

A NEW FLAVONE METHYL ETHER FROM *HELICTERES ISORA*

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Madurai Kamaraj University, Madurai 625 021 IndiaABSTRACT.—A new flavone, 5,8-dihydroxy-7,4'-dimethoxyflavone (**1**), has been isolated, along with trifolin and hibifolin, from the fresh leaves of *Helicteres isora*.

In a continuation of our study of the flavonoids of the Sterculiaceae (1–4), we report herein the isolation and characterization of a new flavone methyl ether, 7,4'-di-*O*-methylisoscuteallarein (5,8-dihydroxy-7,4'-dimethoxyflavone) (**1**) along with kaempferol-3-*O*-galactoside (trifolin) and herbacetin-8-*O*-glucuronide (hibifolin) from the fresh leaves of *Helicteres isora* L. This is the first report of the occurrence of 7,4'-di-*O*-methylisoscuteallarein in nature. Although 8-oxygenated flavonols (3) and 6-oxygenated flavones (1,2) have been reported earlier from plants of the Sterculiaceae, this is the first record of the occurrence of an 8-oxygenated flavone in this family.

The EtOH extract residue of fresh leaves was fractionated using petroleum ether (bp 60–80°), Et₂O, EtOAc, and methyl ethyl ketone, successively. The Et₂O and EtOAc fractions, on concentration, afforded trifolin and hibifolin, respectively, identified by direct comparison (mmp and co-paper chromatography) with authentic samples (3).

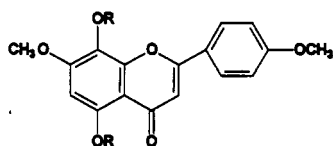
The methyl ethyl ketone fraction on concentration afforded a bright yellow compound (**1**) mp 261° (dec), which gave a gossypetone reaction. The isolate was purple under uv and uv/NH₃, and gave an olive-green color with Fe³⁺. The eims of **1** exhibited a peak at *m/z* 314,

comparable with a molecular formula of C₁₇H₁₄O₆. Compound **1** showed uv absorptions characteristic of a flavone [λ_{max} (MeOH) 281, 305 nm], and its uv spectrum with diagnostic shift reagents revealed the absence of free C-7 and C-4' hydroxyls. The ¹H-nmr spectrum showed the presence of six aromatic protons as two doublets (H-2', H-6' and H-3', H-5') and two singlets (H-3, H-6, or H-8), and also revealed the presence of two methoxyl groups. On acetylation (Ac₂O/HClO₄), **1** afforded a diacetate (**2**), and on demethylation (Ac₂O/HI), it yielded 5,7,8,4'-tetrahydroxyflavone (isoscuteallarein) (5). The presence of a OMe-4' group was also evident by the fragment ion B₂⁺ at *m/z* 135 in the ms of the diacetate (**2**). Based on the above data (color reactions, uv, and ¹H-nmr), **1** was concluded to be 5,8-dihydroxy-7,4'-dimethoxyflavone (7,4'-di-*O*-methylisoscuteallarein).

The structure of **1** was further supported by the ¹³C-nmr spectrum of its diacetate (**2**). The absence of an aromatic methine carbon signal in the range 90–96 ppm indicated that the C-8 was substituted, and the presence of acetoxy groups at C-5 and C-8 was supported by their chemical shifts (δ 169.58 and 167.88) (6).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mps are uncorrected. Ir spectra were recorded in KBr. ¹H- (400 MHz) and ¹³C- (100 MHz) nmr spectra were recorded on a JEOL GSX 400 spectrometer, using TMS as internal standard. Mass spectra (eims) were recorded on a JEOL-DX 300 spectrometer.

PLANT MATERIAL.—Leaves of *Helicteres*

- 1** R=H
2 R=Ac

isora (7) were collected from Alagar Hills, Madurai, India in the autumn of 1992, and identified by Prof. T. Sriganasen (Department of Botany, Madurai College, Madurai, India) and a voucher specimen was deposited at Madurai College Herbarium, Madurai, India.

EXTRACTION AND ISOLATION.—Fresh leaves (1 kg) were extracted with hot 90% EtOH under reflux and the subsequent concentrate was partitioned using petroleum ether, Et₂O, EtOAc, and methyl ethyl ketone, successively. Concentration of the Et₂O fraction afforded trifolin (50 mg), and hibifolin (30 mg) was obtained from the EtOAc fraction. The residue from the methyl ethyl ketone fraction was dissolved in a minimum volume of MeOH and refrigerated for 24 h to yield a greenish yellow solid, which on crystallization (MeOH) yielded a bright yellow compound [**1**] (120 mg); mp 261° (dec), purple under uv and uv/NH₃, olive-green with Fe³⁺; uv (MeOH) λ max (log ε) 281 (4.10), 305 (4.41) nm; (+NaOAc/H₃BO₃) 232, 307 nm; (+AlCl₃/HCl) 287, 320, 347, 426 nm; (+NaOMe) 269, 321 (sh) nm; ir (KBr) ν max 3200 (br), 1650 (C=O), 1595, 1420, 830 (1,4-disubstituted benzene), 750 cm⁻¹; ¹H nmr (DMSO-*d*₆, 400 MHz) δ 3.87 (3H, s, OMe), 3.91 (3H, s, OMe), 6.56 (1H, s, H-3), 6.88 (1H, s, H-6), 7.13 (2H, d, *J*=8 Hz, H-3', H-5'), 8.15 (2H, d, *J*=8 Hz, H-2', H-6'), 8.91 (1H, s, OH-8), 12.44 (1H, s, OH-5); eims *m/z* [M]⁺ 314 (97), 313 (84), 284 (35), 281 (100), 135 (10), 132 (5); *anal.*, calcd for C₁₇H₁₄O₆, C 64.97, H 4.46, found C 63.78, H 4.18.

ACETYLATION OF 1.—Treatment of **1** (60 mg) with Ac₂O (2.0 ml) and HClO₄ (0.2 ml, 70%) at room temperature overnight gave a crystalline diacetate [**2**] (50 mg), mp 236°; ¹H nmr (CDCl₃, 60 MHz) δ 2.41 (6H, s, 2×OAc), 3.85 (3H, s, OMe), 3.90 (3H, s, OMe), 6.47 (1H, s, H-3), 6.68

(1H, s, H-6), 7.00 (2H, d, *J*=8 Hz, H-3', H-5'), 7.70 (2H, d, *J*=8 Hz, H-2', H-6'); eims *m/z* [M]⁺ 398 (5), 314 (100), 312 (4), 135 (10); ¹³C nmr (CDCl₃, 100 MHz) δ 176.24 (C-4), 169.58, 167.88 (acetoxyl carbonyls), 162.51 (C-2), 162.03 (C-4'), 155.05 (C-7), 150.01 (C-5), 147.63 (C-9), 127.83 (C-2', C-6'), 123.72 (C-8, C-1'), 114.59 (C-3', C-5'), 111.19 (C-10), 106.95 (C-6), 104.29 (C-3), 56.64, 55.53 (methoxyl), 21.23, 20.30 (acetoxyl methyls).

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