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5-HYDROXY-7,8,2′,4′-TETRAMETHOXYFLAVONE FROM *LIMNOPHILA RUGOSA*

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Key Word Index—*Limnophila rugosa*, Scrophulariaceae, 5-hydroxy-7,8,2′,4′-tetramethoxyflavone

Abstract—The petrol extract of the aerial parts and roots of *Limnophila rugosa* yielded a new flavone, 5-hydroxy-7,8,2′,4′-tetramethoxyflavone

In course of our studies on plant pigments [1-3] a systematic phytochemical investigation of *Limnophila rugosa* (Roth) Merrill. (*Scrophulariaceae*) [4] has been undertaken. Previously, only essential oil constituents have been reported for this plant [5, 6]. The present paper reports the isolation and structure elucidation of a new flavone, 5-hydroxy-7,8,2′,4′-tetramethoxyflavone (**1**) from the same plant.

5-hydroxy-7,8,2′,4′-tetramethoxyflavone (**1**), $C_{19}H_{18}O_7$ ([M$^+$] at *m/z* 358), gave a positive flavonoid test with magnesium hydrochloric acid and exhibited UV λ_{max}^{EtOH} nm (log ε), 225 (4 28), 280 (4 23) and 330 (4.10) Its IR spectrum shows absorption bands at 3405 (bonded hydroxyl), 1660, 1600 and 1580 cm^{-1} (chelated α,β-unsaturated carbonyl). On methylation with dimethylsulphate it formed a monomethyl derivative, $C_{20}H_{20}O_7$ (**2**). The ^{1}H NMR spectrum (90 MHz, $CDCl_3$) of the parent flavone showed resonances for four methoxyls at δ3.75 (6H, *s*), 3.95 (6H, *s*); one proton singlet at δ6.95 assignable to C_3-proton, the A-ring proton at C-6 appearing as singlet at δ6.45, the presence of three aromatic protons signals at δ6.75 (1H, *d*, $J = 2$ Hz), 6.90 (1H, *q*, $J = 2$ and 9 Hz) and 7.65 (1H, *d*, $J = 9$ Hz) is indicative of a 2′,4′-disubstituted B-ring in **1** The flavone remained unchanged on methylation with diazomethane and did not exhibit any significant change of short wave length band at 280 nm on addition of sodium acetate solution [7] locating respectively a free hydroxyl at C-5 and one of the methoxyls at the C-7 position Compound **1** did not respond to the gossypetone test [8] suggesting the presence of another methoxyl at the C-8 position All these spectral and chemical observations revealed that **1** is 5-hydroxy-7,8,2′,4′-tetramethoxyflavone The structure of **1** was confirmed by the isolation of 2-hydroxy-3,4,6-trimethoxyacetophenone [9] and 2,4-dimethoxybenzoic acid [10] during the hydrolysis of its monomethyl ether (**2**) with 40% caustic potash solution.

EXPERIMENTAL

Mps. uncorr Whole plants of *Limnophila rugosa* (Roth) Merrill were collected from Santiniketan and their identity verified by Mr H R Chowdhury and Mr P. K Dan of Visva-Bharati University. A specimen of the plant is preserved.

Extraction of L. rugosa Air-dried powdered whole plants (1 5 kg) of *L ruqosa* were extracted with petrol (60–80°) in a Soxhlet apparatus for 56 hr. The extract was subjected to CC on 200 g silica gel (60–120 mesh). Fractions 130–155 (C_6H_6) were collected

Isolation of 5-hydroxy-7,8,2′,4′-tetramethoxyflavone (**1**) Fractions 130–155 yielded 5-hydroxy-7,8,2′,4′-tetramethoxyflavone It cryst. from C_6H_6 (yield 3 1 g), mp 188–189°, UV, IR and ^{1}H NMR (90 MHz, $CDCl_3$) data are described in the text

Methylation of **1** *with* Me_2SO_4 5-hydroxy-7,8,2′,4′-tetramethoxyflavone (75 mg) was dissolved in 100 ml Me_2CO and 1 5 g K_2CO_3 added before addition of Me_2SO_4 (4 ml) The mixture was boiled for 50 hr to give, after the usual work-up, compound **2** (50 mg), which cryst from Me_2CO–hexane, mp 173–174°, IR ν_{max}^{KBr} cm^{-1} 1600, 1610 It did not respond to the $FeCl_3$ test

Alkaline degradation of **2**. The monomethyl ether (**2**) (100 mg) was refluxed in a mixture of 40% KOH aq (25 ml) and EtOH (5 ml) under N_2 for 24 hr The reaction mixture was cooled, acidified with 10% HCl aq. and filtered The solid material sepd (30 mg) was shown to be 2,4-dimethoxybenzoic acid It cryst. from H_2O, mp 108–109° The soln was extracted with Et_2O, washed with 10% $NaHCO_3$ until free of acid and the dried Et_2O soln concd to give 2-hydroxy-3,4,6-trimethoxy acetophenone (40 mg), cryst from aq MeOH mp 109–110°, [M$^+$] *m/z* 226, ν_{max}^{KBr} cm^{-1} 3400, 1680

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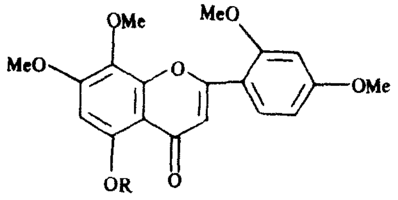

1 R = H

2 R = Me

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STRUCTURE ELUCIDATION OF ROEMERIDINE BY X-RAY CRYSTALLOGRAPHY

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Key Word Index—*Roemeria hybrida*; Papaveraceae, alkaloid roemeridine; X-ray crystallography.

Abstract—The structure of roemeridine, the major alkaloid from *Roemeria hybrida* was established by X-ray crystallography. Structure-significant features of the ^1H and ^{13}C NMR spectra and mass spectral fragmentations are reported.

INTRODUCTION

Roemeridine was isolated for the first time from *Roemeria hybrida* by Platonova and co-workers more than thirty years ago [1]. It was also found to occur in *Papaver pavonium* [1]. Slavík and co-workers [2] succeeded in isolating roemeridine as the main component of the basic fraction of the aerial parts of the latter plant; a particularly high content was found in the roots. The same authors [2] confirmed the elemental composition of roemeridine ($C_{31}H_{39}N_3O_5$) and used IR, UV, ^1H NMR and mass spectral data to discuss the type and number of functional groups present in the molecule. Based on these earlier findings a partial structure of roemeridine was proposed containing the β-carboline and tetrahydroisoquinoline ring systems [3]. The present paper reports the complete structure elucidation of roemeridine by X-ray crystallography aided by NMR and mass spectral measurements.

RESULTS AND DISCUSSION

High-field (9.4 T) ^1H and ^{13}C NMR spectra disclosed the substitution patterns of the heterocyclic moieties. The aromatic ring of the tetrahydroisoquinoline system was found to carry a carbon substituent, a hydroxy group and a methoxyl in a vicinal arrangement. The β-carboline system was found to contain two *ortho*-positioned aromatic methoxy groups each flanked by an aromatic