The genus *Pterocarpus* has received considerable attention in recent years because of its reputation for producing new variants of polyphenolic compounds [1—7]. *Pterocarpus marsupium* Roxb. (Leguminosae) finds use in the Ayurvedic and Unani systems for the treatment of diabetes [8, 9]. Earlier work on the plant has shown the presence of pterostilbene, liquiritigenin and isoliquiritigenin in heartwood and sapwood, l-epicatechin and pterostilbene in kino bark and two phytosterols, pterocarpol A and B, have also been reported [10]. From the rootwood of *Pterocarpus marsupium* the terpenic constituents β-eudesmol, erythrodiol-3-monoacetate and a new sesquiterpene alcohol selin-4(15)-en-1,11-diol, and also pterostilbene were isolated [11] as petroleum ether extractives. We now report detailed account of the isolation and structure elucidation of pterosupin and also the isolation of isoliquiritigenin, the isolation and structure elucidation of pterosupin also pterostilbene were isolated [11] as petroleum ether extractives. We now report detailed account of the isolation and structure elucidation of pterosupin and also the isolation of isoliquiritigenin, liquiritigenin, pseudobaptigenin, liquiritigenin, isoliquiritigenin, garbanzol, 5-deoxy-kaempferol and p-hydroxybenzaldehyde.

**Results and Discussion**

The chemical examination of *Pterocarpus marsupium* root afforded pterosupin, a new C-glucosyl-β-hydroxydihydrochalcone along with pseudobaptigenin, liquiritigenin, isoliquiritigenin, garbanzol, 5-deoxy-kaempferol and p-hydroxybenzaldehyde.

with the molecular formula, C_{21}H_{24}O_{10}, as white powder, m.p. 167—9°, [z]_{B}^{20} = +113.1° (MeOH, c = 0.76). Its chromatographic behaviour (R_{f} 0.60 BAW 4:1:5 and 0.76 15% HOAc) suggested the compound to be a glycoside and the resistance of the compound to acid hydrolysis pointed to C-glycosyl linkage and the sugar was identified as glucose by ferric chloride oxidation [12] and Viscontini-degradation [13]. A violet Fe-III-reaction and UV absorption at \( \lambda_{max} \) 218, 283 and 322 nm and reagent shifts noticed, were typical for a flavanone with free OH in 5 and 7 or a dihydrochalcone with free OH in 2' and 4' positions. The compound formed an octaacetate (m.p. 94—5°) indicating that it is a monoglycoside and the other 4 hydroxyls are present in the diarylpropanoid skeleton. There are 3 phenolic OH groups detected by ¹H-NMR, one of them at δ 13.15 being a chelated hydroxyl. The signals at δ 7.85 and 6.40 ppm (d, \( J = 8.5 \) Hz) showed the presence of only two ortho related protons in the A-ring. The A_{2}B_{2} doublets at δ 7.10 and 6.70 ppm (J = 9 Hz) were significant for a p-hydroxy substitution in B-ring. So the remaining OH must be alcoholic and present on central propanoid moiety. The ABMX pattern discerned with signals at δ 2.70 (dd, \( J = 15 \) & 8 Hz), 3.00 (dd, \( J = 15 \) & 8 Hz), 5.07 (m) and 5.42 (d, \( J = 7 \) Hz, exchangeable) did not agree with a flavanone structure.

Irradiation at δ = 5.07 produced two doublets at δ = 2.76 and 3.00 ppm while decoupling at δ = 2.90
resulted in a singlet at 5.07 ppm. These shift values are in good agreement with the \textsuperscript{1}H-NMR-data of gliricidol [14] \((2',4',3,5,\beta\text{-pentahydroxy-4-methoxy-dihydrochalcone}) which showed \(\delta = 5.21, 2.77,\) and 3.01 ppm for the corresponding signals but not with the data reported for nubigenol [15] \((2',4',6',4,\alpha\text{-pentahydroxydihydrochalcone}) which showed \(\delta = 4.40, 3.10\) and 3.45 ppm.

