EXPERIMENTAL

Isolation The air-dried capsules (without seeds, 640 g) of *M japonicus* Muell Arg were extracted with MeOH at room temp for 4 days The MeOH filtrate was concd to give ppts, which were crystallized from MeOH to afford yellow needles (compound **A**) The filtrate separated from **A** was evaporated to dryness, dissolved in H_2O and extracted with hexane and then with EtOAc to give a hexane extract (9 7 g) and an EtOAc extract (24 3 g) The latter was purified on a Sephadex LH-20 column ($CHCl_3$–MeOH, 1 1) followed by repeated CC on Si gel (hexane–$CHCl_3$ and then hexane–EtOAc) to afford additional **A** and compound **B**

Compound A Yellow needles (2 4 g) from MeOH, mp 188–189° (uncorr) UV λ_{max}^{EtOH} nm(ϵ) 293 (23 200), IR ν_{max}^{KBr} cm^{-1}, 3310 (OH), 3220, 1615, 1595, 1558, 1434, 1390, 1365, 1260, 1208, 1172, 1128, MS *m/z* 444 $[M]^+$, 389 $[M-55]^+$, 249, 235, 209, 195, 181, NMR Tables 1 and 2 (Found C, 64 35, H, 6 44 $C_{24}H_{28}O_8$ requires C, 64 85, H, 6 35%) *Pentamethyl ether of A* A MeOH soln of **A** (14 1 mg) was treated with CH_2N_2–Et_2O The resulting products purified by CC on Si gel gave a colourless oil (4 2 mg), MS *m/z* 514 $[M]^+$, ^1H NMR $\delta(CDCl_3)$ 1 68, 1 75 (3H, *br s* each, Me), 2 15 (3H, *s*, Me), 2 51 (6H, *s*, Ac), 3 31 (2H, *d*, $J = 6\ 2$ Hz), 3 46, 3 59 (3H, *s* each, OMe), 3 50, 3 70 (6H, *s* each, OMe), 4 00 (2H, *s*, CH_2 between rings), 5 16 (1H, *t*, $J = 6\ 2$ Hz) *Penta-acetate of A* **A** (20 mg) was acetylated with Ac_2O (1 ml) and pyridine (1 ml) at room temp for 10 min After usual treatment the resulting products were purified by CC on Si gel **A** colourless oil (15 mg) was obtained, MS *m/z* 654 $[M]^+$, ^1H NMR Table 1

Compound B Yellow needles (88 mg) from MeOH, mp 197–199° (uncorr) UV λ_{max}^{EtOH} nm(ϵ) 232 (22 600), 289 (18 600), 323 (16 400), IR ν_{max}^{KBr} cm^{-1} 3320 (OH), 3230, 1603, 1415, 1362, 1292, 1170, 1128, MS *m/z* 460 $[M]^+$, 417 $[M-43]^+$, 389 $[M-71]^+$, 209, 195, 181, NMR Tables 1 and 2 (Found C, 62 34, H, 6 23 $C_{24}H_{28}O_9$ requires C, 62 60, H, 6 13%) *Hexa-acetate of B* Using acetylation as described for **A**, a colourless oil was obtained, MS *m/z* 712 $[M]^+$, ^1H NMR Table 1

Reductive alkaline cleavage of A **A** (120 mg) dissolved in 5% NaOH (60 ml) was mixed with Zn powder (0 6 g) and warmed for 5 min at 100° The filtrate of the reaction mixture was acidified with 10% H_2SO_4 and extracted with Et_2O After evaporation of Et_2O the residue was purified through a Si gel column (hexane–EtOAc, 13 5) to afford yellow needles (32 5 mg), mp 197–200° (uncorr) MS *m/z* 196 $[M]^+$, 181, ^1H NMR (CD_3OD) δ 1 91 (3H, *s*, Me), 2 63 (3H, *s*, Ac), 3 81 (3H, *s*, OMe), 6 00 (1H, *s*) It was identified by comparison with an authentic sample of 2, 6-dihydroxy-3-methyl-4-methoxyacetophenone [6] by mmp and comparison of spectral data

Acknowledgement—We wish to thank Professor S Matsuura, Gifu Pharmaceutical Collage for an authentic sample of 2, 6-dihydroxy-3-methyl-4-methoxyacetophenone

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CANDIDOL, A FLAVONOL FROM *TEPHROSIA CANDIDA*

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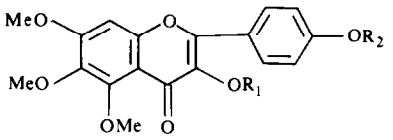
Key Word Index—*Tephrosia candida*, Leguminosae, flavonol, candidol, 3,4'-dihydroxy-5,6,7-trimethoxyflavone

Abstract—The seeds of *Tephrosia candida* have yielded a new flavonol, characterized here as 3,4'-dihydroxy-5,6,7-trimethoxyflavone

