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ENANTIOMULTIJUGIN, A FLAVONE FROM *TEPHROSIA VICIODES**

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Key Word Index—*Tephrosia viciodes*; Leguminosae; Tephrosieae; flavone; enantiomultijugin.

Abstract—Investigation of the aerial parts of *Tephrosia viciodes* resulted in the isolation of a new enantiomeric *bis*furanoflavone, enantiomultijugin.

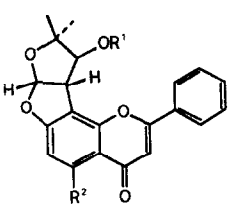
INTRODUCTION

Previous phytochemical studies involving the large (over 400 species) pantropical genus *Tephrosia* (Leguminosae: subfamily Papilionoideae, tribe Tephrosieae) have led to the isolation of numerous flavonoid derivatives (isoflavones, rotenoids and coumestans) some of which possess pronounced insecticidal and fish-poisoning properties. Several reports on the genus have demonstrated the presence of flavonoids with a 5,7-oxygenated pattern characterised by the presence of a C-8 prenyl unit. In many cases, the prenylated flavones have undergone further substitution and cyclisation leading to complex molecules [1–4]. As part of our systematic chemical study of the genus *Tephrosia* we have previously investigated several Mexican species and isolated a number of new flavonoids [5–7]. In continuation of our survey, a study of *T. viciodes*, an endemic species from the south west part of México, has now been undertaken.

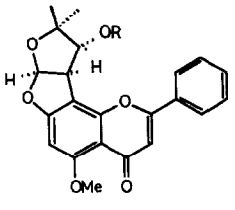
RESULTS AND DISCUSSION

The dichloromethane extract of the aerial parts of *T. viciodes*, on chromatographic separation gave a new flavonoid which we named enantiomultijugin (**1**).

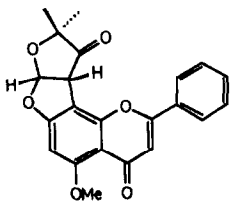
Enantiomultijugin (**1**), mp 232–233°, $[\alpha]_D$ −194.4°, was characterised as a non-phenolic flavone (positive Shinoda and negative $FeCl_3$ tests). Both the UV (262, 315 nm) and IR (1640 cm^{-1}) absorptions were typical of flavones. Further IR absorptions at 1730 and 1230 cm^{-1} suggested the presence of a non-phenolic acetate. The EI mass spectrum showed the $[M]^+$ at *m/z* 422 together with other significant fragmentation peaks at *m/z* 362 $[M-HOAc]^+$, 347 $[M-HOAc-Me]^+$, 333 $[M-HOAc-Me-CH_2]^+$, 319 $[M-HOAc-Me-CO]^+$ and 43. The structure of **1** followed from the EI mass spectrum and the ^1H and ^{13}C NMR spectra. The ^1H NMR confirmed the presence of an acetate, since it showed a sharp three proton singlet at δ2.22. Further three proton singlets at δ3.95, 1.28 and 1.11 indicated the presence of one methoxyl group and two geminal methyl groups. Two one proton singlets at δ6.67 and 6.38 could be assigned to H-6 and H-3, suggesting a 5,7,8-trisubstituted A-ring as in most of the flavonoids from *Tephrosia* species. The remaining signals, two doublets at δ6.58 and 4.21 (J = 6.5 Hz) and a broadened singlet at δ5.58 were associated with a dihydro-bis-furane moiety, as present in multijugin [8], purpurin [9] and semiglabrin [4], all constituents of other *Tephrosia* species. Furthermore, all the above data are in agreement with the structure of multijugin (**2**), except for the optical rotation value $[\alpha]_D$ −194.4°, which suggested that compound **1** isolated from *T. viciodes* must be the enantiomeric isomer of multijugin, which has an optical rotation $[\alpha]_D$ +206.2 [8]. The ^{13}C NMR data of **1** were very similar to those reported for semiglabrin (**1b**) [1], except for the presence of one extra methyl carbon at δ56.7, and the different chemical shifts of C-5, C-6, C-8 and C-4a associated with the introduction of one methoxyl group at C-5. APT experiments indicated the presence of four methyl, ten methine and eight tetrasubstituted carbon atoms.



	R^1	R^2
1	Ac	OMe
1a	H	OMe
1b	Ac	H



	R
2	Ac
2a	H



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*Part 9 in the series 'Flavonoids from *Tephrosia* species'. For Part 8 see ref. [7]. This is contribution No. 1112 of Instituto de Química, UNAM, in commemoration of its 50th anniversary.

Further evidence for the structure **1** for enantiomultijugin was obtained as follows. Alkaline hydrolysis of the acetate group in **1** afforded the alcohol **1a**, $C_{22}H_{20}O_6$ ([M]$^+$ *m/z* 380), mp 291–294°. The presence of a secondary hydroxyl group in **1a** was evident from the IR absorption and the upfield shift (δ1.27) of the C-3″ methine proton in the ^{1}H NMR spectrum. All spectroscopic data of **1a** were almost identical to those reported for multijuginol (**2a**) [8], except for the optical rotation value $[\alpha]_D$ −173°, which confirmed its identity as enantiomultijuginol **1a**. Oxidation of **1a** with CrO_3–pyridine gave the corresponding enantiomultijuginone **3**, $C_{20}H_{18}O_6$ ([M]$^+$ *m/z* 378), mp 320–325°, $[\alpha]_D$ −168.1°. Accordingly from this data the compound isolated from *T. viciodes* must be the enantiomeric isomer of multijugin, which we have named enantiomultijugin (**1**).

