

EXPERIMENTAL

The ^{13}C NMR spectra of compounds **3** to **7** were recorded at 15 MHz in $\text{DMSO}-d_6$ with TMS ($\delta = 0$) as int. ref. using micro-cells. FT-NMR conditions were as follows: spectral width, 4 kHz; number of data points, 8192; pulse repeat time, 1.2 sec; number of pulses, 5000–100000; pulse flipping angle, 45° . The ^{13}C NMR spectra of compounds **1** and **2** were recorded at 25.05 MHz in $\text{DMSO}-d_6$ with TMS ($\delta = 0$) as int. ref. using 1.8 mm tubes. FT-NMR conditions were as follows: spectral width, 5 kHz; number of data points, 8192, 4096; pulse repeat time, 1.5, 1.0 sec; number of pulses, 40000–60000; pulse flipping angle, 60° , 70° . Samples of phillyrin (**5**) and (+)-pinocresinol- β -D-glucoside (**6**) were obtained from the fruit of *Forsythia suspensa* Vahl as described in ref. [5].

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BAVACHROMANOL: A NEW CHALCONE FROM THE SEEDS OF PSORALEA CORYLIFOLIA

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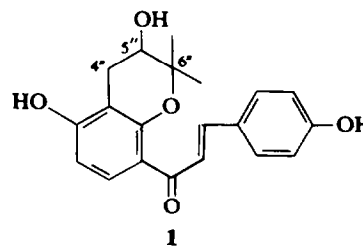
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Key Word Index—*Psoralea corylifolia*; Leguminosae; 4,4',5"-trihydroxy-6",6"-dimethyldihydropyrano-(2",3":2'.3')-chalcone.

In our earlier communication [1], the isolation of psoralenol, a new isoflavone from the seeds of *Psoralea corylifolia*, was reported. In the present paper we describe the isolation and characterization of bavachromanol, a new chalcone. It was obtained by repeated column chromatography of the ether extract of the defatted seeds over Si gel.

Bavachromanol (**1**) crystallized from EtOAc as light yellow granules. High resolution MS gave its molecular formula as $\text{C}_{20}\text{H}_{20}\text{O}_5$. Its chalcone structure was indicated by its UV bands at 242, 308 and 350 nm. A bathochromic shift of 72 nm of the longer wavelength band along with an increase in the intensity with NaOMe showed the presence of a 4-OH group. The appearance of a long wavelength shoulder with NaOAc showed that 4'-OH may be present. Absence of a bathochromic shift with AlCl_3 showed the absence of any chelated OH groups. Its IR (KBr) showed characteristic absorptions at 1638 cm^{-1} due to chalcone carbonyl, at 1378 and 1362 cm^{-1} due to gem dimethyl and at 830 cm^{-1} due to a *para*-substituted benzene ring. The compound formed a triacetate indicating the presence of three OH groups.



^1H NMR ($\text{Me}_2\text{CO}-d_6$) of the compound gave two sharp singlets at δ 1.43 and 1.49 for gem dimethyl protons. A multiplet at δ 2.81 showed the presence of two benzylic protons. The presence of a methine proton attached to a carbon bearing a secondary hydroxyl group was shown by a triplet at δ 3.92, which in conformity with its assigned character, shifted downfield to δ 5.09 in the ^1H NMR of its triacetate. Further, there was an *ortho*-coupled doublet centred at δ 6.92 integrating for two protons at C-3 and C-5 and an A_2B_2 system of a *para*-substituted B-ring, the other doublet for C-2 and C-6 protons merging with a complex multiplet between δ 7.36 and 7.66 integrating for five protons. Another *ortho*-coupled doublet at δ 6.54 integrating for one proton could be assigned to

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the C-5' proton indicating that the 5' and 6' positions of the A-ring were free. The corresponding downfield doublet for C-6' and the signal for α and β protons of the chalcone molecule appeared in the multiplet between δ 7.36 and 7.66. $^1\text{H NMR}$ (CDCl_3) of the triacetate showed the presence of three OAc groups, thus confirming the presence of three OH groups in bavachromanol. The presence of a 4-OH group was confirmed by subjecting bavachromanol to alkali hydrolysis; *p*-hydroxybenzoic acid was identified as one of the products. Based on the above data, bavachromanol can be assigned the structure 4,4',5"-trihydroxy-6'',6''-dimethyldihydropyrano (2'',3'':2',3')-chalcone (**1**). An alternative structure in which the isopentanyl side chain is linked to the 4'-OH group was ruled out, because it did not show the characteristic bathochromic shift in the longer wavelength band in its UV absorption with AlCl_3 [2a].

The proposed structure was supported by MS, the major fragmentation pathways being those characteristic of chalcones [2b] with a 2,2-dimethylchroman ring [3] and compounds containing a hydroxychroman ring [4].

