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CORYLINAL: A NEW ISOFLAVONE FROM SEEDS OF *PSORALEA CORYLIFOLIA*

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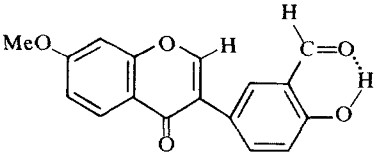
Key Word Index—*Psoralea corylifolia*; Leguminosae; derivatives of neobava-isoflavone; 7-*O*-methyl, 3′-formyl, 4′-hydroxy isoflavone

In a previous paper [1], we reported the isolation and constitution of corylidin, a new coumestane from seeds of *Psoralea corylifolia.* We now report the isolation of a new isoflavone and neobava-isoflavone, as their Me ethers, from the same seeds.

Due to difficulty in separating the phenolic isoflavones, the crystalline mixture from an Et_2O extract was partially methylated with CH_2N_2 followed by chromatography over Si gel. Corylinal Me ether (1) separated as white crystalline needles from MeOH (mp 223–224°). The compound did not correspond to any of the naturally occurring isoflavones by TLC, so that the possibility of it occurring naturally as a Me ether is ruled out.

The compound analysed for $C_{17}H_{12}O_5$, M^+ 296.0686 ($C_{17}H_{12}O_5$ requires M^+ 296.0684). λ_{max}^{EtOH} nm: 260, 305 and 345 (inf.). IR ν_{max}^{KBr} cm^{-1}: 3063 (—OH), 2875 and 2850 (ϕ-CHO), 1663 and 1632 (C=O), 1617 and 1605 (C=C), 1569, 1443, 1265, 932, 890, 838 and 825. PMR (100 MHz, d_6-DMSO) a sharp singlet at δ 3.90 (3H, —OMe), one proton doublet at 7.14 (J = 8 Hz, 1H, C-5′), a double doublet at 7.18 (J = 8 and 2 Hz, 1H, C-6), a doublet at 7.24 (J = 2 Hz, 1H, C-8), a double doublet at 7.8 (J = 8 and 2 Hz, 1H, C-6′), a doublet at 7.95 (J = 2 Hz, 1H, C-2′), a doublet at 8.09 (J = 8 Hz, 1H, C-5), a downfield singlet at 8.57 (1H, C-2) and a sharp singlet at 10.37 (1H, —C$\underline{H}$O).



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The MS showed prominent peaks at *m/e* (rel. int.) 296 (M^+, 54.7%), 281 (2.1), 268 (60), 240 (8.5), 140 (100), 139 (40), 122 (43.1) alongwith a retro Diels–Alder fragments at 151 (36.8), 150 (30.5) and 146 (8.0).

EXPERIMENTAL

Whole seeds of *Psoralea corylifolia* (5 kg) were extracted first with petrol (40–60°) and then with Et_2O The Et_2O extract (700 g) was dissolved in EtOH, boiled with a small quantity of activated charcoal and filtered hot. Solvent was completely removed and the residue dissolved in $CHCl_3$. Petrol was added to the $CHCl_3$ soln until it became turbid. On cooling a semisolid residue was obtained. This was washed with cold Et_2O and the yellow powder thus obtained showed the presence of two isoflavones which co-eluted on TLC (C_6H_6–Me_2Co, 4:1) R_f (0.32 and 0.30). The mixture was taken up in Et_2O and treated with CH_2N_2 and the reaction product showed on TLC that both isoflavones were methylated. After removing the solvent the reaction product (~3 g) was chromatographed on a Si gel column. Elution was carried out with petrol (40–60°), C_6H_6 and EtOAc mixtures of increasing polarity. Elution with C_6H_6–EtOAc (49:1) yielded compound A named corylinal methyl ether (1) as white needles (from MeOH) (50 mg) mp 223–224°, R_f 0.37. It gave a positive test with aq. $FeCl_3$ soln and also responded to 2:4—DNP reagent.

Isolation of neobava-isoflavone-7-O-methyl ether. The last fractions of the C_6H_6–EtOAc (49.1) eluate yielded white crystalline needles (compound B) from Me_2CO–petrol, mp 148–9°. R_f 0.47. It analysed for $C_{21}H_{20}O_4$, M^+ 336.1343 ($C_{21}H_{20}O_4$ req. M^+ 336.1360). λ_{max}^{EtOH} nm. 250, 265 and 308 (inf.). IR ν_{max}^{Nujol} cm^{-1}: 3360 and 1620. Compound B formed a monoacetate mp 96° and analysed for $C_{23}H_{22}O_5$, M^+ 378.1455 ($C_{23}H_{22}O_5$ req. M^+ 378.1465) and its IR ν_{max}^{KBr} cm^{-1}: 1750, 1637, 1628 and 1600. Compound B underwent cyclodehydrogenation with DDQ in dry C_6H_6 and the resulting compound gave white crystalline needles from Me_2CO–petrol, mp 101° (identical with natural corylin Me ether, lit. [2] mp 101°). B on further methylation with CH_2N_2 formed a Me ether which crystallised from petrol, mp 68–9°. From spectral data and the above reactions, B was identified as 7-*O*-Me ether of neobava-isoflavone [3].

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