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PRENYLFLAVANS FROM *TEPHROSIA WATSONIANA**

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Abstract—The aerial parts of *Tephrosia watsoniana* afforded five new flavonoids named tephrowatsin A, B, C, D and E Their structures and stereochemistries were established by spectroscopic methods and chemical transformations

INTRODUCTION

Various rotenoids, isoflavones, flavones, chalcones, flavonols and flavanones have been isolated from plants of genus *Tephrosia* [1] Some of them possess insecticidal activity [2] As part of our chemosystematic study of plants of the genus *Tephrosia*, we previously investigated *T madrensis*, *T nitens* and isolated 5,7-dimethoxy-8-prenylflavan (**1**), 5-hydroxy-7-methoxy-8-prenylflavanone (**2a**) [3] and nitenin (**3**) [4]

We now wish to report the isolation from *Tephrosia watsoniana* of the known 5,7-dimethoxy-8-prenylflavan (**1**) [3], 5-hydroxy-7-methoxy-8-prenylflavanone (**2a**) [3], ninetin (**3**) [4], 5-methylquercetin, and a mixture of sitosterol and stigmasterol, and also the isolation and structure elucidation of five new flavonoids which we have named tephrowatsins A (**4**), B (**5**), C (**6**), D (**7**) and E (**8**)

RESULTS AND DISCUSSION

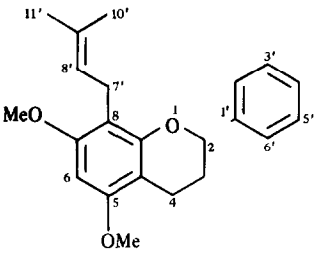
Tephrowatsin A (**4**), $C_{22}H_{26}O_4$ (M^+ 354), $[\alpha]_D$ −43 3°, was a colourless oil whose IR spectrum demonstrated the presence of hydroxyl (3440 cm^{-1}) but not carbonyl groups The UV spectrum λ_{max} nm (ε), 209 (57 998), 273 (1309) indicated the presence of an unconjugated aromatic system The structure of **4** was deduced from the ^1H NMR spectrum (Table 1) which was in part close to that of the flavanone **2b** [5] The presence of two one-proton doublet of doublets at δ5 15 (J = 3 Hz, J = 12 Hz) and 5 0 (J = 3 Hz, J = 4 Hz) and one two-proton multiplet at δ2 2 suggested that the tephrowatsin A must be the 4-hydroxyflavan **4** Confirmation of structure and stereochemistry of tephrowatsin A (**4**) was achieved by Sarett oxidation which gave the corresponding flavanone **2b** All the spectroscopic data of the product obtained were identical to those of the 5,7-dimethoxy-8-prenylflavanone (**2b**) [5]

Tephrowatsin B (**5**), $C_{22}H_{24}O_3$ (M^+ 336) was an oil Its IR spectrum indicated the absence of hydroxyl and carbonyl groups The ^1H NMR spectrum (Table 1) indicated that tephrowatsin B must be the dehydration product of **4**, since it showed two olefinic proton signals as a doublet of doublets at δ6 79 (J = 10 Hz, J = 3 Hz) and 5 62 (J = 10 Hz, J = 4 Hz) and the H-2 signal as a doublet of doublets at 5 8 (J = 4 Hz, J = 3 Hz) indicating an allylic interaction between H-2 and H-4 The mass spectrum showed peaks at m/z 336 $[M]^+$, 321 $[M-Me]^+$, 281 $[M-C_4H_7]^+$ and 105 $[C_7H_5O]^+$ which were consistent with the proposed structure for tephrowatsin B (**5**) Final confirmation of structure of **5** was achieved by dehydration of tephrowatsin A (**4**) with $MgSO_4$ which furnished tephrowatsin B (**5**)

