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PRENYLFLAVANOLS FROM *TEPHROSIA QUERCETORUM**

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Key Word Index—*Tephrosia quercetorum*; Leguminosae; roots; new prenylflavanols.

Abstract—The roots of *Tephrosia quercetorum* afforded three new flavonoids named quercetols A, B and C. Their structures were established by spectroscopic methods, mainly ^{1}H NMR.

INTRODUCTION

Previous studies of various Mexican *Tephrosia* species (Leguminosae) have provided a number of novel flavonoids [1–4]. We have now undertaken a study of a new species, *T. quercetorum*, a herb endemic to the southeast of México.

RESULTS AND DISCUSSION

Extraction of the roots of *Tephrosia quercetorum* with petrol, petrol–ethyl acetate (1:1) and methanol, followed in each case by CC and prep. TLC over silica gel (see Experimental), gave three new flavanols quercetols A(**1**), B(**2**), and C(**3**). In addition, the known compounds 5-hydroxy-7-methoxy-8-prenylflavanone (**4**), [1], 5,7-dimethoxy-8-prenylflavanone (**4a**) [5], obovatin methyl ether (**5**) [6], tephrowatsin A (**6**) [3], and methylhidgartol B (**7a**) [8], were isolated.

Quercetol A(**1**) analysed for $C_{21}H_{22}O_5$ (M^+ 354). Its IR spectrum showed the presence of hydroxyl (3440 cm^{-1}) but not carbonyl groups. The UV spectrum suggested a flavan-3,4-diol structure [9]. The structure of **1** was deduced from the ^{1}H NMR spectrum (Table 1) which was similar to that of tephrobbottin (**7**), previously isolated from *Tephrosia abbottiae* [7]. Quercetol A(**1**) differs from **7** by the presence of an extra hydroxyl group at C-3. According to the ^{1}H NMR, the two-proton multiplet at δ2.15 (H-3) was replaced by a one-proton signal at δ3.92 (J = 10, 8, 4 Hz), which collapsed to a doublet of doublets upon D_2O addition. Moreover the H-4 signal appeared as a broad doublet at δ4.95 (J = 4 Hz) which was also sharpened on D_2O addition and there was an H-2 signal as a doublet at δ4.92 (J = 10 Hz). A broad singlet at δ2.80 and a doublet at δ2.65 (J = 8 Hz) were assigned to the hydroxyl protons at C-3 and C-4, respectively, since these signals were interchangeable with D_2O. As in tephrobbottin (**7**), the MS showed a base peak at m/z 219 due to the $[A_1-Me]^+$ fragment and a molecular ion at m/z 354, which confirmed the presence of an extra oxygen in the molecule. Acetylation of **1** afforded the corresponding diacetate **1a**. The ^{1}H NMR of **1a** clearly exhibited two sharp acetate peaks at δ1.80 and 2.15 and a downfield shift of the H-3 and H-4 signals. It is important to point out that all the flavan-3,4-diols of natural origin, whose structure and stereochemistry have been fully characterized, have been isolated from the wood or bark of Acacia species (Leguminosae) [10].

Quercetol B (**2**) was isolated as a colourless oil. The UV and IR spectra indicated the presence of an unconjugated aromatic system with no carbonyl and hydroxyl group. The structure of **2** followed from the MS and ^{1}H NMR. The MS displayed a molecular ion and a base peak at m/z 368 $[M]^+$ and 249 $[A_1-Me]^+$, which indicated that **2** differs from **6** by 14 mass units. The ^{1}H NMR spectrum of **2** closely resembled that of tephrowatsin A(**6**) previously isolated from *T. watsoniana* [3], except for the appearance of a peak for an extra methoxyl group at δ3.46 and the different chemical shift associated with the replacement of the C-4 hydroxyl group by a methoxyl group. Accordingly, the H-4 signal located at δ5.0 in tephrowatsin A(**6**) was shifted upfield to 4.54 ppm.

The IR and the UV spectra of quercetol C suggested a hydroxyflavanone structure. The ^{1}H NMR confirmed the above assumption, since it showed the characteristic ABX signals of the flavanone nucleus at δ5.40 (H-2) and 2.95 (H-3). The structure of **3** clearly followed from the ^{1}H NMR which was very similar to that of 5,7-dimethoxy-8-prenylflavanone (**4a**). Quercetol C(**3**) differs from **4a** by the presence of tertiary hydroxyl groups and two vinyl protons in the side chain. Accordingly the ^{1}H NMR of **3** showed the following differences: the two vinyl methyl broad singlets (δ1.62) of **4a** were replaced by a pair of overlapping singlets at δ1.35. A pair of downfield doublets (δ6.55 and 6.75, J = 16 Hz) characteristic of a *trans* double bond appeared instead of the typical signals for the prenyl group. The MS showed a molecular ion at m/z 368 together with peaks at m/z 353 $[M-Me]^+$, 350 $[M-H_2O]^+$, 249 $[A_1-H_2O]^+$, 91 and 77 which are consistent with the structure **3**. The negative value of the optical rotation of compound **3** indicated the absolute configuration '*S*' at C-2, [11].

