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A *C*-FORMYLATED CHALCONE FROM *PSORALEA CORYLIFOLIA*

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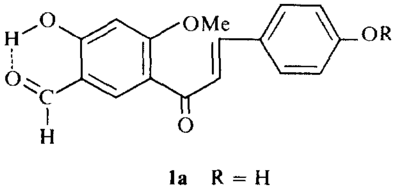
Key Word Index—*Psoralea corylifolia*; Leguminosae; seeds; roots; 5′-formyl-4,4′-dihydroxy-2′-methoxy-chalcone; trilaurin; daidzein; coumestrol.

Earlier workers [1, 2] have reported the isolation and constitution of a *C*-formylated chalcone, neobavachalcone, from the seeds of *Psoralea corylifolia*. We now report the isolation and characterization of a new chalcone, isoneobavachalcone, which is spectrally similar to neobavachalcone except in the IR region. It was obtained by repeated column chromatography of the ether extract of the defatted seeds over Si gel. A survey of the literature shows that no work has been done on the roots of this plant. We have, therefore, also carried out a thorough investigation of the roots and hereby report the isolation of trilaurin, daidzein and coumestrol for the first time.

Isoneobavachalcone (**1a**) crystallized from EtOH as yellow granules, mp 231–232°. High resolution MS gave its molecular formula as $C_{17}H_{14}O_5$. Its chalcone structure was indicated by its UV bands at 230, 266, 306 and 378 nm. A bathochromic shift of 50 nm of the longer wavelength band, along with an increase in intensity with NaOMe, showed the presence of a 4-OH group. Presence of a bathochromic shift with $AlCl_3$ which did not undergo any change with the addition of HCl showed the presence of chelated OH group. This was further confirmed from its IR (KBr) spectra which showed a characteristic absorption at 1660 cm^{-1} due to a salicylaldehyde moiety. It also showed characteristic absorption at 1629 cm^{-1} due to chalcone carbonyl and at 842 cm^{-1} due to a *para*-substituted benzene ring. The compound formed a monoacetate (**1b**) (Ac_2O–Py/ at water bath temperature), but complete methylation gave a trimethyl ether. ^1H NMR (DMSO-d_6) of the parent compound showed the presence of one–OMe group at δ 4.1. Thus, it has two free OH groups, one of which is strongly hydrogen-bonded. A singlet at δ 10.0 integrating for one proton clearly showed the presence of a chelated formyl group.

^1H NMR ($CDCl_3$, 100 MHz) of the acetate gave a sharp singlet at δ 2.34 for the protons of a single acetoxy group and a sharp singlet at 4.00 for the protons of a single methoxyl. Further there was a sharp singlet at 6.52 integrating for one proton at C-3′, an *ortho*-coupled doublet centred at 7.20 integrating for two protons at C-3 and C-5 of an A_2B_2 system of a *para*-substituted B-ring; the other doublet for C-2 and C-6 appeared at 7.82. α- and β-protons of the chalcone molecule appeared as a sharp singlet at 7.68. A singlet of one proton which appeared very downfield at 8.48 was assigned to the C-6′ proton and a sharp singlet at 9.37 to the formyl group at C-5′. The presence of a downfield singlet at 12.95 integrating for one proton was due to a chelated phenolic hydroxyl group at C-4′. The ^1H NMR ($CDCl_3$, 60 MHz) of the dimethyl ether of **1a** showed the presence of three OMe groups as singlets at δ3.7, 3.9 and 4.0, thus confirming the presence of two free OH groups in addition to the one which already exists in the natural compound as a monomethyl ether. An attempt to cyclize the chalcone by refluxing it in anhydrous pyridine containing some piperidine (for 36 hr) failed to yield any flavanone, proving that oxygen function at C-2′ is blocked.



1a R = H
1b R = Ac

The presence of the 4-OH group was confirmed by subjecting isoneobavachalcone to alkali degradation, *p*-hydroxybenzoic acid being identified as one of the products. Based on the above data, isoneobavachalcone can be assigned the structure 5′-formyl-4,4′-dihydroxy-2′-methoxychalcone. The proposed structure was also supported by MS which showed similar major fragmentation to that of neobavachalcone [2].

There are only a few compounds known in the literature [3–5] where the 2′-hydroxyl position of the chalcone is alkylated.

EXPERIMENTAL

Isolation of isoneobavachalcone from the seeds. Whole seeds of *Psoralea corylifolia* (3 kg) were defatted and extracted with Et_2O. Removal of the solvent yielded a viscous mass (350 g) which was subjected to column chromatography over Si gel. The column was successively eluted with C_6H_6, C_6H_6–Et_2O (1:1), Et_2O, Et_2O–$CHCl_3$ (1:1), $CHCl_3$ and $CHCl_3$–MeOH (9:1). The combined residues from the Et_2O and Et_2O–$CHCl_3$ (1:1) eluates were repeatedly subjected to column chromatography over Si gel and eluted with C_6H_6 and C_6H_6–EtOAc with increasing polarity. The C_6H_6–EtOAc (9:1) eluate gave a yellow residue which on crystallization from EtOH yielded a yellow amorphous compound isoneobavachalcone (**1a**), mp 231–232° (100 mg, R_f 0.42, C_6H_6–EtOAc, 4:1). The compound gave a yellow colour with NaOH, orange–red with conc H_2SO_4 and positive reactions with 2:4-DNPH and ferric chloride. The compound analysed for $C_{17}H_{14}O_5$; M^+ 298.0845 ($C_{17}H_{14}O_5$ requires M^+ 298.0837).