Tephrowatsin C (**6**) was isolated as colourless needles, mp 72–74°, it analysed for $C_{21}H_{24}O_5$ (M^+ 356) Its IR spectrum showed strong absorption at 1640 cm^{-1} (chelated C=O) and 3400 cm^{-1} (OH) The UV spectrum λ_{max} nm (ε) 290 (19 090), 339 (4236) suggested a flavanone structure The structure of **6** clearly followed from the ^1H NMR spectrum (Table 1) which showed the typical ABX system, due to H-2 and H-3 protons of the flavanone nucleus As in case of the flavonoids **4** and **5**, tephrowatsin C (**6**) has an unsubstituted B-ring and trisubstituted A-ring The ^1H NMR showed signals for one methoxyl group at δ3 84 and a chelated hydroxyl group at δ12 05, therefore the hydroxyl group must be at C-5 and the methoxyl group could be placed at C-7 While tephrowatsin A (**4**) and B (**5**) have a prenyl side chain at C-8, tephrowatsin C (**6**) has a 3-hydroxyisopentyl group as indicated by the sharp singlet at δ1 2 (6H) and two methylene multiplets at 1 60 and 2 65 in the ^1H NMR spectrum of **6** The negative value of the optical rotation, $[\alpha]_D$ − 50°, indicated the absolute configuration '*S*' at C-2 in tephrowatsin C (**6**) [6] Confirmation on structure **6** was achieved by dehydration with $MgSO_4$ which furnished the known 7-methylglabranin (**2a**), mp 128–129°, identified by the IR, ^1H NMR and mass spectra and comparison with an authentic sample

Tephrowatsin D (**7**), $C_{23}H_{28}O_4$ (M^+ 368) was isolated as a colourless oil The UV spectrum λ_{max} nm (ε) 206 (31 542), 270 (932), 276 (943) suggested the presence of an unconjugated aromatic system The IR indicated the absence of carbonyl and hydroxyl groups The ^1H NMR spectrum (Table 1) of **7** was very similar to that of 5,7-dimethoxy-8-prenylflavan (**1**) previously isolated from *Tephrosia madrensis* [3] Tephrowatsin D (**7**), differs from **1** by the presence of an extra methoxy group at the C-2 position, since the ^1H NMR spectrum of **7** lacked the H-2 doublet of doublets, instead it showed a sharp methoxyl

*Contribution No 687 from Instituto de Química de la UNAM (México)



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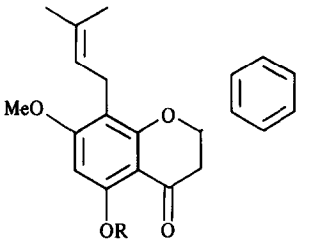

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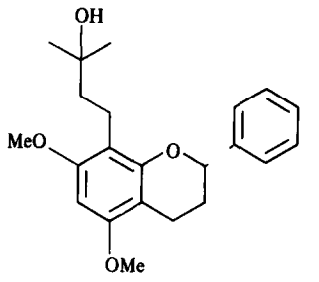
2b R = Me



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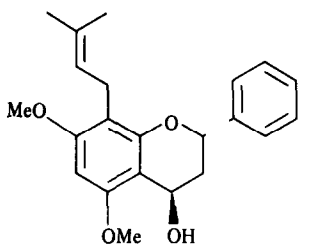

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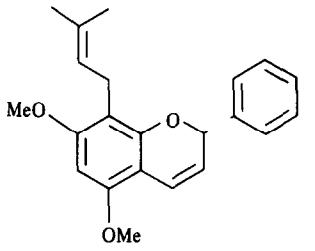

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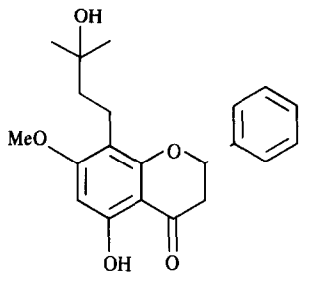

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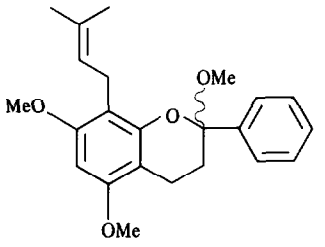

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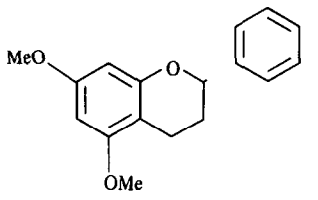