Finally, Jones oxidation of tephrowatsin (A) (**6**) afforded **8** as an orange solid, mp 114–116°; it analysed for $C_{13}H_{18}O_3$ (M^+ 222). Its IR spectrum demonstrated the

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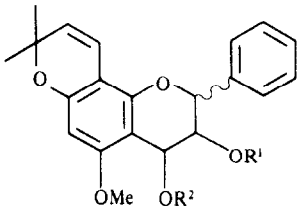
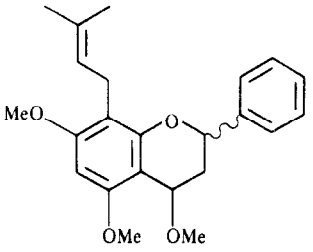
Table 1. ^{1}H NMR data* of flavanols **1**, **2** and **3**

H	1	2	3	8
2	4.92 *d* (10)	5.29 *dd* (4,12)	5.4 *dd* (5,11)	
3	3.92 *ddd* (10, 8, 4)	2.34 *m*	2.95 *m*	
4	4.95 *d* (4)	4.54 *t* (3)		5.8 *s*
6	6.03 *s*	6.12 *s*	6.09	5.8 *s*
$-\phi$	7.41 *m*	7.39 *m*	7.35 *m*	
7′	6.52 *d* (10)	3.26 *d* (7)	6.75 *d* (16)	3.13 *d* (7)
8′	5.34 *d* (10)	5.1 *t* (7)	6.55 *d* (16)	5.13 *t* (7)
gem-Me	1.35 *s*	1.62 *s*	1.35 *s*	1.6 *s*
–OMe	3.8 *s*	3.46 *s*	3.9 *s*	1.72 *s*
		3.81 *s*	3.9 *s*	3.76 *s*
		3.85 *s*	1.35 *s*	3.76 *s*
–OH				6.65 *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.



1 $R^1 = R^2 = H$
1a $R^1 = R^2 = Ac$



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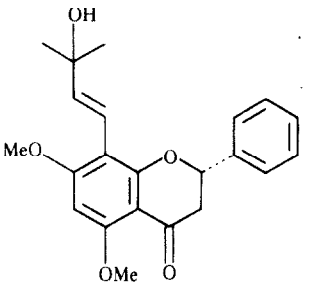

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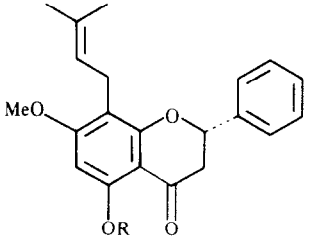
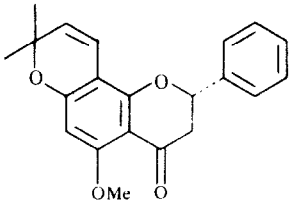


4 R = H
4a R = Me



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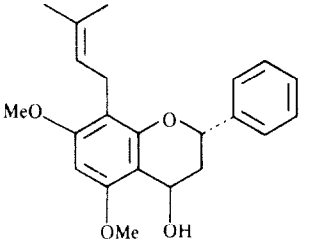

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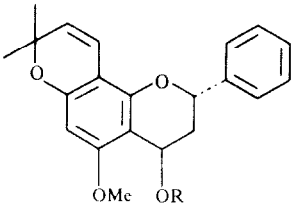
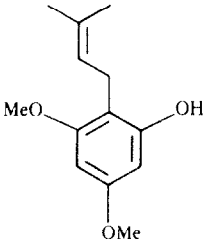


7 R = H
7a R = Me



8

presence of an hydroxyl group (3270 cm^{-1}), an olefinic double bond (1675 cm^{-1}) and aromatic double bonds (1630, 1610 cm^{-1}). The ^1H NMR indicated the presence of two aromatic methoxy groups at δ3.76 (6H), two aromatic protons at 5.8 (2H), one phenolic hydroxy group at δ6.65 and the typical signals for the prenyl group (see Table 1). Based on the above data, **8** must be the 2-prenyl-3,5-dimethoxyphenol derived from the A-ring of tephrowatsin A (**6**) by decarboxylation of the corresponding acid.

EXPERIMENTAL

Mps: uncorr. *Tephrosia quercetorum* Wood was collected in Guerrero, México, *ca* 21 km from Taxco, during December 1982. A voucher is on deposit at the Herbarium of Instituto de Biología (UNAM), México.

