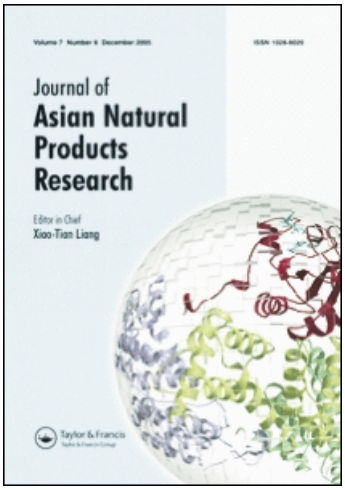

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A NEW BIFLAVONOID FROM *OCHNA BEDDOMEI*

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A new biflavonoid, 2,3-dihydroochnaflavone 7,4′,7″-tri-*O*-methyl ether (**1**) together with two known biflavonoids namely, 2,3-dihydroochnaflavone (**2**) and ochnaflavone (**3**) were isolated from the stem bark of *Ochna beddomei*. The structures were determined by means of spectral and chemical studies.

Keywords: *Ochna beddomei*; Ochnaceae; Biflavonoids; 2,3-Dihydroochnaflavone 7,4′,7″-tri-*O*-methyl ether; 2,3-Dihydroochnaflavone; Ochnaflavone

INTRODUCTION

The genus *Ochna* belonging to the family Ochnaceae of the order Ochnales is represented in India by 11 species [1–3]. Several members of this genus are used in folk medicine for the treatment of epilepsy, menstrual complaints, asthma, lumbago, ulcers and skin diseases. In continuation of our investigations on *Ochna* species [4–7], we examined the stem bark of *Ochna beddomei* Gamble and report here the isolation of a new biflavonoid (**1**) besides two known biflavonoids, 2,3-dihydroochnaflavone (**2**) [6] and ochnaflavone (**3**) [8].

RESULTS AND DISCUSSION

Compound (**1**) was obtained as pale yellow crystals and showed a pseudomolecular ion at *m/z* 583.1604 in its positive HRCIMS corresponding to the molecular formula $C_{33}H_{26}O_{10}$. This was corroborated by the decoupled ^{13}C-NMR spectrum of **1**, which showed 33 carbon resonances. The IR spectrum exhibited a broad OH absorption band at 3441 cm^{-1} and a chelated carbonyl band at 1645 cm^{-1}. The molecular formula and the presence of two carbonyl resonances at δ 196.6 and 182.0 suggested that compound **1** could be a biflavonoid.

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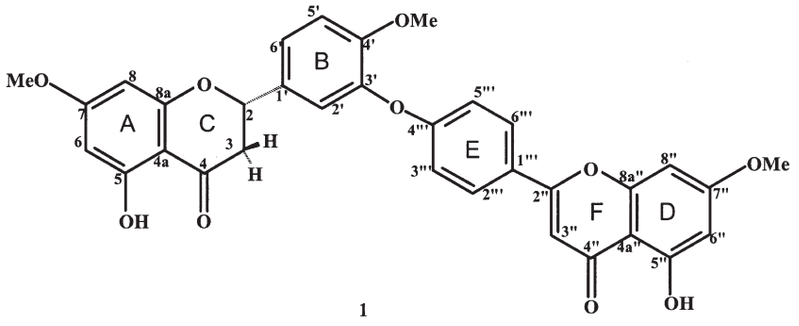
The ^{1}H-NMR spectrum of **1** exhibited an ABX spectrum at δ 5.60 (1H, dd, $J = 12.7$, 3.1 Hz), 3.29 (1H, dd, $J = 17.1$, 12.7 Hz) and 2.84 (1H, dd, $J = 17.1$, 3.1 Hz) characteristic of the C-2 and C-3 protons of a flavanone moiety. Two downfield signals at δ 12.10 and 12.90 (exchangeable with D_2O) were assigned to chelated hydroxyls at the 5 and 5″ positions. It also showed the presence of three methoxyl groups at δ 3.80 (6H, s) and 3.89 (3H, s). Four *meta* coupled doublets at δ 6.05, 6.10, 6.34, and 6.72 were attributed to protons at the C-6, C-8, C-6″, and C-8″ positions of rings A and D. A sharp singlet at δ 6.85 integrating for one proton was assigned to the C-3″ proton of ring F of the flavone moiety. A set of *ortho* coupled doublets at δ 8.06 and 7.01, each integrating for two protons, accounted for the C-2‴, C-6‴ and C-3‴, C-5‴ protons of the *p*-substituted aromatic ring E of the flavone moiety. The signals at δ 7.40 (1H, d, $J = 2.1$ Hz), 7.28 (1H, d, $J = 8.5$ Hz) and 7.47 (1H, dd, $J = 8.5, 2.1$ Hz) were ascribed to C-2′, C-5′ and C-6′ protons of ring B of the flavanone moiety. The above assignments obviously indicate that the three methoxyls are placed at carbons C-7, C-4′ and C-7″ as these carbons showed correlations with the methoxyl protons in the HMBC spectrum (Fig. 1).

