Two New 5-Deoxyflavones from *Albizia odoratissima*

Yerra KOTESWARA RAO,[a] Mopur VIJAYA BHASKAR REDDY,[a] Chunduri VENKATA RAO,*,[a]
Duvvuru GUNASEKAR,[a] Alan BLOND,[b] Cristelle CAUX,[b] and Bernard BODO[b]

[a] *Natural Products Division, Department of Chemistry, Sri Venkateswara University; Tirupati 517 502, India: and* [b] *Laboratoire de Chimie des Substances Naturelles, ESA 8041 CNRS-GDR 790 CNRS, Museum National d'Histoire Naturelle; 63 rue Buffon, 75005 Paris, France.* Received April 15, 2002; accepted June 4, 2002

Two new 5-deoxyflavones, 7,8-dimethoxy-3′,4′-methylenedioxyflavone (1) and 7,2′,4′-trimethoxyflavone (2) together with a known flavone, 7,4′-dimethoxy-3′-hydroxyflavone (3) were isolated from the rootbark of *Albizia odoratissima*. The structures of these new compounds were elucidated by electrospray ionization mass spectrometry (ESI-MS) and 1D and 2D-NMR spectral studies including ^{1}H–^{1}H correlation spectroscopy (COSY), heteronuclear single quantum coherence (HSQC), heteronuclear multiple bond connectivity (HMBC) and nuclear Overhauser enhancement spectroscopy (NOESY).

Key words *Albizia odoratissima*; Mimosaceae; 5-deoxyflavone

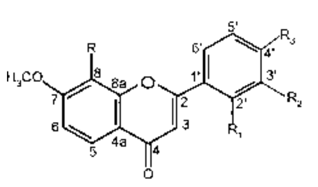
Albizia odoratissima LINN. (Mimosaceae) is a tree found throughout the Western Ghats of South India.[1] In traditional Indian Medicine *A. odoratissima* is used in the treatment of leprosy, ulcers and cough.[2] Previously, terpenilic acid[3] and saponins,[4,5] from seeds, and flavones[6] from heartwood were reported from *A. odoratissima*. In continuation of our search for new flavonoids, we have investigated the rootbark of *A. odoratissima*, and report here two new 5-deoxyflavones, 7,8-dimethoxy-3′,4′-methylenedioxyflavone (**1**) and 7,2′,4′-trimethoxyflavone (**2**) in addition to a known flavone, tithonine (**3**).

Results and Discussion

Compound **1**, an amorphous powder, showed $[M+K]^+$, $[M+Na]^+$ and $[M+H]^+$ ions at *m/z* 365.0547, 349.0788 and 327.0983 in its positive electrospray ionization mass spectrometry (ESI-MS) corresponding to the molecular formula $C_{18}H_{14}O_6$. This was corroborated by the decoupled ^{13}C-NMR distortionless enhancement by polarization transfer (DEPT) spectrum which showed signals for all the eighteen carbons of the molecule. The UV absorption in MeOH (254, 325 nm) suggested compound **1** to be a flavone.[7] The IR absorption bands at 1648, 1620 and 1596 cm^{-1} and negative ferric chloride test indicated compound **1** to be a non-phenolic flavone.

The ^{1}H-NMR spectrum of **1** showed two methoxyl singlets at δ 3.97 and 4.01, a two-proton singlet at δ 6.05 assigned to a methylenedioxy group and a sharp one-proton singlet at δ 6.61 ascribed to H-3. The electron impact mass spectrometry (EI-MS) of **1** showed two *retro*-Diels Alder fragments at *m/z* 181 $[A_1+H]^+$ and 146 $[B_1]^+$ indicating the presence of two methoxyl groups in ring-A and a methylenedioxy group in ring-B, respectively. The ^{1}H-NMR spectrum of **1** further showed two *ortho*-coupled aromatic doublets at δ 7.91 and 7.01 and they were assigned to H-5 and H-6, respectively as the former showed HMBC correlations with C-6, C-7, C-4, C-4a and C-8a, and the latter with C-4a, C-5, C-7 and C-8 (Fig. 2). It also displayed three aromatic proton signals at δ 7.50 (1H, dd, J=8.2, 1.6 Hz), 7.36 (1H, d, J=1.6 Hz) and 6.91 (1H, d, J=8.2 Hz) assigned to H-6′, H-2′ and H-5′ respectively, characteristic of 3′,4′-dioxygenated flavone.[8] This fixes the attachment of a methylenedioxy group at δ 6.05 to 3′ and 4′ positions, further evidenced by the ^3J correlation of the methylene protons with C-3′ (δ 148.4) and C-4′ (δ 150.4). Of the two methoxyl groups in ring-A, the one at δ 3.97 was placed at C-8 as it resonated at 61.6 ppm in its ^{13}C-NMR spectrum which is characteristic of a di-*ortho*-substituted methoxyl group.[9] This fixes the placement of another methoxyl group at (δ 4.01) to C-7. Thus from the foregoing spectral studies the structure of compound **1** was characterised as 7,8-dimethoxy-3′,4′-methylenedioxyflavone.