Extraction. The air-dried roots (600 g) of *T. quercetorum* were coarsely powdered and extracted successively with petrol, petrol–Me_2CO (1:1) and MeOH. After evapn of solvents, the green syrups A (27.8 g), B (12.5 g) and C (23.9 g) respectively, were obtained. The petrol extract A (27.8 g) was chromatographed over 450 g silica gel using petrol and mixtures of petrol–EtOAc as eluants. From the fraction eluted with petrol, 5-hydroxy-7-methoxy-8-prenylflavanone (**4**) (2.3 g) was obtained. Fractions eluted with petrol–EtOAc (8:2) afforded 5-methylobovatin (**5**) (100 mg), tephrobbottin (**7**) (520 mg) and quercetol A (150 mg). The petrol–Me_2CO (1:1) extract B (12.5 g) was chromatographed over 75 g silica gel using petrol and mixtures of petrol–Me_2CO. From the fractions eluted with petrol 5-hydroxy-7-methoxy-8-prenylflavanone (**4**) (205 mg) and tephrowatsin A (**6**) (35 mg) were obtained. Fractions eluted with petrol–Me_2CO afforded tephrobbottin (**7**) (80 mg), 5,7-dimethoxy-8-prenylflavanone (**4a**) (30 mg), quercetol A (**1**) (45 mg) and quercetol C (**3**) (120 mg). In the same way, extract C (23.9 g) afforded 5-hydroxy-7-methoxy-8-prenylflavanone (**4**) (150 mg), tephrobbottin (**7**) (35 mg), 5-methyl obbovatin (**5**) (20 mg), 5,7-dimethyl-8-prenylflavanone (**4a**) (18 mg), methylhidgartol B (**7a**) (30 mg) and quercetol B (**2**) (35 mg).

Quercetol A (**1**). $C_{21}H_{22}O_5$ colourless needles, mp 99–100°. $[\alpha]_D$ −2.71° ($CHCl_3$, *c* 0.221 g/100 ml). UV λ_{max}^{MeOH} nm (ε): 203 (11 078), 234 (32 253), 286 (41 142). IR ν_{max}^{KBr} cm^{-1}: 3440, 1585, 1490. EIMS (probe) 70 eV, *m/z* (rel. int.): 354 $[M]^+$ (20), 339 $[M-15]^+$ (47), 321 $[M-15-18]^+$ (31), 291 (100), 120 (5).

Quercetol A diacetate (**1a**). Acetylation of **1** (59 mg) with Ac_2O–pyridine gave, after prep. TLC, the diacetate **1a**. UV λ_{max}^{MeOH} nm (ε): 204 (20 106), 235 (27 660), 287 (6085); IR ν_{max}^{film} cm^{-1}: 1745, 1620, 1585, 1490, EIMS (probe) 70 eV, *m/z* (rel. int.): 438 $[M]^+$ (16), 423 $[M-Me]^+$ (71), 381 $[423-C_2H_2O]^+$ (5), 321 $[381-C_2H_4O]^+$ (20), 219 (100).

Quercetol B (**2**). $C_{23}H_{28}O_4$, colourless oil, $[\alpha]_D$ −42.18° ($CHCl_3$, *c* 0.192). UV λ_{max}^{MeOH} nm (ε): 211 (66240), 277 (1648). IR ν_{max}^{film} cm^{-1}: 1610, 1500. EIMS (probe) 70 eV, *m/z* (rel. int.): 368 $[M]^+$ (70), 337 $[M-OMe]^+$ (47), 353 $[M-Me]^+$ (4), 249 $[M-C_8H_8]^+$ (100), 221 $[249-CO]^+$ (75).

Quercetol C (**3**). $C_{22}H_{24}O_5$, colourless needless, mp 198–200°, $[\alpha]_D$ −66° ($CHCl_3$, *c* 0.1). UV λ_{max}^{MeOH} nm (ε): 207 (20 392), 263 (27 416), 283 (12 482), 337 (3006). IR ν_{max}^{KBr} cm^{-1}: 3430, 1660, 1590, 1560, 790. EIMS (probe) 70 eV *m/z* (rel. int.): 368 $[M]^+$ (26), 350 $[M-H_2O]^+$ (15), 353 $[M-Me]^+$ (10), 249 (47), 205 (100), 104 (10), 91 (13), 77 (18).

Oxidation of tephrowatsin A (**6**). Jones oxidation of **6** (8 mg) gave, after prep. TLC the phenol **8** (8 mg), IR ν_{max}^{film} cm^{-1}: 3270, 1675, 1630, 1610, EIMS (probe) 70 eV, *m/z* (rel. int.): 222 $[M]^+$ (8), 207 $[M-Me]^+$ (100), 192 $[M-2Me]^+$ (29), 69 (C_5H_4) (15).

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