Phytochemistry, 1980, Vol. 19, pp. 1272–1273. © Pergamon Press Ltd. Printed in England. 0031-9422/80/0601-1272 $02.00/0

TEPHROSOL, A NEW COUMESTONE FROM THE ROOTS OF *TEPHROSIA VILLOSA*

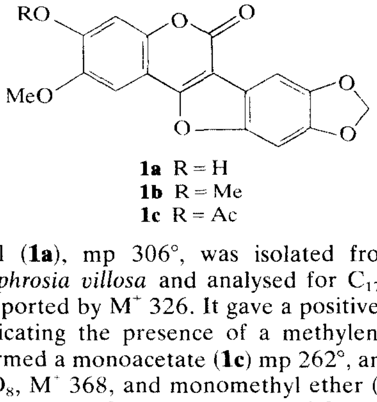
P. Pulla Rao and G. Srimannarayana

Department of Chemistry, Osmania University, Hyderabad-500 007, India

(*Received 7 September* 1979)

Key Word Index—*Tephrosia villosa*; Leguminosae; new coumestone; tephrosol; 3-hydroxy-2-methoxy-8,9-methylenedioxy-coumestone.

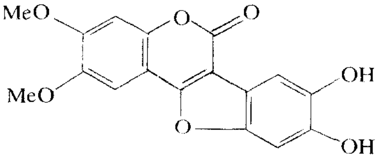
Tephrosia villosa (L.) Pers is a herbaceous plant grown widely in south India. The pods and roots of *T. villosa* were reported to have physiological properties [1]. Earlier, from the pods of *T. villosa*, six new rotenoids were reported [2, 3]. Rangaswamy and Sastry [4] isolated three crystalline compounds from the roots of the above plant which were considered to be isoflavones. In this communication the isolation and structural elucidation of a new coumestone, tephrosol, is discussed.



1a R = H
1b R = Me
1c R = Ac

Tephrosol (**1a**), mp 306°, was isolated from the roots of *Tephrosia villosa* and analysed for $C_{17}H_{10}O_7$ which is supported by M^+ 326. It gave a positive Labat test [5] indicating the presence of a methylenedioxy group. It formed a monoacetate (**1c**) mp 262°, analysed for $C_{19}H_{12}O_8$, M^+ 368, and monomethyl ether (**1b**) on treatment with Me_2SO_4–K_2CO_3 in Me_2CO, mp 245° (decomp.) analysed for $C_{18}H_{12}O_7$ and M^+ 340. Thus the presence of one phenolic hydroxyl group in tephrosol was indicated. In the IR spectrum (KBr) of tephrosol the absorptions due to the phenolic hydroxyl (3210 cm^{-1}), δ-lactone carbonyl (1710 cm^{-1}), aromatic C—O (1265 cm^{-1}) and methylenedioxy group (935 cm^{-1}) are discernible. Its UV spectral data $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε) 245 (4.59), 285 (4.10), 315 (3.97), 355 (4.45) is strikingly similar to that of a natural coumestone, wedelolactone [6]. The alcoholic solution of tephrosol exhibits fluorescence, a phenomenon commonly noted in coumarins and coumestones. Therefore a coumestone structure was considered for tephrosol. The UV spectrum of tephrosol showed a bathochromic shift [7] of 30 nm ($\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε) 385 (4.59)), in the long wavelength band in the presence of NaOAc indicating a hydroxyl group at the 3-position of coumestone skeleton. The mass spectral fragmentation of tephrosol, M^+ (326, 100%), M − Me (311, 44%), M − Me − CO (283, 28%) and M − Me − CO − CO (255, 8%) is in agreement with fragmentation of coumarins [8]. Particularly, considerable intensity of the M − Me ion is the characteristic of 6-methoxycoumarins [8]; therefore a methoxy group may be located at the 2-position. The ^{1}H NMR spectrum of its acetate (**1c**) ($CDCl_3$) revealed the presence of one methoxyl group (δ4.06, 3H, *s*), one acetoxyl group (2.42, 3H, *s*), one methylenedioxy group (6.2, 2H, *s*) and four aromatic protons (7.3, 1H, *s*; 7.44, 1H, *s*; 7.54, 1H, *s*; 7.64, 1H, *s*). Since there was no *ortho* or *meta* coupling pattern of protons in the aromatic proton region, the two pairs of aromatic protons may be *para*-oriented. Therefore the methylenedioxy group may be located at 8,9-positions. Thus tephrosol is 3-hydroxy-2-methoxy-8,9-methylenedioxycoumestone (**1a**). This assignment was confirmed by an authentic synthesis of its methyl ether.

4-Hydroxy-6,7-dimethoxycoumarin [9], on dehydrogenative coupling with catechol in the presence of $K_3Fe(CN)_6$–NaOAc in aq. acetone medium [10], afforded 2,3-dimethoxy-8,9-dihydroxycoumestone (**2**). On condensation with CH_2I_2 in dry Me_2CO–K_2CO_3 this furnished 2,3-dimethoxy-8,9-methylenedioxycoumestone (**1b**). It was identical with the methyl ether of tephrosol in all respects (mp, mmp, TLC and IR).