This is the first report of the occurrence in *Psoralea* seeds of a chalcone containing a chroman ring closed upon the 2'-hydroxyl position. Rottlerins are among other chalcones known to contain this type of 2'-linkage [3,5].

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Defatted whole seeds (1.5 kg) were extracted with Et_2O at room temp. Removal of the solvent yielded a viscous mass (200 g) which was subjected to column chromatography over Si gel. The column was successively eluted with C_6H_6 and C_6H_6 -EtOAc mixtures with increasing polarity, and finally with EtOAc. The combined residue from C_6H_6 -EtOAc (1:1) and EtOAc eluates which showed one major spot on TLC (R_f 0.52, CHCl_3 -MeOH, 9:1; red colour with ceric ammonium sulphate reagent) was rechromatographed over Si gel. C_6H_6 -EtOAc (3:2) eluates yielded an amorphous solid which on crystallization from C_6H_6 -EtOAc and recrystallization from EtOAc afforded light yellow granules of bavachromanol (**1**), mp 235–236°. The compound gave a yellow colour with NaOH, orange-red with conc H_2SO_4 and a positive reaction with 2:4-DNPH. The compound analysed for $\text{C}_{20}\text{H}_{20}\text{O}_5$, M^+ , 340.1299 ($\text{C}_{20}\text{H}_{20}\text{O}_5$ requires: M^+ , 340.1309). $\lambda_{\text{max}}^{\text{MeOH}}$ (log ϵ) nm: 242 (4.06), 308 sh (4.11), 350 (4.39); +NaOMe 263 (4.08), 318 (3.98), 422 (4.55); +

NaOAc 308 sh, 350, 436 sh; + AlCl_3 240, 308 sh, 352. $^1\text{H NMR}$ (60 MHz, $\text{Me}_2\text{CO}-d_6$): δ 1.43 and 1.49 (6H, $2 \times s$ Me_2C -), 2.81 (2H, multiplet, ϕ - CH_2 at C-4''), 3.92 (1H, *t*, C-5''), 6.54 (1H, *d*, $J = 8$ Hz, C-5'), 6.92 (2G, $dJ = 8$ Hz, C-3 and C-5), 7.36–7.55 (5H, complex multiplet, α - and β -H, C-2, C-6 and C-6'). MS m/e (%): 340 (M^+ , 24), 339 (3), 322 (2.9), 312 (20), 307 (4.3), 282 (7.1), 281 (3.5), 279 (8.6), 269 (11), 268 (31.1), 254 (24), 253 (17.1), 240 (21.4), 225 (3), 221 (5.4), 161 (14.3), 150 (17), 149 (100), 147 (18.6), 122 (16), 121 (14.3), 120 (19), 119 (20), 118 (7.1) and 107 (14.2).

Bavachromanol triacetate was obtained (Ac_2O , Py) as colourless needles, mp 153–154° (Me_2CO -petrol mixture). It analysed for $\text{C}_{26}\text{H}_{26}\text{O}_8$, M^+ , 466.1614 ($\text{C}_{26}\text{H}_{26}\text{O}_8$ requires: M^+ , 466.1624). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1765, 1737, 1655. $^1\text{H NMR}$ (60 MHz, CDCl_3): δ 1.36 (6H, *s*, Me_2C -), 2.10 (3H, *s* *o*-COMe), 2.33 (6H, *s*, $2 \times \text{O-COMe}$), 2.83 (2H, *m*, ϕ - CH_2 at C-4''), 5.06 (1H, *t*, C-5''), 6.76 (1H, *d*, $J = 8$ Hz, C-5'), 7.13 (2H, *d*, $J = 9$ Hz, C-3 and C-5), 7.5–7.69 (5H, complex multiplet, C-2, C-6, C-6' and α - and β -H of the chalcone molecules). MS m/e (%): 466 (M^+ , 3.3), 424 (5.3), 407 (5.3), 406 (16.6), 392 (12.5), 391 (50), 382 (3.3), 381 (4.5), 365 (9), 364 (25), 355 (12), 350 (25), 349 (95), 340 (1.6), 322 (36), 312 (3), 307 (100), and fragments as shown for **1**.

Alkaline hydrolysis of bavachromanol. 5.0 mg **1** was refluxed with aq. KOH (50%, 5 ml) for 3 hr. The soln was cooled, acidified with HCl and extracted with Et_2O . The Et_2O soln was extracted with 5% aq. NaHCO_3 , the alkaline soln was neutralized and then re-extracted with Et_2O . The conc Et_2O extract contained *p*-hydroxybenzoic acid, by PC (*n*-BuOH-5% HOAc, 1:1; R_f 0.87) comparison with an authentic sample.

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