8

Table 1 ^{1}H NMR data* of flavans 4, 5, 6, 7 and 8

	4	5	6	7	8
H-2	5 15 *dd* (3, 12)	5 8 *dd* (3, 4)	5 38 *dd* (6, 12)	—	5 0 *dd* (4, 10)
H-3	2 2 *m*	5 62 *dd* (4, 10)	2 95 *m*	2 2 *m*	2 15 *m*
H-4	5 0 *dd* (3, 4)	6 79 *dd* (3, 10)	—	2 63 *m*	2 7 *m*
H-6	6 12 *s*	6 0 *s*	6 07 *s*	6 15 *s*	6 15 *d* (3)
H-8	—	—	—	—	6 08 *d* (3)
-ϕ	7 36 *br m*	7 3 *br m*	7 4 *br s*	7 4 *br m*	7 37 *br s*
H-7'	3 29 *d* (7)	3 18 *d* (7)	2 65 *m*	3 4 *d* (7)	—
H-8'	5 1 *ob*†	5 05 *tq* (7)	1 6 *m*	5 3 *tq* (7)	—
H-10'	1 65 *s*	1 63 *s*	1 2 *s*	1 70 *s*	—
H-11'	1 63 *s*	1 57 *s*	1 2 *s*	1 64 *s*	—
-OMe	3 86 *s*	3 77 *s*	3 84 *s*	3 83 *s*	3 85 *s*
	3 83 *s*			3 80 *s*	3 75 *s*
				3 05 *s*	
-OH	—	—	12 05 *s*	—	—
			1 70 *s*		

*Run at 80 MHz in $CDCl_3$ with TMS as internal standard Values are in ppm (δ) Values in parentheses are coupling constants in Hz

†*ob* = signal obscured

singlet at δ3 05 The mass spectrum of 7 supported the proposed structure, it showed a molecular ion peak at *m/z* 368 and other significant peaks at *m/z* 337 $[M-OMe]^+$, 234 $[A_1]^+$, 219 $[A_1-Me]^+$

Tephrowatsin E (**8**), $C_{17}H_{18}O_3$ (M^+ 270), was another flavan which was also similar to the flavan **1** It differs from **1** by the absence of the prenyl side chain at C-8 The ^{1}H NMR spectrum of **8** showed the following differences from that of **1** The prenyl group signals were missing and instead an extra aromatic proton doublet appeared as part of an AB system metacoupled (J = 3 Hz) Hence the AB system must be due to H-8 and H-6 protons The mass spectrum of tephrowatsin E (**8**) supported the proposed structure **8**, since the molecular ion peak was observed at *m/z* 270 and other peak at *m/z* 166 $[A_1]^+$, 104 $[B_1]^+$ derived from the retro-Diels–Alder fragmentation

EXPERIMENTAL

Mps were determined on a Kofler block and are uncorr

Tephrowia watsoniana was collected in Guerrero, México, *ca* 20 km W of Tlapa, March 1982 A voucher is on deposit at the Herbarium of Instituto de Biología (UNAM), México

The air-dried plant material, leaves and flowers (866 g) were extracted with boiling petrol (10 l) and then × 2 with $CHCl_3$ (10 l) and the solvent removed *in vacuo* The petrol extract (15 g) was percolated on a column packed with 60 g of Tonsil optimum extra (supplied by Tonsil Mexicana) and eluted with petrol and mixtures of petrol–$CHCl_3$ (1 1), $CHCl_3$ and $CHCl_3$–Me_2CO (2 1) From the fraction eluted with petrol a mixture of sitosterol and stigmasterol, 5,7-dimethoxy-8-prenylflavan (**1**) (617 mg), 5-hydroxy-7-methoxy-8-prenylflavanone (**2a**) (235 mg) and nitenin (**3**) (9 mg) were obtained Fractions eluted with petrol–$CHCl_3$ (1 1) and $CHCl_3$ (3 g) were combined and rechromatographed over silica gel (30 g) affording tephrowatsin C (**6**) (15 mg) and tephrowatsin E (**8**) (7 mg) Rechromatography of the later fractions eluted with $CHCl_3$–Me_2CO (2 1) afforded tephrowatsin D (**7**) (5 mg)

The $CHCl_3$ extract (133 g) was chromatographed over 1 3 kg silica gel using petrol–$CHCl_3$ and mixtures of $CHCl_3$–Me_2CO as eluants From the fractions eluted with petrol–$CHCl_3$ tephrowatsin A (**4**) (80 mg) and tephrowatsin B (**5**) (50 mg) were obtained

Tephrowatsin A (**4**), $C_{22}H_{26}O_4$, colourless oil, $[\alpha]_D$ −43 3° ($CHCl_3$, *c* 0 45) UV λ_{max}^{MeOH} nm (ε) 209 (57 998), 273 (1309) IR ν_{max}^{film} cm^{-1} 3400, 1610, 1500 EIMS (probe) 70 eV, *m/z* (rel int) 354 $[M]^+$ (5), 336 $[M-H_2O]^+$ (37), 245 $[M-H_2O-C_7H_7]^+$ (95), 91 $[C_7H_7]^+$ (100)

