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A PRENYLATED FLAVAN FROM *TEPHROSIA MADRENSIS**

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Key Word Index—*Tephrosia madrensis*; Leguminosae, 5,7-dimethoxy-8-prenylflavan

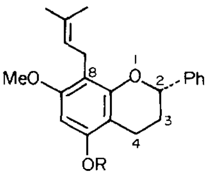
Abstract—5,7-Dimethoxy-8-prenylflavan has been isolated and identified from aerial parts of *Tephrosia madrensis*.

INTRODUCTION

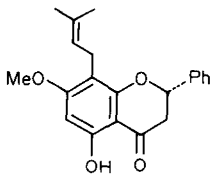
The genus *Tephrosia* is known to contain rotenoids, 7-oxygenated and 5,7-dioxygenated flavonoids characterized by the presence of a C-8 prenyl unit [1]. In the present paper we report the isolation and structure elucidation of a new prenylated flavan **1a** from *Tephrosia madrensis*,† an endemic species of the Oaxaca Valley in México. The known 5-hydroxy-7-methoxy-8-prenylflavanone (**2**), D-(+)-pinitol, sitosterol and stigmasterol were also obtained.

RESULTS AND DISCUSSION

The flavan, **1a**, analysed for $C_{22}H_{26}O_3$ (M^+ 338), mp 76–77°. The UV spectrum λ_{max} nm (ε): 209 (57 339), 263 (sh 787), 271 (904) and 276 (sh 814) indicated the presence of an unconjugated aromatic system. The IR spectrum indicated the absence of carbonyl and hydroxyl groups The ^1H NMR spectrum showed a symmetrical multiplet at δ 7.3 (5H) corresponding to an unsubstituted phenyl group. Three singlets at δ 3.78, 3.80 (3H each) and 6 06 (1H) were indicative of a 5,7-dimethoxyflavan nucleus, substituted at C-8 or C-6 The aliphatic CH appears at δ 4.95 (1H) as a doublet of doublets (J = 4, 10 Hz) and two methylene multiplets at δ 2.64 and 2.1 (2H each). The remaining protons were observed as a broad singlet at δ 1.6 (6H) for two methyl groups, one doublet at 3 25 (2H) and a triplet at 5.2 (1H) for an isolated olefinic proton. These resonance are typical for a prenyl side chain [2] and permitted the assignment of either structure **1a** or the 6-prenyl isomer. The mass spectrum showed peaks at m/z 338 $[M]^+$, 234, 247, 219, 104, 91 which were consistent with the proposed fragmentation pattern of flavans [3].



1a R = Me
1b R = H



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Confirmation of the structure and stereochemistry of **1a** was achieved by partial synthesis as follow. Reduction of 5-hydroxy-7-methoxy-8-prenylflavanone (**2**) with sodium borohydride [4] resulted in the hydroxyflavan, **1b**, which was methylated with dimethyl sulfate to afford the methyl ether, **1a**. All the spectroscopic data of the obtained product were identical to those of the isolated flavan **1a**. This is the first flavan isolated from genus *Tephrosia* containing a prenyl side chain.

EXPERIMENTAL

Mps were determined on a Koffler block and are uncorr Analysis was determined by Dr F Pascher, West Germany *Tephrosia madrensis* was collected in Oaxaca, Mexico *ca* 15 km NW of Silacayaopilla, October 1980 A voucher is on deposit at the Herbarium of Instituto de Biología (U N.A M), México

Dried leaves and flowers (400 g) were extracted with hot EtOH The crude syrup after elimination of the solvent was washed several times with hexane, filtered and concd *in vacuo* From the combined hexane washings, 7 5 g of crude syrup were obtained and percolated on a column packed with 75 g Tonsil optimum extra (supplied by Tonsil Mexicana) and eluted with hexane and mixtures of hexane–$CHCl_3$ (1 1), $CHCl_3$ and $CHCl_3$–Me_2CO (2 1) From the fraction eluted with hexane–$CHCl_3$ (1 1) a mixture of sitosterol, stigmasterol and 5-hydroxy-7-methoxy-8-isoprenylflavanone (**2**) was obtained

Isolation of 5,7-dimethoxy-8-prenylflavan (**1a**) Fraction 2 eluted with hexane–$CHCl_3$ and purified by TLC, afforded 85 mg **1a**, mp 75–77° from hexane–Me_2CO, $[\alpha]_D - 79\ 5°$ ($CHCl_3$, c 0 088) UV λ_{max}^{MeOH} nm (ε) 209 (57, 339), 263 (sh 787), 271 (904), 276 (sh 314). IR ν_{max}^{film} cm^{-1} 1610, 1500 EIMS (probe) 70 eV m/z (rel int) 338 $[M]^+$ (34), 234 $[M - C_8H_8]^+$ (15), 247 $[M - C_7H_7]^+$ (3), 219 $[C_{13}H_{16}O_3]^+$ (100), 104 $[C_8H_8]^+$ (17 5), 91 $(C_7H_7]^+$ (33) (Found C, 78 28, H, 7 86, O, 14 10 $C_{22}H_{26}O_3$ requires C, 78 07, H, 7 74, O, 14 18 %)

