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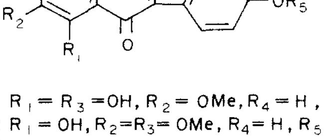
Key Word Index—*Milletia auriculata*, Leguminosae, pods, isoaurmillone, 5,7-dihydroxy-6-methoxy-4′-*O*-prenyloxyisoflavone

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 δ8 0 in the NMR spectrum are indicative of the presence of an isoflavone system [4]. Functional group analysis revealed the presence of OMe-1 (δ4.0, 3H, *s*), 2-phenolic hydroxyl groups (1H, singlets at δ8 5 and 17 7, exchangeable with D_2O) and a prenyloxy system [2, 5] (δ4 87, 2H, *d*, J = 7 Hz,–O–CH_2, δ1 80, 6H, *d*, = C Me_2, δ5 57, 1H, *m*, –CH=). The spectrum also disclosed four aromatic protons constituting an A_2B_2 system (2H, *d*, J = 9 Hz at δ7 06 and 7.49) which are assignable to a *p*-disubstituted phenyl nucleus [4, 5] and an aromatic singlet at δ6 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 $R_1 = R_3 = OH, R_2 = H, R_4 = OMe, R_5 = CH_2CH{=}CMe_2$

EXPERIMENTAL

Isolation of **1** The dried pods were extracted with petrol and the concd extract was chromatographed over Si gel C_6H_6 eluates afforded a yellow solid which was further purified by rechromatography over Si gel Elution of the chromatogram with C_6H_6–petrol (8 2) furnished a yellow solid which crystallized from $CHCl_3$–petrol (1 1) as yellow needles, mp 162 5–163 5°, $[\alpha]_D \pm 0°$, $C_{21}H_{20}O_6$ (M^+ 368), UV λ_{max}^{MeOH} 269 nm, $\lambda_{max}^{MeOH-AlCl_3-HCl}$ 279 nm, $\lambda_{max}^{MeOH-NaOAc}$ 283 nm, IR ν_{max}^{KBr} 1655 cm^{-1}, NMR δ4 0 (3H, *s*, OMe-1), 6.5 (*s*, one phenolic OH), 12 7 (*s*, one chelated phenolic OH), 4.87 (2H, *d*, $J = 7$ Hz, $-OCH_2$), 1 8 (6H, 2 × *s*, $=CMe_2$), 5 57 (1H, *m*, $-CH=$), 7 06 (2H, *d*, $J = 9$ Hz), 7 49 (2H, *d*, $J = 9$ Hz), 6 5 (*s*, ArH-1), 8 0 (1H, *s*, C-2-proton)

Monomethylation of **1**. Compound **1** on methylation with CH_2N_2 for 24 hr gave a yellow crystalline compound (**2**), mp 118–119°, $C_{22}H_{22}O_6$ (M^+ 382), UV λ_{max}^{MeOH} 266 nm, $\lambda_{max}^{MeOH-AlCl_3-HCl}$ 276 nm IR ν_{max}^{KBr} 1650 cm^{-1}, NMR δ1 52 (3H, *s*, Me), 1 8 (3H, *br s*, Me), 3 91 (3H, *s*, OMe-1), 3 97 (3H, *s*, OMe-1), 4 53 (2H, *d*, $J = 7$ Hz, $-OCH_2-$), 5 53 (1H, *m*, $CH=$), 6 45 (*s*, ArH-1), 7 0 (2H, *d*, $J = 9$ Hz), 7 47 (2H, *d*, $J = 9$ Hz), 7 94 (1H, *s*, C-2-proton)

Dimethylation of **1** Methylation of **1** with Me_2SO_4–K_2CO_3 in Me_2CO for 45 hr afforded the dimethyl ether **3** after usual work-up, mp 220–222°, $C_{23}H_{24}O_6$ (M^+ 394), IR ν_{max}^{KBr} 1655 cm^{-1}, NMR δ1 78 (6H, *d*, $=CMe_2$), 5 55 (1H, *m*, $-CH=$), 4 6 (2H, *d*, $J = 7$ Hz, $-OCH_2-$), 3 90 (3H, *s*, OME-1), 3 94 (3H, *s*, OMe-1), 3 98 (3H, *s*, OMe-1), 6 48 (*s*, ArH-1), 7 0 (2H, *d*, $J = 9$ Hz), 7 48 (2H, *d*, $J = 9$ Hz), 8 15 (1H, *s*, C-2-proton)

Acid hydrolysis of **1** Compound **1** was hydrolysed with HOAc–HCl (25 1) for 2 hr and extracted with EtOAc The concd extract on crystallization from $CHCl_3$–petrol (1 1) furnished the deprenylated derivative which was identical with tectorigenin (**4**), mp 224–226°, $C_{16}H_{12}O_6$ (M^+ 300)

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