The above spectral studies suggested that compound **1** could be a biflavonoid consisting of a flavanone and a flavone moiety with an $-O-$ linkage since only 9 out of the 10 oxygen atoms in **1** have been accounted for by the presence of two chelated hydroxyls, three methoxyls, two pyranone and two pyrone oxygen atoms. Comparison of ^{13}C-NMR spectral data of **1** with those of 7,4′-di-*O*-methylnaringenin [9] and genkwanin [10,11] (Table I) showed that C-3′ of ring B should be involved in the interflavonoid ether linkage [12] with C-4‴ of ring E, as the resonance of C-3′ has shifted downfield by 27.7 ppm from the corresponding carbon resonance of 7,4′-di-*O*-methylnaringenin. The HMBC spectrum of **1** further confirmed the involvement of C-3′ and C-4‴ in the interflavonoid ether linkage as these carbons showed correlations with H-2′ and H-5′, and H-2‴, H-6‴, H-3‴ and H-5‴, respectively. The absolute configuration at C-2 was shown to be *S* [13] as the CD spectrum of **1** exhibited positive and negative Cotton effects at 334 and 288 nm, respectively. Thus from the foregoing spectral studies, the structure of compound **1** was elucidated as 2,3-dihydroochnaflavone 7,4′,7″-tri-*O*-methyl ether.



1

EXPERIMENTAL SECTION

General Experimental Procedures

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. UV spectra were determined in MeOH on a Shimadzu UV-240 spectrophotometer. The CD spectrum was recorded in MeOH at 15°C on a JASCO J-715 spectropolarimeter. IR spectra were obtained in KBr discs on a Perkin–Elmer 283 double beam spectrophotometer.

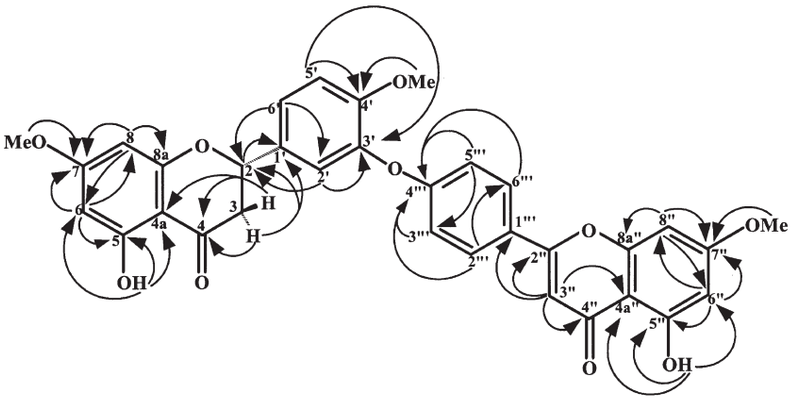


FIGURE 1 HMBC correlations of **1**.

^{1}H- and ^{13}C-NMR spectra were recorded in DMSO-d_6 with TMS as internal standard on a Bruker AC 300 MHz spectrometer operating at 300 and 75 MHz, respectively. HMBC spectrum was obtained using standard pulse sequences. EIMS were obtained on Nermag R 10–10 and Hewlett-Packard 5989X mass spectrometers at 70 eV by direct inlet probe. HRCIMS was obtained on a 700 JEOL mass spectrometer by direct inlet probe using CH_4 as the ionizing gas at 500°C. Column chromatography was performed on Acme silica gel finer than 200 mesh (0.08 mm).

Plant Material

The stem bark of *O. beddomei* was collected from Tirumala hills, Andhra Pradesh, India in April, 1998. The plant material was identified by Dr K. Madhava Chetty, Department of Botany, Sri Venkateswara University, Tirupati, India, where a voucher specimen (DG-987) was deposited.

TABLE I ^{13}C-NMR chemical shifts of **1**, 7,4′-di-*O*-methylnaringenin and genkwanin

C	*Flavanone moiety of* ***1***	*7,4′-Di-O-methylnaringenin*	*C*	*Flavone moiety of* ***1***	*Genkwanin*
2	77.0	79.2	2″	163.3	164.6
3	42.0	43.2	3″	104.2	103.4
4	196.6	196.5	4″	182.0	182.3
4a	102.9	103.3	4a″	104.8	105.0
5	163.2	164.0	5″	161.3	157.7
6	94.6	95.2	6″	98.0	98.2
7	167.5	168.3	7″	165.3	165.6
8	94.0	94.4	8″	93.0	92.9
8a	162.6	163.3	8a″	157.3	161.8
1′	131.7	130.8	1‴	124.3	121.6
2′	120.9	128.0	2‴	128.5	128.8
3′	142.1	114.4	3‴	116.0	116.3
4′	151.6	160.2	4‴	161.0	161.8
5′	113.5	114.4	5‴	116.0	116.3
6′	125.1	128.0	6‴	128.5	128.8
7-OMe	55.8	54.4	7″-OMe	56.0	56.0
4′-OMe	55.8	55.8			

Extraction and Isolation

Shade-dried and powdered stem bark of *O. beddomei* (2.5 kg) was successively extracted with *n*-hexane, Me_2CO and MeOH. The Me_2CO extract was defatted with *n*-hexane and the residue obtained (30 g) on purification over a silica gel column (180 g) using *n*-hexane/EtOAc step gradient mixtures (1:1, 3:7 and 1:9) as eluents yielded **1** (30 mg), **2** (25 mg), and **3** (60 mg), respectively.

