

5-METHOXYFURANO(2'',3'':7,8)FLAVONE FROM THE STEMS OF *OCHNA SQUARROSA*

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(Revised received 14 September 1982)

Key Word Index—*Ochna squarrosa*; Ochnaceae; 5-methoxyfurano(2'',3'':7,8)flavone.

Abstract—A new furanoflavone, 5-methoxyfurano(2'',3'':7,8)flavone, is reported from the stems of *Ochna squarrosa*.

Ochna squarrosa L., is a small shrub grown in the tropics. It is reported to have physiological properties; the bark as a digestive tonic and the root for its curative effect against asthma [1]. Earlier, from the leaves, biflavonoids [2] and flavonoid glycosides [3] were reported. We now report the isolation of a new furanoflavone (**1a**) from the stem tissue of this plant.

Compound **1a** analysed for $C_{18}H_{12}O_4$ and this was supported by 292 $[M]^+$. A positive Shinoda test [4] indicated its flavonoid nature and UV spectral data [λ_{Max}^{MeOH} nm (log ϵ): 270 (4.20), 316 (4.46)] were similar to those of flavones [5]. The IR spectrum of **1a** in potassium bromide revealed an absorption at 1635 cm^{-1} assignable to a flavone carbonyl group. Further, the absorptions at 760 and 729 cm^{-1} are characteristic of the C–H out-of-plane bending vibrations of an unsubstituted side phenyl ring and the absorptions at 885 and 833 cm^{-1} are due to the C–H out-of-plane bending vibrations of a furan ring. The compound did not form a methyl ether, on treatment with dimethyl sulphate in acetone and potassium carbonate, or an acetate, on treatment with acetic anhydride and pyridine, indicating that it did not have any free hydroxyl groups.

The ^1H NMR spectrum (CDCl_3) showed a singlet at $\delta 6.8$ (1H) assignable to C-3 of the flavone [5]. The spectrum also revealed the presence of two AB doublets, one at $\delta 7.7$ ($d, J = 2\text{ Hz}$) and the other at $\delta 7.1$ ($d, J = 2\text{ Hz}$) assignable to H-2'' and H-3'' of the benzofuran nucleus [6], respectively. Further, protons due to a methoxyl group at $\delta 4.06$ (3H, s) and a monosubstituted phenyl group at $\delta 7.9$ (2H, m) and $\delta 7.4$ (3H, m) were also found in the ^1H NMR spectrum. The singlet at $\delta 7.5$ (1H) is assignable to C-6 of flavone.

Compound **1a** on demethylation furnished a hydroxy compound (**1b**), which gave a green colour with alcoholic ferric chloride solution indicating a chelated hydroxyl group. Further the IR spectrum of **1b**, showed a chelated hydroxyl group at 3350 cm^{-1} and a carbonyl group at 1620 cm^{-1} . Compound **1b** was found to be identical (TLC, mp and mmp) with an authentic synthetic sample of 5-hydroxyfurano(2'',3'':7,8)flavone [7].

Thus, from the analytical, chemical and spectral evidence the 5-methoxyfurano(2'',3'':7,8)flavone structure was assigned to **1a**. The mass spectral fragmentation of **1a** m/z (%) 292 $[M]^+$ (72), 264 $[M - \text{CO}]^+$ (19), 277 $[M$

$-\text{Me}]^+$ (3), 249 $[M - \text{Me} - \text{CO}]^+$ (5), RDA ions 190 (71) (II), 102 (100) (III) and 77 $[\text{C}_6\text{H}_5]^+$ is in agreement with the assigned structure. The presence of RDA fragment ions II and III confirm the presence of a methoxy group as well as furano group in the A-ring of the flavone molecule.

Compound **1a** was found to be identical in all respects (TLC, mp, mmp, superimposable IR) with an authentic synthetic sample of 5-methoxyfurano(2'',3'':7,8)flavone [7]. This is the first report of **1a** as a natural product although it has been previously synthesized [8, 9].

EXPERIMENTAL

Plant material of *Ochna squarrosa* L. was collected from the Mannanore Forest, Andhra Pradesh and verified by Dr. S. T. Ramachandra Chary, Department of Botany, Osmania University, Hyderabad. The stems (6 kg) were coarsely powdered and extracted successively with petrol (60–80°), CHCl_3 and MeOH in a Soxhlet extractor. The CHCl_3 extract was concd to yield a semi-solid (20 g) which was chromatographed on Si gel (200 mesh) and eluted successively with petrol (60–80°), C_6H_6 and $\text{C}_6\text{H}_6\text{--CHCl}_3$ (9:1). The $\text{C}_6\text{H}_6\text{--CHCl}_3$ eluent (6 \times 50 ml) yielded **1a** which crystallized from Me_2CO as colourless crystals (0.20 g; 0.33%) mp 185–186° (lit. 180–181° [8], 185° [9]), M^+ 292. (Found C, 73.96; H, 4.12. $\text{C}_{18}\text{H}_{12}\text{O}_4$ requires C, 73.98; H, 4.10%).

Demethylation of 1a Compound **1a** (0.073 g; 0.25 μmol) was refluxed with dry AlCl_3 (0.033 g; 0.25 μmol) in dry C_6H_6 (50 ml) for 20 min. The solvent was removed under red. pres. and the residue mixed with H_2O . An almost colourless solid separated on keeping it overnight which crystallized from MeOH as colourless crystals of 5-hydroxyfurano(2'',3'':7,8)flavone (**1b**), mp 201–203°, identical with an authentic synthetic sample of 5-hydroxyfurano(2'',3'':7,8)flavone [7] [mmp, TLC, Si gel G ($\text{C}_6\text{H}_6\text{--CHCl}_3$, 1:1) and exposure to I_2 vapour].

Acknowledgements—We are grateful to Professor C. V. Ratnam, Department of Chemistry, Osmania University for providing facilities. We are also thankful to Dr. R. N. Khanna, Department of Chemistry, Delhi University, New Delhi, for providing authentic samples of 5-hydroxyfurano(2'',3'':7,8)flavone and 5-methoxyfurano(2'',3'':7,8)flavone. We thank the Chief Conservator of Forests, Government of Andhra Pradesh, Hyderabad (India) for supplying the plant material and Dr. S. T. Ramachandra Chary, Department of Botany, Osmania

University for verification. One of us (K.C.R.) is grateful to the UGC for the award of JRF.

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