 170°. It was found to be glycosidic in nature [1]. 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 the 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, $C_{16}H_{12}O_4$ was characterized as an aurone on the basis of colour reactions [2] and UV spectral data [3]. ^{1}H NMR studies showed six aromatic protons suggesting a trisubstituted aurone. A multiplet at δ7.69–7.9 (2H) was due to C-2′ and -6′ and multiplet at δ6.8–7.0 (2H) for C-3′ and -5′ protons. There was a singlet at δ6.67 for benzylic proton (=CH–) [4]. A singlet at δ1.44 was assignable to 3H of the –Me group. On acetylation it gave a diacetate, mp 96°, showing the presence of two hydroxyl groups. The positions of hydroxyls were shown to be at C-4′ and C-6 of aglycone by UV spectral shifts (bathochromic shift of 45 and 46 nm of band 1 with sodium methoxide and sodium acetate respectively). The presence of a free –OH at C-4′ position in the glycoside was confirmed by a large bathochromic shift in λ_{max}^{MeOH} (*ca* 70 nm) upon addition of sodium methoxide and (68 nm) with sodium acetate. C-7 position of –Me group was confirmed by NMR.

Mass spectral data showed a molecular ion peak at 414. Two fragments at m/z 150 and m/z 118 showed that one hydroxyl group was present in the B ring and –Me was present in the A ring. Thus the structure of **1** is confirmed. This compound has not been reported earlier from any other plant source.

Compound **2**, a yellow crystalline compound analysed for $C_{21}H_{20}O_{10}$, mp 264°, was found to be glycosidic in nature [1]. On hydrolysis it gave rhamnose (co-PC) and an aglycone which was shown to be an aurone by its colour reactions [2] and UV spectrum [3]. ^{1}H NMR studies of the aglycone showed five aromatic protons suggesting a tetrasubstituted nucleous. On acetylation it gave a tetraacetate, mp 182°, showing the presence of four hydroxyl groups. The aglycone was found to be the same as a [synthetic] sample of aureusidin (4,6,3′,4′-tetrahydroxyaurone) on the basis of chromatography and spectroscopy [5, 6]. The UV spectrum of the glycoside showed that the sugar was not at C-4 (a large bathochromic shift of 60 nm by aluminium chloride) or C-4′ (bathochromic shift of 85 nm in alkali). Methylation of the glycoside, followed by acid hydrolysis gave a product which was chromatographically and spectrally identical with a [synthetic] sample of 6-hydroxy-4,3′,4′-trimethoxyaurone. Thus the structure of **2** is confirmed; this is a new glycoside but the aglycone has been reported earlier [5, 6].

The structures of aglycones were further confirmed by synthesis. Aglycone of **1** was synthesized by condensing 6-hydroxy-7-methylcoumaranone and *p*-hydroxybenzaldehyde. Aureusidin, the aglycone of **2** was prepared from 4,6-dihydroxycoumaranone and 3,4-dihydroxybenzaldehyde.

EXPERIMENTAL

The heartwood of *P. marsupium* was collected from Bahraich and identified by the Allahabad branch of the Botanical Survey of India. It was crushed and extracted with water at room temp. The water extract was concd in a rotary evaporator at red. pres. The concd extract (150 ml) was mixed with absolute EtOH. A dark yellow ppt. was removed by filtering. The filtrate was concd and chromatographed over silica gel. Compound **1** was obtained from the C_6H_6–EtOAc fraction and crystallized from MeOH. Compound **2** was obtained from the EtOAc fraction and crystallized from MeOH. Purity of the compounds was checked by PC and TLC.

Compound **1**, mp 170°, $C_{22}H_{22}O_8$ (Found C 63.7, H 5.3. Calc. for $C_{22}H_{22}O_8$ C 64.0, H 5.26%). UV λ_{max}^{MeOH} nm: 260 (sh), 340 (sh), 404; +NaOMe 262 (sh), 348 (sh), 474; +NaOAc 260 (sh), 344 (sh), 472; $AlCl_3$ 260 (sh), 340 (sh), 404. IR ν_{max}^{KBr} cm^{-1}: 3365 (–OH), 1634 (C=O), 730, 678. ^1H NMR (90 MHz, $CDCl_3$) δ: 1.19 (3H, *d*, rhamnose-Me), 4.3 (1H, *s*, H-1"), 3.55–3.8 (4H, *br*, sugar protons), 7.7–7.89 (2H, *m*, H-2′ and 6′), 6.8–7.0 (2H, *m*, H-3′ and 5′), 6.1 (1H, *d*, J = 9cps, H-5), 6.4 (1H, *d*, J = 9cps, H-4), 6.7 (1H, *s*, =CH–). MS (70 eV) *m/z*: 414 $[M]^+$, 268 (100%) 150, 118.