Compound **2**, obtained as yellow amorphous powder, showed $[M+H]^+$ ion peak at *m/z* 313.1000 in its positive ESI-MS, consistent with the molecular formula $C_{18}H_{16}O_5$, and was corroborated by decoupled ^{13}C-NMR DEPT spectrum, which showed signals for all the eighteen carbons of the molecule. The UV absorption maxima of **2** in MeOH at



1: R = OCH_3, R_1 = H, R_2–R_3 = –O–CH_2–O–
2: R = R_2 = H, R_1 = R_3 = OCH_3
3: R = R_1 = H, R_2 = OH, R_3 = OCH_3

Fig. 1. Structures of Compounds **1**—**3**

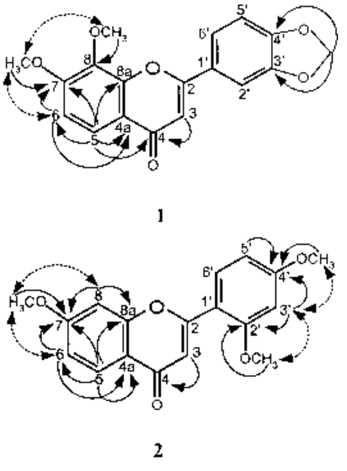


Fig. 2. Significant HMBC (→) and NOESY (↔) Correlations for **1** and **2**

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* To whom correspondence should be addressed. e-mail: cvr_svu@yahoo.com

Table 1. ^{13}C-NMR Data (75 MHz, $CDCl_3$) of **1**, **2** and **3**

Carbon	**1**	**2**	**3**
2	162.6	160.4	162.5
3	105.9	111.1	105.3
4	178.0	178.3	176.3
4a	118.6	117.6	117.1
5	120.9	126.8	126.2
6	109.8	113.9	114.5
7	156.6	163.8	163.8
8	136.9	100.2	100.8
8a	150.5	158.0	157.4
1′	125.8	113.5	123.5
2′	106.3	159.4	112.9
3′	148.4	98.8	146.8
4′	150.4	163.0	150.8
5′	108.8	105.2	112.1
6′	121.4	130.2	118.4
7-OMe	56.4	55.7	56.0
8-OMe	61.6	—	—
2′-OMe	—	55.6	—
4′-OMe	—	55.5	55.7
–O–CH_2–O–	101.9	—	—

238 and 339 nm is typical of a flavone.[7] The IR absorption bands at 1640, 1600, 1509, 1440 cm^{-1} and negative ferric chloride test indicated compound **2** also to be a non-phenolic flavone.

The ^{1}H-NMR spectrum of **2** displayed three methoxyl singlets at δ 3.83, 3.86 and 3.87 and a sharp one-proton singlet at δ 7.03 characteristic of H-3 of 2′-oxygenated flavone.[10] The EI-MS of **2** showed the $[M]^+$ ion peak at *m/z* 312 and two *retro*-Diels Alder fragments at *m/z* 151 $[A_1+H]^+$ and 162 $[B_1]^+$ consistent with the presence of one methoxyl group in ring-A and two methoxyl groups in ring-B, respectively. The ^{1}H-NMR spectra of **2** further revealed two aromatic ABX spin coupled systems, at δ 8.07 (1H, d, J=8.8 Hz), 6.90 (1H, dd, J=8.8, 2.3 Hz) and 6.85 (1H, d, J=2.3 Hz) assigned to H-5, H-6 and H-8, and δ 7.82 (1H, d, J=8.1 Hz), 6.57 (1H, dd, J=8.1, 2.3 Hz) and 6.50 (1H, d, J=2.3 Hz) assigned to H-6′, H-5′ and H-3′, confirming the presence of mono substitution in ring-A and disubstitution in ring-B. The three methoxyl groups at δ 3.83, 3.86 and 3.87 were placed at C-4′, C-2′ and C-7 positions as these methoxyls protons showed HMBC correlations with these carbons at 163.0, 159.4, 163.8 ppm, respectively. The placement of methoxyl groups were further supported by the NOE studies (Fig. 2). Thus from the foregoing spectral studies compound **2** was established as 7,2′,4′-trimethoxyflavone. The isolation of **2** constitutes the first report of the occurrence of a 2′-oxygenated flavone from *Albizia* genus.