EXPERIMENTAL

T. vicoides was collected in Carrizalillo near Puerto Escondido, in the state of Oaxaca (México) in 1982. The plant material was identified by Oswaldo Tellez and a voucher specimen deposited at the Herbarium of the Instituto de Biología, UNAM (MEXU). Air-dried and powdered aerial parts of the plant (1.2 kg) were extd with CH_2Cl_2 under reflux. The combined exts yielded a dark green residue (8.3 g) which was sepd by CC using petrol and petrol–CH_2Cl_2 mixts as eluants. The low polarity frs afforded the ubiquitous β-sitosterol. The medium polarity frs, after further purification by CC yielded 161 mg of **1**.

Enantiomultijugin (**1**). $C_{24}H_{22}O_7$, ([M]$^+$ *m/z* 422). Colourless crystals, mp 232–233° (CH_2Cl_2–MeOH). $[\alpha]_D$ −194.4° ($CHCl_3$; *c*3.6). UV λ_{max}^{MeOH} nm (ε): 210 (37724), 262 (31010), 315 (8088). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730, 1640. EIMS (probe) 70 eV *m/z* (rel. int.): 422 [M]$^+$ (100), 362 (17), 347 (20), 333 (40), 319 (19), 43 (36). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.11, 1.28 (6H, *s*, *gem* Me_2), 2.22 (3H, *s*, OCOMe), 3.95 (3H, *s*, OMe), 4.21 (*d*, *J* = 6.5 Hz, H-3″), 5.58 (*s*, H-3‴), 6.38 (*s*, H-6), 6.58 (*d*, *J* = 6.5 Hz, H-2″), 6.67 (*s*, H-3), 7.48 and 7.85 (5H, *m*, $-\phi$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 177.1 (*s*), 169.5 (*s*), 163.6 (*s*), 162.9 (*s*), 160.2 (*s*), 154.5 (*s*), 131.3 (*d*), 131.2 (*s*), 128.9 (*d*), 126.0 (*d*), 112.6 (*d*), 109.3 (*s*), 104.0 (*s*), 91.1 (*d*), 88.0 (*s*), 80.2 (*d*), 56.7 (*q*), 52.8 (*d*), 27.5 (*q*), 23.1 (*q*), 20.8 (*q*).

Alkaline hydrolysis of **1**. A soln of **1** (190 mg) and KOH (250 mg) in aq. MeOH (90% MeOH, 30 ml) was stirred at room temp. for 30 min. The mixt. was dild with H_2O (15 ml) and extd with CH_2Cl_2. The residue was purified by CC and recrystallised from petrol–Me_2CO to give **1a** (156 mg), mp 291–294°, $[\alpha]_D$ −173° ($CHCl_3$; *c*1.82). UV λ_{max}^{MeOH} nm (ε): 211 (41011), 265 (35855), 320 (10945). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3460, 1648. EIMS (probe) 70 eV *m/z* (rel. int.): 380 [M, $C_{22}H_{20}O_6$]$^+$ (100), 362 (20), 347 (23), 333 (28), 319 (12), 179 (23), 43 (31). ^{1}H NMR (80 MHz, $CDCl_3$) δ: 1.07, 1.40 (6H, *s*, *gem* Me_2), 3.93 (3H, *s*, OMe), 4.23 (*d*, *J* = 6.5 Hz, H-3″), 4.3 (*s*, H-3‴), 6.35 (*s*, H-6), 6.60 (*d*, *J* = 6.5 Hz, H-2″), 7.4, 7.7 (5H, *m*, $-\phi$).

Oxidation of **1a**. A soln of **1a** (100 mg) in CH_2Cl_2 (30 ml) was treated with a soln of CrO_3 (500 mg) in pyridine (2 ml) for 12 hr. Usual work-up and purification of the residue afforded 3 (20 mg) as colourless crystals, mp 320–325° (petrol–Me_2CO), $[\alpha]_D$ −168.1° ($CHCl_3$; *c*1.82). UV λ_{max}^{MeOH} nm (ε): 209 (27672), 262 (26702), 315 (10079). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1765, 1646. EIMS (probe) 70 eV *m/z* (rel. int.): 378 [M, $C_{20}H_{18}O_6$]$^+$ (100), 349 (21), 291 (38), 263 (47), 246 (42). ^{1}H NMR (80 MHz, $CDCl_3$) δ: 1.25, 1.42 (6H, *s*, gem Me_2), 3.96 (3H, *s*, OMe), 4.42 (*d*, *J* = 6.5 Hz, H-3″), 6.42 (*s*, H-6), 6.70 (*s*, H-3), 6.72 (*d*, *J* = 6.5 Hz, H-2″), 7.5, 8.09 (5H, *m*, $-\phi$).

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