Acid hydrolysis (7% H_2SO_4) of **1** yielded an aglycone (R_f 0.73, solvent *n*-BuOH–HOAc–H_2O, 4:1:5, spray I_2 vapours) and rhamnose. Aglycone of **1**, mp 200°, $C_{16}H_{12}O_4$ (Found C 71.15, H 4.5; Calcd for $C_{16}H_{12}O_4$ C 71.6, H 4.4%). UV λ_{max}^{MeOH} nm: 262 (sh), 340 (sh), 404; +NaOMe 262 (sh), 346 (sh), 452; +NaOAc 260 (sh), 344 (sh), 450; +$AlCl_3$ 260 (sh), 340 (sh), 404. ^1H NMR (90 MHz, $CDCl_3$) δ: 6.15 (1H, *d*, H-5), 6.45 (1H, *d*, H-4), 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 115° (Found: C 69.24, H 4.13, acetyl 24.78; Calc for $C_{20}H_{16}O_6$ C 68.16, H 4.45, acetyl 24.43%).

Compound **2**, mp 264°, $C_{21}H_{20}O_{10}$ (Found: C 61.02, H 4.70, Calcd for $C_{21}H_{20}O_{10}$ C 58.33, H 4.63, %), UV λ_{max}^{MeOH} nm: 256 (sh), 270 (sh), 340 (sh), 404; +NaOMe 254 (sh), 272 (sh), 346 (sh), 489; +$AlCl_3$ 256 (sh), 272 (sh), 344 (sh), 464. IR ν_{max}^{KBr} cm^{-1}: 3364 (OH), 1636 (C=O), 728, 680. ^1H NMR (90 MHz, $CDCl_3$) δ: 1.21 (3H, *d*, rhamnose-Me), 4.2 (1H, *s*, H-1″) 3.6–3.8 (4H, *br*, sugar protons) 6.1 (1H, *d*, J = 2 Hz, H-5) 6.3 (1H, *d*, J = 2 Hz, H-7) 7.4–7.68 (2H, *m*, C-2′, 6′) 6.94 (1H, *d*, J = 8 Hz, C-5′), 6.7 (1H, *s*, =CH–). MS (70 eV) *m/z*: 432 $(M)^+$, 286 (100%), 152, 134; 124.

Acid hydrolysis (7% H_2SO_4) of **2** yielded an aglycone and rhamnose. Aglycone of **2**, mp 302°, $C_{15}H_{10}O_6$ (Found: C 64.25, H, 3.45%). R_f 0.57 in BuOH–HOAc–H_2O, 4:1:5, spray I_2 vapours) λ_{max}^{MeOH} nm: 254, 269, 335 (sh) 398; +NaOMe (very unstable), +$AlCl_3$ 256, 270, 405 (sh), 458. Acetete (pyridine–Ac_2O, 24 hr. at room temp.) mp 182° (Found: C 59.62, H 4.13, acetyl 38.20; Calc C 60.79, H 3.96, acetyl 37.89%).

Synthesis of 6,4 *-dihydroxy* 7*-methylaurone.* 6*-Hydroxy-*7*-methyl coumaranone.* Dry HCl was passed for 4 hr into a stirred mixture of 2,6-dihydroxytoluene (75 g), 50 g chloroacetonitrile 20 g powdered dry $ZnCl_2$ and 500 ml dry Et_2O. A second phase, oily at first and later solid, separated. The mixture was allowed to stand overnight, the solid separated and was washed with fresh Et_2O. The light yellow solid was dissolved in 500 ml ice-water and the solution heated under reflux for 1 hr. The solid that separated on cooling was boiled for 5 hr in a solution of 100 g KOAc in 2 l of H_2O. The hot solution was treated with decolorizing carbon and filtered. The product separated as yellow needles, mp 132° (dec).

Synthesis of aurone. Equimolecular amounts (100 mg) of 6-hydroxy-7-methylcoumaranone and *p*-hydroxybenzaldehyde were dissolved in 5 ml HOAc and 0.2 ml conc. HCl. After 3–5 hr at room temp. the solution was poured into H_2O and the product collected and recrystallized from aq. EtOH, mp 190–192°. It was identical in every respect with the natural product.

Synthesis of aureusidin. It was prepared by condensing 4,6-dihydroxycoumaranone and 3,4-dihydroxybenzaldehyde using the same work-up as above.

Synthesis of 6*-hydroxy-*4,3′,4′*-trimethoxy aurone.* Condensation of 6-hydroxy-4-methoxy coumaranone and veratraldehyde gave the required product [5]. Yellow needles mp 270° (dec.) Anal. Found: C 64.95, H 5.01 calcd for $C_{18}H_{16}O_6$ C 65.85, H 4.9.

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