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A CHALCONE AND FLAVANONES FROM *DIDYMOCARPUS PEDICELLATA*

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Key Word Index—*Didymocarpus pedicellata*; Gesneriaceae; 3′-hydroxy-2′,4′,5′,6′-tetramethoxychalcone; 5-hydroxy-6,7,8-trimethoxyflavanone; 6-hydroxy-5,7-8-trimethoxyflavanone; isopedicin; structural determination.

Eleven flavonoids have been isolated previously from *Didymocarpus pedicellata* R.Br. [1–5]. Recently we have synthesized 7-hydroxy-5,6,8-trimethoxyflavanone and contradicted [6] the structure assigned to didymocarpin [3], a new flavanone reported from the leaves of *D. pedicellata*. This led to a chemical re-investigation of *D. pedicellata* to identify didymocarpin and other related minor components. The present communication reports the isolation and characterization of three flavonoids, 3′-hydroxy-2′,4′,5′,6′-tetramethoxychalcone (**1**), 5-hydroxy-6,7,8-trimethoxyflavanone (**3**) and 6-hydroxy-5,7,8-trimethoxyflavanone (**4**). Of these, **1** and **3** are new natural products while **4** has been reported earlier from *D. pedicellata* [3].

The IR ($>$C=O) and NMR spectrum of **1** and its methyl ether **2** showed that it is a chalcone with four methoxyls and one hydroxyl group. In the mass spectrum, the appearance of peaks at *m/z* 267 and 241 corresponding to the loss of phenyl and styrene fragments from M^+ confirmed that the B-ring in **1** is unsubstituted and that the four methoxyls and one hydroxyl are present in ring A. The absence of a bathochromic shift in the UV spectrum (λ_{max}^{MeOH} 289 nm) on addition of $AlCl_3$ or NaOAc suggested that the 2′-, 4′- and 6′-positions are not hydroxylated. Hence, the hydroxyl group must be present at the 3′- or 5′-positions. These being equivalent, structure **1** has been assigned to the new chalcone.

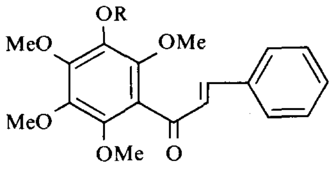
The mass fragmentation pattern and NMR spectrum of **3** and its methyl ether **5** confirmed that it is a flavanone with no B-ring substitution. A bathochromic shift in the UV spectrum of **3** on addition of $AlCl_3$/HCl fixed position 5 for the hydroxyl group and therefore structure **3** was assigned to the new flavanone. Previously, Rao *et al.* [7] converted 5,6,8-trihydroxy-7-methoxyflavanone into **3** by methylation with CH_2N_2 and recorded only its melting point.

EXPERIMENTAL

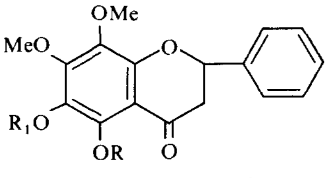
Isolation. Dried whole plant (3 kg) of *Didymocarpus pedicellata*, devoid of any dust on the under leaf surface, was obtained from the Pratap Nursery and Seed Stores, Dehradun and identified by the Department of Botany, University of Delhi. It was successively extracted with petrol, C_6H_6 and EtOH. The C_6H_6 extract was concd and chromatographed on Si gel (400 g) with a petrol → C_6H_6 → EtOAc gradient. The fractions eluted with EtOAc–C_6H_6 (1:9) on cryst. (EtOAc–petrol) afforded **1**. The EtOH extract was also concd and chromatographed on Si gel (500 g) using a $CHCl_3$ → MeOH gradient. The fractions eluted with $CHCl_3$–MeOH (49:1) gave **3** while those eluted with $CHCl_3$–MeOH (24:1) gave **4**.

