

A New Flavone from *Limnophila heterophylla*

K. S. MUKHERJEE*, G. BRAHMACHARI, T. K. MANNA and P. MUKHERJEE

Department of Chemistry, Visva-Bharati University, Santiniketan-731 235

Manuscript received 10 March 1997, revised 8 July 1997, accepted 12 August 1997

The benzene extract of the aerial parts and roots of *Limnophila heterophylla* yielded a new flavone, 5,2'-dihydroxy-7,8,4'-trimethoxyflavone.

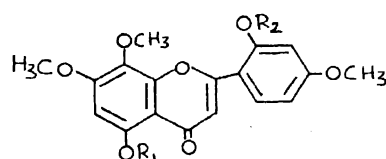
In continuation of our previous works^{1,2} on *Limnophila heterophylla* (Scrophulariaceae)³, we now report the isolation of a novel flavonoid compound, 5,2'-dihydroxy-7,8,4'-trimethoxyflavone (**1**) from the benzene extract of the aerial parts and roots of the same plant.

The flavone (**1**), C₁₈H₁₆O₇ ([M⁺] at *m/z* 344), m.p. 190–91°, gives a positive flavonoid test with magnesium hydrochloric acid and exhibits $\lambda_{\max}$ (EtOH) (log ϵ) 225 (4.25), 280 (4.20) and 335 (4.10) nm, and $\nu_{\max}$ (KBr) 3400 (bonded hydroxyl), 1655, 1600 and 1575 cm⁻¹ (chelated α,β -unsaturated carbonyl). On methylation with diazo-methane, it forms a monomethyl derivative (**2**), C₁₉H₁₈O₇, m.p. 188–89°, and with dimethylsulphate it yields a dime-thyl derivative (**3**), C₂₀H₂₀O₇, m.p. 173–74°, suggesting thereby the presence of two hydroxyl functions in **1**, one of which being bonded in nature.

The ¹H nmr spectrum (90 MHz; CDCl₃) of the parent flavone displays signals for (i) three methoxyls at δ 3.85 (3H, s), 3.95 (3H, s) and 3.98 (3H, s), (ii) C₃-proton as one-proton singlet at δ 6.95, (iii) one-proton singlet at δ 13.30 due to chelated phenolic hydroxyl, (iv) C₆-proton appearing as a singlet at δ 6.50 and (v) three aromatic protons of B-ring at δ 7.0 (1H, d, *J* 2 Hz), 7.19 (1H, dd, *J* 2 and 9 Hz) and 7.88 (1H, d, *J* 9 Hz). Such appearance of signals of three aromatic protons of B-ring is indicative of a 2',4'-disubstituted B-ring in **1**. The mass spectral data of **1** reveal the presence of ion peaks at *m/z* 344 (M⁺), 329 (M⁺–CH₃), 316 (344–CO), 314 (329 M⁺–CH₃), 313 (344–OCH₃), 301 (329–CH₃), 196 (r.D.A. around ring C), 197 (196 + H), 168 (196–CO), 153 (168–CH₃), 148 (another portion of r.D.A. around ring C), 133 (148–CH₃), 132 (133–H), and this is clearly in accordance with the presence of two methoxyls and one hydroxyl functions in ring-A and one methoxyl and one hydroxyl group in ring-B.

The flavone (**1**) does not respond to Gossypetone test⁴, which suggests that its C₈-position is blocked. Further, the compound does not exhibit any significant change of short wavelength band at 280 nm on addition of sodium acetate indicating thereby that one of the methoxyls is located at C₇-position⁵. Again, the monomethyl derivative (**2**) and dimethyl derivative (**3**) obtained from the methylation of **1**

respectively with diazomethane and dimethylsulphate, were found to be completely identical respectively with 5-hydroxy-7,8,2',4'-tetramethoxyflavone^{2,6} and 5,7,8,2',4'-pentamethoxyflavone⁶ by co-tlc, co-ir and m.m.p. determination. Finally, the isolation of 2,6-dihydroxy-3,4-dimethoxyacetophenone⁷ (m.p. 166–67°) and 2-hydroxy-4-methoxybenzoic acid⁸ (m.p. 157°) during the hydrolysis of the parent flavone (**1**) with 40% caustic potash solution led us to formulate this new flavone as 5,2'-dihydroxy-7,8,4'-trimethoxyflavone (**1**) which gets further confirmation from its ¹³C nmr spectral analysis (Table 1).



1; R₁ = R₂ = H
2; R₁ = H; R₂ = CH₃
3; R₁ = R₂ = CH₃

TABLE 1—¹³C NMR SPECTRAL DATA OF COMPOUND **1** (100 MHz, CDCl₃)

C-atom	δ	C-atom	δ
2	162.4	1'	122.2
3	108.9	2'	148.3
4	182.2	3'	107.8
5	156.5	4'	150.5
6	96.0	5'	114.6
7	158.4	6'	119.5
8	128.3	7-OCH ₃	56.5
9	148.9	8-OCH ₃	61.0
10	103.8	4'-OCH ₃	55.8

Acknowledgement

The authors are thankful to R.S.I.C., I.I.T., Madras, and R.S.I.C., C.D.R.I., Lucknow, for spectral measurements and also to U.G.C., New Delhi, for awarding a Senior Research Fellowship to one of the authors (G.B.). They are also grateful to Dr. H. R. Chowdhury and Dr. P. K. Dan for the identification of the plant.

References

1. K. S. MUKHERJEE, G. BRAHMACHARI, and T. K. MANNA, *Phytochemistry*, 1995, **38**, 1273; *J. Indian Chem. Soc.*, 1997, **74**, 738.
2. K. S. MUKHERJEE, T. K. MANNA, S. LAHA, and G. BRAHMACHARI, *J. Indian Chem. Soc.*, 1994, **71**, 655.
3. J. D. HOOKER, "Flora of British India", L. Reeve and Co., London, 1882, Vol. IV, p. 170; V. V. SIVARAJAN and I. BALACHAND-RAN, *Ancient Sci. Life*, 1986, **5**, 250.
4. A. G. PERKIN, *J. Chem. Soc.*, 1913, 650.
5. T. J. MABRY, K. R. MARKHAM, and M. B. THOMAS, "The Systematic Identification of Flavonoids", Springer, New York, 1970, p. 48.
6. K. S. MUKHERJEE, C. K. CHAKRABORTY, and T. P. CHATTERJEE, *Phytochemistry*, 1980, **38**, 1778.
7. "Dictionary of Organic Compounds", Eyre & Spottiswoode, London, 1965, Vol. 2, p. 1055.
8. Ref. 7, Vol. 5, p. 3002.