5-Hydroxy-7-methoxy-8-prenylflavan (**1b**) Formed by reduction of 5-hydroxy-7-methoxy-8-prenylflavanone (**2**) (100 mg) in HOAc (20 ml) with $NaBH_4$ added over 4 hr (the reaction being monitored by TLC) Dilution with H_2O and extraction with Et_2O gave **1b** (19 mg), IR ν_{max}^{film} cm^{-1} 3390, 1615, 1600, 1500, EIMS (probe) 70 eV m/z (rel int) 324 $[M]^+$ (43), 309 $[M - 15]^+$ (17), 205 $[C_{12}H_{13}O_3]^+$ (100), 177 $[C_{11}H_{13}O_2]^+$ (41 5), 104 $[C_8H_8]^+$ (4 8), 91 $[C_7H_7]^+$ (14 6)

5,7-Dimethoxy-8-prenylflavan (**1a**) Compound **1b** in dry

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†We thank Mr O Telles of Instituto de Biología (U.N A M) for collecting and identifying the plant material

Me_2CO (20 ml), Me_2SO_4 (0.5 ml) and dry K_2CO_3 (100 mg) was refluxed for 2 hr and worked-up as usual Purification by TLC-$AgNO_3$ of the reaction residue yielded a crystalline compound which was identical to flavan **1a** in all respects

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ISOAURMILLONE, AN ISOFLAVONE FROM THE PODS OF *MILLETIA AURICULATA*

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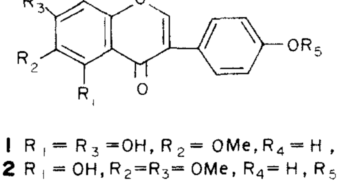
Key Word Index—*Milletia auriculata*, Leguminosae, pods, isoaurmillone, 5,7-dihydroxy-6-methoxy-4′-*O*-prenyloxyisoflavone

Abstract—The pods of *Milletia auriculata* have yielded a new substance, 5,7-dihydroxy-6-methoxy-4′-*O*-prenyloxy-isoflavone.

In continuation of our studies on plants exhibiting pesticidal activity we became interested in the pods of *Milletia auriculata*, the roots of which are reported to possess insecticidal and piscicidal properties [1] A number of isoflavonoids have already been isolated from the roots [2], leaves and stems [3] of *M auriculata* From the petrol extract of the dried pods of *M auriculata* we have isolated another new isoflavone, isoaurmillone, to which we have assigned the structure **1**

Isoaurmillone (**1**) $C_{21}H_{20}O_6$ was obtained in poor yield (0.002 %) from the petrol (bp 60–80°) extract of the dried pods of *M auriculata*. The colour reaction (green ferric colour), UV λ_{max}^{MeOH} 269 nm and IR data ν_{max}^{KBr} 1655 cm^{-1} (=C=O) coupled with a low field singlet at $\delta 8.0$ in the NMR spectrum are indicative of the presence of an isoflavone system [4]. Functional group analysis revealed the presence of OMe-1 ($\delta 4.0$, 3H, *s*), 2-phenolic hydroxyl groups (1H, singlets at $\delta 8.5$ and 17.7, exchangeable with D_2O) and a prenyloxy system [2, 5] ($\delta 4.87$, 2H, *d*, $J = 7$ Hz, –O–CH_2, $\delta 1.80$, 6H, *d*, = C Me_2, $\delta 5.57$, 1H, *m*, –CH=). The spectrum also disclosed four aromatic protons constituting an A_2B_2 system (2H, *d*, $J = 9$ Hz at $\delta 7.06$ and 7.49) which are assignable to a *p*-disubstituted phenyl nucleus [4, 5] and an aromatic singlet at $\delta 6.5$. Further, the UV spectrum of **1**, showing a bathochromic shift of 10 and 14 nm upon addition of aluminium chloride–hydrochloric acid and sodium hydroxide, respectively, suggested the presence of hydroxyl groups [4] at C-5 and C-7

Although the physical data of isoaurmillone (**1**) showed resemblance with those of aurmillone (**5**) the latter, on direct comparison (mp, mmp and co-TLC) with isoaurmillone (**1**), proved to be different The monomethyl (**2**) and dimethyl (**3**) ethers of **1** also showed differences with aurmillone (**5**) Acid hydrolysis of isoaurmillone gave a compound (M^+ 300), the physical and spectral data of which were found to be in agreement with tectorigenin, 5,7,4′-trihydroxy-6-methoxyisoflavone (**4**) [6] On the basis of these results, isoaurmillone was identified as 5,7-dihydroxy-6-methoxy-4′-*O*-prenyloxyisoflavone (**1**) which is a positional isomer of aurmillone (**5**) [7]



1 $R_1 = R_3 = OH, R_2 = OMe, R_4 = H, R_5 = CH_2CH{=}CMe_2$
2 $R_1 = OH, R_2 = R_3 = OMe, R_4 = H, R_5 = CH_2CH{=}CMe_2$
3 $R_1 = R_2 = R_3 = OMe, R_4 = H, R_5 = CH_2CH{=}CMe_2$
4 $R_1 = R_3 = OH, R_2 = OMe, R_4 = R_5 = H$
5 $R_1 = R_3 = OH, R_2 = H, R_4 = OMe, R_5 = CH_2CH{=}CMe_2$