The \textsuperscript{13}C-NMR interpretation clarified the presence of C-glucopyranosyl sugar and 2',4'-dihydroxy substitution of A-ring. Since the \(\alpha\text{-CH}_2\) signal at \(\delta 40.1\) and \(\beta\text{-CHO}\) at 73.3 ppm (triplet and doublet in off resonance spectrum) show a similar absorbance to the shifts assigned to flavanone C-3 and C-2 respectively [15], a dihydrochalcone with a hydroxy group in \(\alpha\)-position to the carbonyl can be excluded. Thus pterosupin is 3'-\(\beta\text{-D-glucopyranosyl-2',4',4',\beta\text{-pentahydroxydihydrochalcone}) which showed \(\delta = 5.21, 2.77,\) and 3.01 ppm for the corresponding signals but not with gliricidol [14] \((2',4',3,5,\beta\text{-pentahydroxydihydrochalcone}) which showed \(\delta = 4.40, 3.10\) and 3.45 ppm.

Interestingly the flavonoids obtained in this work are 5-deoxy type and this observation has biogenetic significance.

**Experimental**

Mps were determined on Gallenkemp hot stage melting block and are uncorrected. IR and NMR spectra were recorded in KBr and DMSO-d\(_6\) or CDCl\(_3\) respectively. \textsuperscript{13}C-NMR was recorded at 20.15 MHz and MS at 70 eV by direct probe insertion.

**Plant material:** The main root of the plant was collected at the Mamandur forests, Andhra Pradesh, India.

**Extraction and fractionation:** The chips of the root (3.3 kg) were extracted with acetone and the concentrate was fractionated with light petroleum \((60-80^\circ),\) benzene, ether and ethyl acetate. The light petroleum soluble part on work up afforded the terpenic compounds \(\beta\text{-eudesmol, selin-4-(15)-en-1,8,11-diol and erythrodiol-3-monoacetate, and also pterosupin.}\) These compounds were identified by mp, UV, IR, NMR and MS studies and confirmation by mmp and co-chromatography with authentic samples. The ethyl acetate soluble fraction on repeated preparative PC in BAW \((4:1:5)\) and 15% HOAc resulted in compound G (200 mg), which is named pterosupin.