The structure of the known compound as 7,4′-dimethoxy-3′-hydroxyflavone (**3**) was established by comparison of its spectral data with literature values.[11]

Experimental

General Procedures Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded in KBr discs on a Bio-Rad win FT-IR spectrophotometer and UV spectra on a Shimadzu UV-240 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were determined on a Bruker AC 400 spectrometer operating at 400.13 and 75.46 MHz, respectively using tetramethylsilane (TMS) as an internal standard. ^{1}H–^{1}H COSY, HSQC, HMBC and the phase-sensitive NOESY (with 150 ms mixing time) spectra were recorded using the standard pulse sequences. ESI-MS was recorded on a API Q-STAR PULSA of Applied Biosystem. EI-MS were recorded at 70 eV (direct probe) on a Nermag R 10—10 mass spectrometer. CC was performed on Acme silica gel finer than 200 mesh (0.08 mm).

Plant Material The rootbark of *A. odoratissima* was collected in January 2000 at Tirumala Hills, Tirupati, Andhra Pradesh, India.

Extraction and Isolation The air-dried and powdered rootbark (2 kg) of *A. odoratissima* was successively extracted with *n*-hexane, Me_2CO and MeOH. The *n*-hexane extract was purified over a silica gel column using *n*-hexane and EtOAc, 9 : 1, 8 : 2, to yield **1** (20 mg) and **2** (16 mg) respectively. The acetone extract on similar purification using hexane and EtOAc, 6 : 4 yielded **3** (25 mg).

7,8-Dimethoxy-3′,4′-methylenedioxyflavone (**1**): Yellow amorphous powder, mp 252—254 °C (MeOH). UV λ_{max} (MeOH) nm (log ε): 254 (4.23), 325 (4.14). IR (KBr) ν_{max} cm^{-1}: 1648 (>C=O), 1620, 1596, 1544, 1490. ^{1}H-NMR ($CDCl_3$) δ: 7.91 (1H, d, J=8.9 Hz, H-5), 7.50 (1H, dd, J=9.9, 1.7 Hz, H-6′), 7.36 (1H, d, J=1.6 Hz, H-2′), 7.01 (1H, d, J=8.9 Hz, H-6), 6.91 (1H, d, J=8.2 Hz, H-5′), 6.61 (1H, s, H-3), 6.05 (2H, s, –O–CH_2–O–), 4.01 (3H, s, OMe-7), 3.97 (3H, s, OMe-8). ^{13}C-NMR ($CDCl_3$): see Table 1. EI-MS *m/z* (%): 326 (100), 312 (6), 181 (20), 166 (18), 152 (42), 146 (10), 138 (20), 105 (25). ESI-MS *m/z* 327.0983 $[M+H]^+$ (Calcd for $C_{18}H_{15}O_6$: 327.3015).

7,2′,4′-Trimethoxyflavone (**2**): Yellow amorphous powder, mp 128—130 °C (MeOH). UV λ_{max} (MeOH) nm (log ε): 238 (4.18), 339 (4.03). IR (KBr) ν_{max} cm^{-1}: 1640 (>C=O), 1600, 1509, 1440, 1376. ^{1}H-NMR ($CDCl_3$) δ: 8.07 (1H, d, J=8.8 Hz, H-5), 7.82 (1H, d, J=8.7 Hz, H-6′), 7.03 (1H, s, H-3), 6.90 (1H, dd, J=8.8, 2.3 Hz, H-6), 6.85 (1H, d, J=2.3 Hz, H-8), 6.57 (1H, dd, J=8.7, 2.3 Hz, H-5′), 6.50 (1H, d, J=2.3 Hz, H-3′), 3.87 (3H, s, OMe-7), 3.86 (3H, s, OMe-2′), 3.83 (3H, s, OMe-4′). ^{13}C-NMR ($CDCl_3$): see Table 1. EI-MS *m/z* (%): 312 (78), 270 (10), 217 (40), 180 (22), 162 (50), 152 (100), 151 (22), 146 (10), 120 (40). ESI-MS *m/z* 313.1000 $[M+H]^+$ (Calcd for $C_{18}H_{17}O_5$: 313.3239).

7,4′-Dimethoxy-3′-hydroxyflavone (**3**): Colourless needles, mp 190—192 °C (MeOH). UV λ_{max} (MeOH) nm (log ε): 235 (4.41), 314 sh, 338 (4.20). IR (KBr) ν_{max} cm^{-1}: 3278 (OH), 2972, 2840, 1643 (>C=O), 1602, 1511, 1440, 1379. ^{1}H-NMR (DMSO-d_6) δ: 9.44 (1H, s, OH-3′), 7.89 (1H, d, J=8.9 Hz, H-5), 7.51 (1H, d, J=9 Hz, H-6′), 7.43 (1H, s, H-2′), 7.21 (1H, s, H-8), 7.03 (2H, m, H-5′,6), 6.70 (1H, s, H-3), 3.88 (3H, s, OMe-7), 3.84 (3H, s, OMe-4′). ^{13}C-NMR (DMSO-d_6) δ: see Table 1. EI-MS *m/z* (%): 298 (100), 283 (5), 270 (4), 255 (11), 165 (10), 151 (32).

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