Tephrowatsin B (**5**), $C_{22}H_{24}O_3$, colourless oil, UV λ_{max}^{MeOH} nm (ε) 208 (3500), 245 (1325), 295 (840) IR ν_{max}^{film} cm^{-1} 1680, 1610, 1500 EIMS (probe) 75 eV, *m/z* (rel int) 336 $[M]^+$ (40), 321 $[M-Me]^+$ (40), 281 $[M-C_4H_7]^+$ (10), 105 $[C_7H_5O]^+$ (100)

Tephrowatsin C (**6**), $C_{21}H_{24}O_5$ colourless needles, mp 72–74°, $[\alpha]_D$ −5109 ($CHCl_3$, *c* 0 182) UV λ_{max}^{MeOH} nm (ε) 210 (31 600), 290 (19 093), 339 (4236) IR ν_{max}^{film} cm^{-1} 3450, 1640, 1590, 1500 EIMS (probe) 70 eV, *m/z* (rel int) 356 $[M]^+$ (18), 338 $[M-H_2O]^+$ (20), 283 $[M-C_4H_9O]^+$ (34), 179 $[C_9H_7O_4]^+$ (100), 104 $[C_8H_8]^+$ (18), 91 $[C_7H_7]^+$ (14)

Tephrowatsin D (**7**), $C_{23}H_{28}O_4$, colourless oil, IR ν_{max}^{film} cm^{-1} 1605, 1500 UV λ_{max}^{MeOH} nm (ε) 206 (31 542), 270 (932), 276 (943) EIMS (probe 70 eV, *m/z* (rel int) 368 $[M]^+$ (73), 337 $[M-OMe]^+$ (28), 313 $[M-C_4H_7]^+$ (9), 219 $[C_{13}H_{15}O_3]^+$ (100), 234 $[C_9H_{10}O]^+$ (24), 91 $[C_7H_7]^+$ (15)

Tephrowatsin E (**8**), $C_{17}H_{18}O_3$, colourless oil IR ν_{max}^{film} cm^{-1} 1600, 1500 UV λ_{max}^{MeOH} nm (ε) 207 (20 782), 257 (485), 263 (478), 267 (491) EIMS (probe) 70 eV, *m/z* (rel int) 270 $[M]^+$ (100), 239 $[M-OMe]^+$ (10), 166 $[C_9H_{10}O_3]^+$ (78), 138 $[C_8H_{10}O_2]^+$ (34), 104 $[C_8H_8]^+$ (10), 91 $[C_7H_7]^+$ (12)

Oxidation of tephrowatsin A (**4**) A soln of **4** (60 mg) in the minimum volume of pyridine was triturated with chromic anhydride (100 mg) in pyridine (1 ml) for 2 hr The mixture was diluted with water and extracted with $CHCl_3$ to give **2b** (12 mg), mp 85–86° IR ν_{max}^{film} 1660, 1600, 1570 UV λ_{max}^{MeOH} nm (ε) 205 (34 600), 236 (17 104), 282 (18 285), 320 (5622)

Dehydration of tephrowatsin A (**4**) Dry $MgSO_4$ (200 mg) was added to a soln of 20 mg **2** in C_6H_6 and refluxed for 30 min, the reaction being monitored by TLC When the reaction was completed the $MgSO_4$ was filtered and the solvent evaporated yielding 7 mg of tephrowatsin A (**5**) after TLC purification

Dehydration of tephrowatsin C (**6**) Dry $MgSO_4$ (150 mg) was added to a soln of **6** in C_6H_6 and refluxed for 15 min, the reaction being monitored by TLC When the reaction was completed the $MgSO_4$ was filtered and the solvent evaporated yielding 6 mg of 7-methylglabranin (**2a**), mp 128–129° (lit 123–125°) [6] identified by its IR, ^{1}H NMR and mass spectra and comparison with authentic sample

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REFERENCES

1 Waterman, P A and Khalid, A S (1980) *Phytochemistry* **19**, 1909

2 Sinha, B Natu, A A and Nanavati, D D (1982) *Phytochemistry* **21**, 1468

3 Gómez, F , Quijano, L , García, G , Calderón, J S and Ríos, T (1983) *Phytochemistry* **22**, 1305

4 Gómez, F , Quijano, L , Calderón, J S , Crúz, O and Ríos, T (1984) *Chem Ind* 632

5 Jayaraman, I , Ghanim, A and Khan, N A (1980) *Phytochemistry* **19**, 1267

6 Whalley, W B (1962) in *The Chemistry of Flavonoid Compounds* (Geissman, T A , ed), p 441 Pergamon Press, New York