**Pterosupin** (1): White amorphous powder, m.p. 167.9\(^\circ\), \([\alpha]_D^15 = +113.1^\circ\) (MeOH, c = 0.76). PC: \(R_f 0.60\) (BAW, 4:1:5), 0.76 (15% HOAc). With alc. FeCl\(_3\) it gave violet colour but did not answer colour reactions with Zn/HCl, Mg/HCl and Na-Hg/HCl. With dil. alkali it gave yellow colouration. UV: \(\lambda_{\text{max}}\) (MeOH): 218, 241 sh, 283, 322 nm; + AlCl\(_3\): 225, 245 sh, 312, 360 nm; + AlCl\(_3\)/HCl: 225, 245 sh, 310, 362 nm; + NaOAc: 264, 285 sh, 341 nm; + NaOAc/H\(_3\)BO\(_3\): 278, 330 nm; + NaOMe: 220, 241 sh, 283, 323 nm. IR: \(\nu_{\text{max}}\) (KBr) 3380 (OH), 1620 (C = O), 1518, 1500, 1445 (Ar), 1255 cm\(^{-1}\) (C - O). X H-NMR: \(\delta 13.15 (s, 1H, \beta\text{-OH}), 9.1 (1H, 4-OH), 7.85 (d, J = 8.5 Hz, 1H, H-6'), 7.10 (d, J = 9 Hz, 2H, H-2 & 6), 6.70 (d, J = 9 Hz, 2H, H-3 & 5), 6.40 (d, J = 8.5 Hz, 1H, H-5'), 5.40 (d, J = 7 Hz, 1H, \(\beta\text{-OH}), 5.07 (m, 1H, \beta\text{-CH}), 3.00 (dd, J = 15 & 5 Hz, 1H, \alpha\text{-CH}), 2.76 (dd, J = 15 & 8 Hz, 1H, \alpha\text{-CH}). MS: \(m/z\) \(216\) (M\(^+\), 0.002), 418 (2), 400 (14.1), 312 (52.6), 294 (33.3), 281 (59.0), 263 (35.9), 245 (46.2), 233 (62.8), 219 (14.1), 217 (15.38), 215 (12.8), 205 (12.8), 191 (23.1), 189 (19.2), 179 (26.9), 163 (29.5), 1518, 1500, 1445 (Ar), 1255 cm\(^{-1}\) (C - O). X H-NMR: \(\delta 13.15 (s, 1H, \beta\text{-OH}), 9.1 (1H, 4-OH), 7.85 (d, J = 8.5 Hz, 1H, H-6'), 7.10 (d, J = 9 Hz, 2H, H-2 & 6), 6.70 (d, J = 9 Hz, 2H, H-3 & 5), 6.40 (d, J = 8.5 Hz, 1H, H-5'), 5.40 (d, J = 7 Hz, 1H, \(\beta\text{-OH}), 5.07 (m, 1H, \beta\text{-CH}), 3.00 (dd, J = 15 & 5 Hz, 1H, \alpha\text{-CH}), 2.76 (dd, J = 15 & 8 Hz, 1H, \alpha\text{-CH}). MS: \(m/z\) \(216\) (M\(^+\), 0.002), 418 (2), 400 (14.1), 312 (52.6), 294 (33.3), 281 (59.0), 263 (35.9), 245 (46.2), 233 (62.8), 219 (14.1), 217 (15.38), 215 (12.8), 191 (23.1), 189 (19.2), 179 (26.9), 163 (29.5), 162 (25.6), 161 (28.2), 136 (23.1), 135 (33.3), 108 (51.3), 107 (100), 106 (30.8), 91 (25.6), 77 (61.5).
204.7 (C = O), 164.1 (C-4'), 163.8 (C-2'), 159.3 (C-4), 132.1 (C-6'), 130.4 (C-2 & 6), 128.1 (C-1), 115.2 (C-3 & 5), 112.5 (C-1'), 108.5 (C-3'), 108.1 (C-5'), 81.4 (C-5''), 79.0 (C-3''), 73.8 (C-1''), 73.3 (C-ß), 71.2 (C-2''), 70.6 (C-4''), 61.4 (C-6''), 40.1 (C-α).

Pterosupin octaacetate: (Py/Ác2O); m. p. 94-5°

1H-NMR: (CDCl3, TMS int. standard) δ 7.80 (d, J = 8.5 Hz, 1H, H-6'), 7.25 (d, J = 8.5, 2 H, H-2 & 6), 7.02 (d, J = 8.5, 2H, H-3 & 5), 6.72 (d, J = 8.5 Hz, 1H, H-5'), 5.27 (m, 1H, β-CH), 4.76 (br. d, J = 10 Hz, 1H, H-1''), 3.12 (m, 2H, α-CH2), 2.44, 2.40, 2.30, (9H, 2', 4',4'-OAc), 2.23, 2.1, 1.80, (15 H, 2'', 3'', 4'', 6'', β-OAc).

FeCl3 oxidation: A mixture of pterosupin (50 mg) and ferric chloride (250 mg) in water (1.5 ml) was heated at 125° in an oil bath for 6 h. After usual work up and chromatographic examination the sugar was identified as glucose.

Viscontini degradation: To 2 mg of pterosupin in 0.1 ml of aqueous DMSO, 2 mg of sodium metaperiodate was added and kept at room temperature for 4 h. Then 2 mg of sodium borohydride in 0.1 ml of water was added and left over night. After usual work up the product was identified as glycerol by chromatography.

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