Identification. **1** was obtained as light yellow crystals (100 mg), mp 80°. $C_{19}H_{20}O_6$ (M^+ 344); R_f: 0.80 (Si gel, EtOAc–C_6H_6, 1:9); 0.61 (Si gel, $CHCl_3$–MeOH, 250:1); UV λ_{max}^{MeOH} nm (log ε): 289 (4.20); $AlCl_3$, 289; NaOAc, 289; IR ν_{max}^{KBr} cm^{-1}: 1632, 1565, 1415, 1225, 1055, 970, 750 and 631; MS *m/z*: 329 ($M^+ - 15$: $M^+ - Me$), 316 ($M^+ - 28$; $M^+ - CO$), 267 ($M^+ - 77$; $M^+ - C_6H_5$), 241 ($M^+ - 103$, $M^+ - C_6H_5CH{=}CH^+$) and 213 *m/z* 241–28; *m/z* 241 − CO); ^{1}H NMR ($CDCl_3$): δ 3.86, 3.88, 3.97 and 4.08 (3 H each, *s*, 4 × —OMe), 5.81 (1 H, *s*, D_2O exchangeable, —OH), 7.06 (1 H, *d*, *J* = 17 Hz, Hα) and 7.46 (6 H, *m*, 5 protons of B ring and Hβ). **1** gave no colour with alcoholic $FeCl_3$ but gave a red colour with conc. H_2SO and aq. NaOH. On methylation with ethereal diazomethane **1** gave **4** methyl ether **2**, mp 93–94°, UV λ_{max}^{MeOH} nm (log ε): 294 (4.43); IR ν_{max}^{KBr} cm^{-1}: 1631, 1458, 1393, 1349, 1245, 1195, 1055, 687; ^{1}H NMR ($CDCl_3$): δ 3.85 and 3.95 (6 H each, *s*, 4 × —OMe), 4.05 (3 H, *s*, —OMe), 6.90 (1 H, *d*, *J* = 17 Hz, Hα), 7.15 (1 H, *d*, *J* = 17 Hz, Hβ) and 7.41 (5 H, *m*, B-ring protons). **2** was identified as 2′,3′,4′,5′,6′-pentamethoxychalcone (pedicellin) [3] on direct comparison (co-TLC, mmp and co-IR) with an authentic sample obtained from the collections of the late Professor T. R. Seshadri.

3 cryst. from EtOAc–petrol as light yellow needles (30 mg), mp



1 R = H
2 R = Me



3 R = H, R_1 = Me
4 R = Me, R_1 = H
5 R = R_1 = Me

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98°, $C_{18}H_{18}O_6$ (M^+ 330); R_f: 0.70 (Si gel, $CHCl_3$–MeOH, 19:1); 0.80 (Si gel, C_6H_6–EtOAc, 7:3); UV λ_{max}^{MeOH} nm: 275, 330, $AlCl_3$, 290, 345; $AlCl_3$–HCl, 290, 345; IR ν_{max}^{KBr} cm^{-1}: 1662, 1600, 1485, 1430, 1360, 1310, 1053 and 910; MS m/z: 330 (M^+), 253 ($M^+ - 77$, $M^+ - C_6H_5$) and 226 ($M^+ - 104$, $M^+ - C_6H_5 - CH{=}CH_2^+$); ^1H NMR ($CDCl_3$): δ 2.91 (2 H, *m*, $C_3 - 2$ H), 3.88, 4.02 and 4.10 (3 H each, *s*, 3 × —OMe), 5.41 (1 H, *m*, C_2–1 H), 7.42 (5 H, *s*, B-ring protons). It gave a positive colour with Mg/HCl and alcoholic $FeCl_3$. On methylation (Me_2SO_4), **3** gave **5** as colourless needles, mp 103°; UV λ_{max}^{MeOH} nm: 295; IR ν_{max}^{KBr} cm^{-1}: 1630, 1585, 1400, 1330, 1222, 1010, 890 and 640; ^1H NMR ($CDCl_3$): δ 2.98 (2 H, *m*, C_3–2 H), 3.90, 3.92 and 4.01 (3 H each, *s*, 3 × —OMe), 5.50 (1 H, *m*, C_2–1 H), 7.50 (5 H, *m*, B-ring protons). **5** was identified as 5,6,7,8-tetramethoxyflavanone on direct comparison with an authentic sample (co-TLC, co-IR, mmp and UV) obtained from the collections of the late Professor T. R. Seshadri. Hence, **3** was identified as 5-hydroxy-6,7,8-trimethoxyflavanone.

4, colourless needles, mp 103–104° (EtOAc–petrol); $C_{18}H_{18}O_6$ (M^+ 330); UV λ_{max}^{MeOH} nm: 285, 350; NaOAc: 285, 350; $AlCl_3$ 285, 350; IR ν_{max}^{KBr} cm^{-1}: 1671, 1590, 1422, 1310, 1230, 1160, 1050 and 834; ^1H NMR ($CDCl_3$): δ 2.94 (2 H, *m*, C_3–2 H), 3.86, 3.90 and 4.07 (3 H each, *s*, 3 × —OMe), 5.42 (1 H, *m*, C_2–1 H), 7.41 (5 H, *m*, B-ring protons). On methylation (CH_2N_2), **4** gave a methyl ether, mp 103–104° which was identified as **5** on direct comparison (mmp, co-TLC, co-IR and UV). **4** was therefore identified as 6-hydroxy-5,7,8-trimethoxyflavanone (isopedicin) [3].

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