2,3-Dihydroochnaflavone 7,4′,7″-Tri-O-methyl Ether (1)

Pale yellow crystals from $CHCl_3$, 30 mg, mp 194–196°C; CD $[\theta]_{288}$ −7998°, $[\theta]_{334}$ +2365° (*c* 0.05, MeOH); UV (MeOH) λ_{max} (log ε) 282 (4.08), 333 (3.92) nm; IR (KBr) ν_{max} 3441 (–OH), 2924, 1645 (>C=O), 1614, 1574, 1504, 1443, 1379, 1352, 1303, 1278, 1233, 1191, 1157, 1075, 835 cm^{-1}; ^{1}H-NMR (DMSO-d_6, 300 MHz) δ 12.90 (1H, s, OH-5″), 12.10 (1H, s, OH-5), 8.06 (2H, d, J = 8.9 Hz, H-2‴, H-6‴), 7.47 (1H, dd, J = 8.5, 2.1 Hz, H-6′), 7.40 (1H, d, J = 2.1 Hz, H-2′), 7.28 (1H, d, J = 8.5 Hz, H-5′), 7.01 (2H, d, J = 8.9 Hz, H-3‴, H-5‴), 6.85 (1H, s, H-3″), 6.72 (1H, d, J = 2.2 Hz, H-8″), 6.34 (1H, d, J = 2.2 Hz, H-6″), 6.10 (1H, d, J = 2.3 Hz, H-8), 6.05 (1H, d, J = 2.3 Hz, H-6), 5.60 (1H, dd, J = 12.7, 3.1 Hz, H-2), 3.89 (3H, s, OMe-7″), 3.80 (6H, s, OMe-7, OMe-4′), 3.29 (1H, dd, J = 17.1, 12.7 Hz, H-3_{ax}), 2.84 (1H, dd, J = 17.1, 3.1 Hz, H-3_{eq}); ^{13}C-NMR (DMSO-d_6, 75 MHz), see Table I; EIMS *m/z* 582 $[M]^+$ (46), 567 (10), 553 (11), 539 (3), 416 (5), 403 (6), 401 (1), 390 (12), 315 (1), 299 (2), 283 (2), 267 (2), 263 (2), 255 (2), 252 (2), 227 (1), 193 (3), 167 (7), 149 (21), 109 (13), 69 (29), 45 (100); HRCIMS *m/z* 583.1604 $[M + H]^+$ (calcd for $C_{33}H_{27}O_{10}$, 583.1604).

Acetylation of 1

A measured amount (10 mg) of **1** in C_5H_5N (0.5 ml) was treated with Ac_2O (1.5 ml) for 48 h at room temperature. The reaction mixture on usual workup gave colourless needles (9 mg) from Me_2CO, mp 178–180°C; IR (KBr) ν_{max} 2938, 1772 (>C=O of OAc), 1678, 1644, 1621, 1568, 1509, 1442, 1370, 1194, 1155, 1080, 1028, 835 cm^{-1}; ^{1}H-NMR (Me_2CO-d_6, 300 MHz) δ 8.0 (2H, d, J = 8.9 Hz, H-2‴, H-6‴), 7.46 (1H, dd, J = 8.5, 2.1 Hz, H-6′), 7.41 (1H, d, J = 2.1 Hz, H-2′), 7.29 (1H, d, J = 8.5 Hz, H-5′), 7.0 (2H, d, J = 8.9 Hz, H-3‴, H-5‴), 6.85 (1H, s, H-3″), 6.72 (1H, d, J = 2.2 Hz, H-8″), 6.33 (1H, d, J = 2.2 Hz, H-6″), 6.10 (1H, d, J = 2.3 Hz, H-8), 6.05 (1H, d, J = 2.3 Hz, H-6), 5.62 (1H, dd, J = 12.7, 3.1 Hz, H-2), 3.91 (3H, s, OMe-7″), 3.82 (6H, s, OMe-7, OMe-4′), 3.10 (1H, dd, J = 17.1, 12.7 Hz, H-3_{ax}), 2.76 (1H, dd, J = 17.1, 3.1 Hz, H-3_{eq}), 2.30 (3H, s, OAc-5), 2.25 (3H, s, OAc-5″).

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