Earlier investigations [1, 2, Chibber, S S and Dutt, S K , unpublished] of the seeds of *Tephrosia candida* have revealed the presence of three new flavonoids We report here the isolation and characterization of a flavonol, candidol, from the ethyl acetate extract of the seeds It analysed for $C_{18}H_{16}O_7$ and produced a yellow fluorescence in UV light It responded to Shinoda's test for flavonoids giving a magenta colour



1 $R_1 = R_2 = H$

2 $R_1 = R_2 = Me$

and also gave a brownish-green colour with alcoholic ferric chloride indicating a chelated hydroxyl group The UV spectrum showed λ_{max} in methanol at 270 and 355 nm suggestive of a flavonol The presence of a chelated hydroxyl was supported by a bathochromic shift of 67 nm with aluminium chloride–hydrochloric acid in UV and absorptions at 3430 (ν_{OH}) and 1640 (ν_{CO}) cm^{-1} in the IR spectrum Absence of a shift with sodium acetate indicated the absence of a free hydroxyl at the 7-position However, a bathochromic shift of 35 nm with sodium methoxide suggested a 4'-hydroxyflavonol skeleton [3] This was substantiated by two doublets ($J = 10$ Hz) at δ7 00 and 8 05 in the ^1H NMR spectrum, characteristic of a A_2B_2 pattern, due to the B-ring protons The ^1H NMR spectrum further showed the presence of three methoxyl groups which were indicated by two singlets at δ3 70 and 4 00, integrating for three and six protons, respectively A sharp singlet at δ6 64 integrating for one proton was indicative of the fact that only one position in the A-ring was unsubstituted Absence of any low field deshielded proton suggested that the 5-position was substituted Methylation of candidol yielded a compound which was identified as 3,5,6,7,4'-pentamethoxyflavone (2) [4] This established the oxygenation pattern in candidol and showed the presence of two hydroxyl groups in addition to the three methoxyls The second hydroxyl was assigned to the 3-position on the basis of a negative Gibbs test Hence all three methoxyls must be present in ring A and this was confirmed by oxidation of the dimethyl ether (2), when 2-hydroxy-4,5,6,ω-tetramethoxyacetophenone and anisic acid were obtained The former was identified by direct comparison with an authentic sample prepared by the method of Row and Seshadri [5] A retro-Diels–Alder fragmentation pattern was not observed in the mass spectrum and is in agreement with the observation that such a process is of minor importance in the highly substituted flavones [6, 7] The structure 3,4'-dihydroxy-5,6,7-trimethoxyflavone (1) for candidol, assigned on the basis of spectral and chemical data, was finally confirmed by comparing it with a synthetic sample [8] (mmp and co-TLC)

It is interesting to note that 6-hydroxykaempferol 4'-methyl ether 3,7-dirhamnoside, a flavonol glycoside with the same substitution pattern, has been isolated from the aerial parts of *T candida* [4]

EXPERIMENTAL

Isolation Air-dried, coarsely powdered seeds (1 kg) of *T candida* were extracted with EtOAc after exhaustive treatment with petrol to remove petrol-soluble oils This extract was concd under red pres and subjected to CC over Si gel On elution with C_6H_6–EtOAc (8 2) it gave a pale yellow, crystalline compound (80 mg, mp 253–254°), candidol (1) TLC R_f 0 16 (C_6H_6–EtOAc, 4 1), 0 60 (C_6H_6–EtOAc, 1 1) UV λ_{max}^{MeOH} nm 270, 340, 355, +NaOAc 270, 340 +NaOMe 270, 390, +$AlCl_3$ 235, 275, 345, 422, +$AlCl_3$–HCl 235, 285, 360, 422 IR ν_{max}^{KBr} cm^{-1} 3430, 1640, 1590, 1460, 995 and 800 ^1H NMR (90 MHz, $CDCl_3$) δ 3 70 (3H, *s*, OMe), 4 00 (6H, *s*, 2 × OMe), 6 64 (1H, *s*, Ar -H-8), 7 00 (2H, *d*, $J = 10$ Hz, Ar -H-3', H-5'), 8 05 (2H, *d*, $J = 10$ Hz, Ar -H-2', H-6') MS *m/z* (rel int) 343 $[M-1]^+$ (67), 326 (24), 301 (19), 286 (16), 258 (10), 181 (61), 167 (21), 153 (100), 134 (97) and 121 (97) Methylation (Me_2SO_4, K_2CO_3, Me_2CO) gave the dimethyl ether as brown needles, mp 151–153°, characterized as 3,5,6,7,4'-pentamethoxyflavone (2) by comparing its chemical (mp) and spectral (IR, NMR) data with that reported in the lit [4]

Oxidation of candidol dimethyl ether (50 mg) in KOH (100 mg) and EtOH (50 ml) at 100° and extraction with $NaHCO_3$ gave a compound (10 mg), mp 182–184°, identified as anisic acid The residue crystallized from alcohol as pale yellow prisms (15 mg), mp 76–77° (lit [5] mp 77–78°), identified as 2-hydroxy-4,5,6,ω-tetramethoxyacetophenone by direct comparison (mmp, co-TLC and co-IR) with a synthetic sample

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