

Communication

A Novel Flavonoid C-glycoside from *Sphaeranthus indicus* L. (Family Compositae)

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Abstract: A novel flavonoid C-glycoside, 5-hydroxy-7-methoxy-6-C-glycosylflavone (**1**), was isolated from the aerial part of *Sphaeranthus indicus*. Its structure was elucidated by spectroscopic methods.

Keywords: *Sphaeranthus indicus*; flavonoid C-glycoside; 5-hydroxy-7-methoxy-6-C-glycosylflavone.

Introduction

Sphaeranthus indicus L. is a multi-branched herb with round purple flowers that grows plentifully in rice fields [1, 2] and is distributed throughout India, Ceylon, Malay, China and Africa. It used indigenously in the Indian system of traditional medicine as a remedy for various ailments, being used as a tonic, laxative, digestive, anthelmintic, and the treatment of insanity, tuberculosis, diseases of the spleen, anaemia, bronchitis, elephantiasis, pain of the uterus and vagina, piles, asthma, leucoderma and hemicrania. Almost every part of the plant is useful. Leaves of the plant are eaten as a pot-herb and have anxiolytic [3], macrofilaricidal [4], antimicrobial [5], and insecticidal activities [6]. Earlier work

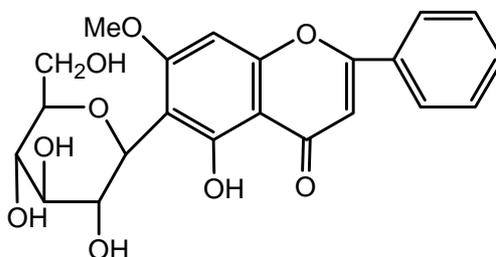
on the aerial parts of this plant revealed it to be quite rich in essential oils, glucosides and eudesmanoids [7], along with some uncharacterized sesquiterpenes, phenolic glycosides, and sesquiterpene lactones [8, 9].

A systematic phytochemical study of the chemical constituents of the plant led us to isolate a new flavonoid C-glycoside compound **1**, together with eight known compounds, namely n-pentacosan, hentriacontane, *n*-triacontanol, β -sitosterol, stigmasterol, β -*D*-glucoside of β -sitosterol, sphaeranthine and a phenolic glycoside (C₂₂H₂₆O₁₂). In this paper we report the isolation and structure elucidation of 5-hydroxy-7-methoxy-6-C-glycosylflavone (**1**) from the aerial parts of the plant.

Results and Discussion

Compound **1** was obtained as pale yellow needles, m.p. 230-232°C. Elemental analysis of compound **1** is consistent with the molecular formula C₂₂H₂₂O₉ (calcd. 430.409). Its IR spectrum indicated the presence of hydroxyl (3403 cm⁻¹) and carbonyl (1645 cm⁻¹) groups. Bands in the 1650-1050 cm⁻¹ range are typical of a flavone skeleton. The UV spectrum exhibited absorption maxima at 260 nm (band II) and 300 nm (band I), that are characteristic absorption bands of a flavone skeleton [10]. No shift in band I of compound **1** was observed with the addition of AlCl₃/HCl, suggesting formation of a hydroxy-keto complex at the 5-OH and the absence of an *O*-dihydroxyl grouping in the B ring [10, 11]. The fragment *m/z* 105 (15%) and 102 (18%) in the mass spectrum supports the unsubstituted nature of the flavonoid ring B.

Figure 1. Structure of Compound 1.



The ¹H-NMR spectrum exhibited a flavonoid pattern and showed signals at δ 6.65 (1H, s), 6.51 (1H, br), typical of the flavone skeleton protons at C-3 and C-8. Chemical shifts of 7.90 (d, H2', H6') and 7.51 (m, H3', H4' and H5') suggested that there is no substitution on the B ring of the flavonoid. The signal at δ 12.80 ppm was assigned to the C-5 hydroxyl. The observed singlet at 3.91 (s, -OCH₃) is evidence for one methoxy group. Signals in the ¹³C-NMR spectrum just below δ 77 ppm indicated the presence of a glucose moiety [12]. The signal at δ 5.84 ppm was assigned to the anomeric proton (H-1'') with a coupling constant (*J* = 10 Hz) indicating a β -configuration [13], sugar proton signals at δ 4.47, multiple attributed to the H-3'', H-4'' and H-5'' respectively. The position of the C-glucose moiety on the C-6 position was based on the above evidence and comparison with the values in literature for the analogous compound isoorientin [14].

Experimental

General

Melting points were measured in open capillary tubes on a Buchi 530 apparatus and are uncorrected. NMR spectra were obtained on a JEOL AL300 FT-NMR spectrometer (300 MHz for ^1H , 75.45 MHz for ^{13}C) in CDCl_3 solutions with tetramethylsilane as an internal reference. EI-MS data was obtained on a JEOL JMS D-300 instrument. UV spectra were recorded on a Cary-14 instrument. IR spectra were recorded on Perkin Elmer 257 infrared spectrometer.

Plant material and product isolation

Aerial parts of plant were collected in September 2006 in a suburb of Varanasi, India. The plant identification was verified by Professor N. K. Dubey, Department of Botany, Faculty of Science, Banara Hindu University, Varanasi, India. A specimen sample of the plant material has been preserved in our laboratory no. 39, Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi, India. The dried plant material (3 Kg) was first extracted with petroleum ether (5 L) for 24 h and then with MeOH (5 L) for 38 h using a Soxhlet apparatus. After concentration of the methanolic extracts (0.5 g), the residues were extracted with CHCl_3 (2 L x 3), EtOAc (3 L x 3) and EtOH (3 L x 2) respectively. The EtOH extract (20.5 g) was chromatographed on silica gel (200-300 mesh; 600 g) and eluted with EtOAc-MeOH- H_2O (4:1:0.1), after rechromatography with MeOH, MeOH- H_2O (1:1) eluates gave pale yellow compound **1** (35 mg).

Compound 1: UV-Visible λ_{max} (nm) MeOH: 252, 260, 300; MeOH+MeONa: 246, 270; MeOH+ AlCl_3 250, 272, 335, 380 nm; IR ν_{max} (KBr, cm^{-1}) 3403, 1645; $^1\text{H-NMR}$: 12.80 (s, HO-5), 7.90 (d, $J = 6.5$, H-2', H-6'), 7.51 (m, H-3', H-4', H-5'), 6.65 (s, H-3), 6.51 (s, H-8), 5.84 (d, $J = 10$, H-1''), 5.20 (t, $J = 8.6$, H-2''), 4.47 (m, H-3'', 4'', 5''), 4.46 (d, $J = 9.6$, H-6''), 3.39 (s, -OCH₃) ppm; $^{13}\text{C-NMR}$: 182.9 (C-4), 164.7 (C-5), 160.5 (C-2), 160.2 (C-7), 157.9 (C-9), 139.9 (C-4'), 130.1 (C-1'), 130 (C-3', C-5'), 127.2 (C-2', C-6'), 110 (C-6), 105.5 (C-3), 104.7 (C-10), 90 (C-8), 83.4 (C-5''), 80.7 (C-3''), 75.3 (C-1''), 72.5 (C-2''), 72.0 (C-4''), 63.0 (C-6''), 56.2 (C-7-OMe); MS m/z (rel. int.): 430 [M⁺] (60%), 429 (10%), 415 (15%), 105 (15%), 102 (18%).

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Sample availability: Contact the Author.