λ_{max}^{EtOH} (log ε) nm: 230 (4.18), 266 (4.36), 306 (4.03, sh), 378 (4.47); +NaOMe 266 (4.39), 328 (4.35), 428 (4.51), +NaOAc 255 (4.33, sh), 268 (4.36), 328 (4.39), 380 (4.32); +AlCl$_3$ 238, 310 inf. 360, 425 inf; +AlCl$_3$ + HCl 238, 310 inf, 360, 425 inf. IR ν_{max}^{KBr} cm^{-1}: 3140, 1660, 1629, 842. ^{1}H NMR (60 MHz, DMSO-d_6): δ 4.1 (3 H, *s*, OMe), 6.85 (1 H, *s*, C-3'), 7.05 (2 H, *d*, *J* = 8 Hz, C-3, C-5), 7.95 (4 H, complex multiplet, α- and β-H, C-2, C-6), 8.7 (1 H, *s*, C-5') and 10.0 (1 H, *s*, –CHO). MS *m/e* (%): 298 (M$^+$, 80.0), 297 (58.7), 281 (18.7), 269 (18.7), 255 (8.0), 205 (46.7), 192 (24.0), 179 (100.0), 147 (38.7), 120 (52.0), 119 (49.3), 107 (52.0) and 91 (53.3).

Isoneobavachalcone monoacetate (**1b**) was obtained (Ac$_2$O–Py) as yellow needles from ether, mp 186–187°. λ_{max}^{EtOH}nm: 228, 267, 315, and 350. IR ν_{max}^{KBr} cm^{-1}: 1740, 1685, 1635 and 840. ^{1}H NMR (100 MHz, CDCl$_3$): δ 2.34 (3 H, *s*, O-COMe), 4.0 (3 H, *s*, OMe), 6.52 (1 H, *s*, C-3'), 7.20 (2 H, *d*, *J* = 8 Hz, C-3, C-5), 7.68 (2 H, *s*, α- and β-H of chalcone), 7.82 (2 H, *d*, *J* = 8 Hz, C-2, C-6), 8.48 (1 H, *s*, C-6'), 9.37 (1 H, *s*, –CHO) and 12.95 (1 H, *s*, D$_2$O exchange, phenolic OH at C-4').

Isoneobavachalcone dimethyl ether was obtained (DMSO$_4$–K$_2$CO$_3$ in Me$_2$CO refluxed for 60 hr) as yellow needles from Me$_2$CO–petrol, mp 141–143° decomp. (lit. [1, 2] mp 140–141°).

Alkaline degradation of isoneobavachalcone. 1.0 mg (**1a**) was refluxed with aq. KOH (50 %, 2.5 ml) for 3 hr. The soln was cooled, acidified with HCl and extracted with Et$_2$O. The Et$_2$O soln was extracted with 5 % aq. NaHCO$_3$, the alkaline soln was neutralized and then re-extracted with Et$_2$O. The conc Et$_2$O extract contained *p*-hydroxybenzoic acid by PC (*n*-BuOH–5 % HOAc, 1:1, R_f 0.85) comparison with an authentic sample.

Isolation of root constituents. Petrol extract (16.7 g) obtained from powdered roots (2.3 kg), on cooling at 10°, gave trilaurin mp 44–45° (lit. [6] mp 49°, yield 1.2 g) and M$^+$ 638. The mother liquor left after the isolation of trilaurin was chromatographed over Si gel and gave angelicin, psoralen and sitosterol. Defatted roots on extraction with EtOAc gave 28 g residue, which were chromatographed over a Si gel column and eluted with C$_6$H$_6$, C$_6$H$_6$–EtOAc and EtOAc–MeOH. The first few fractions of the C$_6$H$_6$–EtOAc (1:1) eluates yielded needles from Me$_2$CO–petrol, mp 314–316° (yield 38 mg). Molecular ion at 254.0569 analysed for $C_{15}H_{10}O_4$ ($C_{15}H_{1.}O_4$ requires: M$^+$, 254.0579). It was identified as daidzein (lit. [6] mp 323°, co-TLC, mmp, IR and ^{1}H NMR). Diacetate, mp 183–184° (lit. [6] 187°). Later fractions of the C$_6$H$_6$–EtOAc (1:1) eluate yielded a violet fluorescent compound from EtOH, mp > 350°, M$^+$ 268 (yield 30 mg). It was identified as coumestrol (lit. [6] mp 385° (block), co-TLC, IR and ^{1}H NMR).

EtOAc–MeOH (9:1) eluate gave sitosterol-D-glucoside, mp 268–270° (lit. [6] mp 283–285°).

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