2

EXPERIMENTAL

Mps were uncorr. ^{1}H NMR spectrum was taken in $CDCl_3$ with TMS as internal standard.

Extraction. The air-dried roots (5 kg) of *T. villosa*, collected locally, were coarsely powdered and extracted successively with petrol (bp 60–80°), $CHCl_3$ and MeOH in a Soxhlet. The petrol extract on concn yielded a semi-solid (20 g), which was kept for further examination. The $CHCl_3$ and MeOH extracts were concd and residues were found to have identical behaviour on TLC. Therefore they were combined (30 g) and from the ether-soluble portion, a semi-solid (12 g) obtained was subjected to column chromatography on Si gel (200 mesh). It was eluted successively with petrol, C_6H_6, $CHCl_3$ and $CHCl_3$–EtOAc (9:1). $CHCl_3$–EtOAc eluents yielded a compound designated as tephrosol (**1a**), which crystallized from MeOH as green–yellow crystals (300 mg, 0.006%) mp 306°, M$^+$ 326. (Found: C, 62.55; H, 3.02. $C_{17}H_{10}O_7$, requires: C, 62.58: H, 3.06%). The monoacetate (**1c**) crystallized from MeOH as colourless crystals (40 mg), mp 262°, M$^+$ 368. (Found: C, 61.92; H, 3.23. $C_{19}H_{12}O_8$ requires: C, 61.95; H, 3.26%). UV λ_{max}^{MeOH} nm (log ε): 245 (4.79), 285 (4.47), 315 (4.13), 355 (4.34), IR ν_{max}^{KBr}: cm^{-1}: 1760, 1740, 1255, 933. The monomethyl ether **1b** crystallized from MeOH, mp 245° (decomp.), M$^+$ 340. (Found: C, 63.51; H, 3.5. $C_{18}H_{12}O_7$ requires: C, 63.53; H, 3.53%). UV λ_{max}^{MeOH} nm (log ε): 250 (4.55), 285 (4.0), 315 (3.77), 355 (4.15); IR ν_{max}^{KBr} cm^{-1}: 1720, 1260, 925.

Synthesis. 6-7-Dimethoxy-4-hydroxycoumarin [10] (1 g) and catechol (0.6 g) were dissolved in aq. Me_2CO (10 ml; 1 : 1) containing NaOAc (3 g). Addition of a soln of $K_3Fe(CN)_6$ (3 g) and NaOAc (3 g) in H_2O (20 ml) to the above soln yielded **2**, a brown ppt. which crystallized from MeOH as pale yellow crystals, mp > 300° (decomp.) (0.8 g). (Found: C, 62.12; H, 3.6. $C_{17}H_{12}O_7$ requires: C, 62.19; H, 3.66%). A mixture of **2** (0.5 g) and CH_2I_2 (5 ml) was refluxed in Me_2CO (120 ml)–K_2CO_3 (10 g) for 8 hr and worked up as usual. The product on crystallization from MeOH gave a pale yellow crystalline compound, mp 245° (decomp.) (0.4 g), identical with **1b**.

Acknowledgements—We thank Prof. T. Navaneeth Rao, Head of the Chemistry Department, for providing facilities. We are thankful to the UGC, New Delhi for awarding a Junior Research Fellowship to one of us (P. P. R.).

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Phytochemistry, 1980, Vol. 19, pp. 1273–1274. © Pergamon Press Ltd. Printed in England. 0031-9422/80/0601-1273 $02.00/0

EHRETININE, A NOVEL PYRROLIZIDINE ALKALOID FROM *EHRETIA ASPERA*

Om P. Suri, Rajinder S. Jamwal, Krishan A. Suri and Chand K. Atal

Regional Research Laboratory, Jammu-Tawi, India

(*Revised received* 4 *September* 1979)

Key Word Index—*Ehretia aspera;* Boraginaceae; pyrrolizidine; retronecanol; *p*-methoxybenzoic acid.

Abstract—The structure for ehretinine, 7-*O*-(*p*-methoxybenzoyl)-retronecanol, a new pyrrolizidine alkaloid isolated from leaves of *Ehretia aspera* has been established by a combination of spectroscopic and chemical methods. To our knowledge this constitutes the first report of the natural occurrence of a retronecanol ester.

INTRODUCTION

Ehretia aspera Willd. [1], a tree growing in Deccan peninsula extending northwards to Uttarpradesh and Punjab has not been chemically investigated. Present investigations on the alkaloids from the leaves of this species have resulted in the isolation and identification of a retronecanol ester of *p*-methoxybenzoic acid.

RESULTS AND DISCUSSION

The ^{1}H NMR ($CDCl_3$) spectrum of ehretinine (**1**) exhibits characteristic signals of a pyrrolizidine nucleus [2] at δ 2.4 (*m*, H-2 and H-6), 2.8 (*m*, H-5), 3.8 (*m*, H-3) and 5.8 (*m*, H-7). The usual position of the H-7 signal in pyrrolizidine secondary esters is *ca* δ 5, this peculiar downfield shift could only be explained after