

PSORALENOL: A NEW ISOFLAVONE FROM THE SEEDS OF *PSORALEA CORYLIFOLIA*

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Continuing our studies on the constituents of the ether extract of *Psoralea corylifolia*, we hereby report the isolation and constitution of a new isoflavone psoralenol. In our previous paper [1], we reported the isolation and constitution of corylinal and neobavaisoflavone 7-O-methyl ether. The mother liquor left after the isolation of the above mentioned isoflavone mixture was repeatedly chromatographed over Si gel. Benzene-EtOAc (1:1) and EtOAc eluates afforded an amorphous solid which on recrystallization from Me_2CO -petrol mixture gave fine crystals of psoralenol (1), mp 240–242°. The compound analysed for $\text{C}_{20}\text{H}_{18}\text{O}_5$. M^+ 338.1143 ($\text{C}_{20}\text{H}_{18}\text{O}_5$ requires: M^+ , 338.1152). $\lambda_{\text{EtOH}}^{\text{max}}$ (log ϵ) nm: 265 (4.29), 310 sh (4.04) and 328 sh (3.54); $\lambda_{\text{EtOH}+\text{NaOAc}}^{\text{max}}$ nm: 260, 310 sh and 345 sh; $\lambda_{\text{EtOH}+\text{NaOH}}^{\text{max}}$ nm: 260, 280 sh and 345; IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3200 (OH), 1624 (C=O), 1585 (C=C), 1490, 1450, 1378 and 1390 (inf.) (gem dimethyl), 1295, 1265, 1192, 1150, 1120, 1092, 1055, 950 and 852. PMR (60 MHz, $\text{Me}_2\text{CO}-d_6$): two sharp singlets at δ 1.27 and 1.37 (6H, $\text{Me}_2\text{C}-$), a triplet at 2.92 (2H, $\phi\text{-CH}_2$ at C-4"), a multiplet at 3.85 (1H, C-5"), a doublet at 6.82 (J = 8.5 Hz, 1H, C-5'), a complex multiplet between 6.9 and 7.1 (2H, C-8 and C-6), another multiplet between 7.25 and 7.5 (2H, C-2' and C-6'), a doublet at 8.13 (J = 7.5 Hz, 1H, C-5), and a singlet at 8.20 (1H, C-2). Positions of C-6, C-8, C-2' and C-6' protons were located with the help of decoupling experiments. The above two complex multiplets (6.9–7.1 and 7.25–7.5) were simplified when irradiated at 487.8 and 409.2 Hz, respectively.

The MS showed prominent peaks at m/e (rel. int.) 338 (M^+ , 100%), 319 (7.3), 305 (14.3), 279 (35.37), 268 (95), 267 (88), 239 (23.5), 237 (26.3), 183 (4.4), 181 (4.4), 169 (11), 137 (41.2), the last two fragments arising as a result of retro Diels-Alder fragmentation of m/e 305.

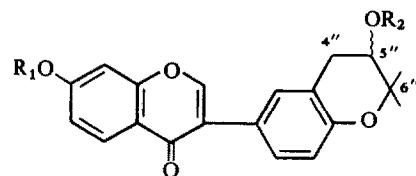
The compound formed a diacetate ($\text{Ac}_2\text{O}/\text{Py}$) indicating the presence of two hydroxyls. It formed a monomethyl ether on treatment with CH_2N_2 which on acetylation gave a monoacetate. This showed that one of the hydroxyls is phenolic while the other is alcoholic.

Psoralenol diacetate (2): mp 175–176° (EtOH) $\lambda_{\text{EtOH}}^{\text{max}}$ (log ϵ) nm: 260 (4.49) and 310 sh (4.00); IR $\nu_{\text{Nujol}}^{\text{cm}^{-1}}$: 1780, 1750 and 1625. PMR (60 MHz, CDCl_3): δ 1.45 (s, 6H, $\text{Me}_2\text{C}-$), 2.17 (s, 3H, O—COCH₃), 2.45 (s, 3H, O—COCH₃), 3.1 (m, 2H, $\phi\text{-CH}_2$ at C-4"), 5.13 (t, 1H, C-5"), 6.95 (d, J = 8 Hz, 1H, C-5'), 7.22 (dd, J = 2 and 8 Hz, 1H, C-6), 7.25–7.42 (complex multiplet, 3H, C-6', C-2' and C-8), 8.0 (s, 1H, C-2) and 8.35 (d, J = 8 Hz, 1H, C-5). The frequency shift of about 75 Hz observed for C-5" proton in the case of (1) and its acetate (2) is in excellent agreement with its assigned character, as it is

well known [2] that a methine proton attached to a carbon bearing secondary hydroxyl group usually exhibits absorption in the PMR at a frequency *ca* 60–70 Hz higher than when the hydroxyl is acetylated. In agreement with the above assignments, irradiation at 501 and 417 Hz by double resonance technique decoupled C-6 and C-6' protons, respectively, resulting in each case in the simplification of the complex multiplet into broad singlets at δ 7.22 and 7.42, respectively. The doublet at δ 8.35 was reduced to a sharp singlet by irradiation at 433 Hz. Similarly the multiplet at 3.1 was reduced to two singlets by irradiation at 308 Hz, while the triplet at 5.13 changed into a sharp singlet by irradiation at 186 Hz. MS showed prominent peaks at m/e (rel. int.) 422 (M^+ , 17.4%), 380 (4.3), 362 (25), 347 (100), 320 (23.4), 319 (28.1), 305 (81.2), 279 (19.5), 268 (40.6), 267 (23.4), 239 (10.5), 237 (17.2), 183 (11.7), 169 (14.4), and 137 (50).

Psoralenol methyl ether (3) crystallized from Me_2CO -petrol mixture as needles, mp 145–147°. $\lambda_{\text{EtOH}}^{\text{max}}$ (log ϵ) nm: 265 (4.5) and 312 sh (4.05). PMR (60 MHz, CDCl_3): δ 1.45 (s, 6H, $\text{Me}_2\text{C}-$), 2.98 (t, 2H, $\phi\text{-CH}_2$ at C-4'), 3.87 (m, 1H, C-5') and 4.0 (s, 3H, OMe).

Psoralenol monomethyl ether monoacetate (4) mp 170–171° (Me_2CO -petrol mixture). $\lambda_{\text{EtOH}}^{\text{max}}$ (log ϵ) nm: 262 (4.39) and 310 sh (3.94). PMR (60 MHz, CCl_4): δ 1.3 (s, 6H, $\text{Me}_2\text{C}-$), 2.03 (s, 3H, O—COCH₃), 2.93 (m, 2H, $\phi\text{-CH}_2$ at C-4"), 3.87 (s, 3H, OMe) and 4.97 (t, 1H, C-5"). The aromatic and C-2 protons both in (3) and (4) were observed in their respective positions.



1 $\text{R}_1 = \text{R}_2 = \text{H}$

2 $\text{R}_1 = \text{R}_2 = \text{Ac}$

3 $\text{R}_1 = \text{Me}$, $\text{R}_2 = \text{H}$

4 $\text{R}_1 = \text{Me}$, $\text{R}_2 = \text{Ac}$

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