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AN UNUSUAL PRENYL BIFLAVANOL FROM *TEPHROSIA TEPICANA**

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Key Word Index—*Tephrosia tepicana*; Leguminosae; prenyl biflavanol; 5,7,5″,7″-tetramethoxy-8,8″diprenyl-4,4″biflavanyl ether; tepicanol A.

Abstract—The roots and aerial parts of *Tephrosia tepicana* afforded a prenyl biflavanol. The structure and stereochemistry were established by spectroscopic methods, some chemical transformations and confirmed by X-ray diffraction. Tepicanol A is the first biflavanol with a 4,4″biflavanyl ether group to be isolated from the genus *Tephrosia*. © 1997 Elsevier Science Ltd

INTRODUCTION

In a continuation of our chemical studies of members of the genus *Tephrosia* [1–4], we have undertaken the study of *Tephrosia tepicana* a species endemic to the northwest of México.

RESULTS AND DISCUSSION

Extraction of the roots and aerial parts of the plant with petrol, ethyl acetate and methanol, followed in each case by column chromatography and preparative TLC over silica gel (see Experimental) gave new flavonoid which we name tepicanol A (**1**); in addition, the known sitosterol, α-amyrin, D(+)-pinitol and the flavonoids, α-toxicarol, 5-hydroxy-7-methoxy-8-prenylflavanone [2], 5,7 dimethoxy-8-prenylflavanone [2], tephrowatsin A (**2a**) and B (**3**) [2], and quercetol B (**2b**) [3] were isolated. Identification of the known compounds was based on comparison with authentic samples and published data.

Tepicanol A (**1**) was isolated as a crystalline product, mp. 138–140°. $[\alpha]_D^{25}$ 260°. Its IR spectrum showed the presence of aromatic bands (1606 cm^{-1}) but lacked hydroxyl and carbonyl absorption. The ^1H NMR spectrum of **1** closely resembled that of quercetol B (**2b**), previously isolated from *T. quercetorum* [3], except for the different chemical shift of H-4, which was shifted downfield to 4.95 ppm, in tepicanol A (**1**). The UV and mass spectra of tepicanol A (**1**) suggested a biflavan structure. The UV spectrum showed two maxima in the region of 208 and 270 nm, the magnitude of the molar extinction coefficients being almost double those for typical flavonoids such as quercetol B (**2b**) [3] and tephrowatsin A (**2a**) [2], thus confirming the above assumption.

The mass spectrum showed a $[M]^+$ peak at *m/z* 690 corresponding to the molecular formula $C_{14}H_{50}O_7$ which is indicative of a prenyl-biflavanol, and also some characteristic fragments at *m/z* 354 [M-$C_{22}H_{24}O_3$] and 336 [M-$C_{22}H_{26}O_4$] which are consistent with structure **1**.

Treatment of **1** with acetic anhydride–acetic acid furnished **4**. This compound is a crystalline product mp. 73–75°. Its *M*, determined by mass spectrometry, is in accord with the molecular formula $C_{22}H_{24}O_5$. The IR spectrum indicated the presence of aromatic groups (1610 cm^{-1}). Structure **4** followed from the typical ^1H NMR signals together with mass spectral peaks and the UV spectrum indicated the presence of a 4,6-dimethoxy-7-prenyl-2-benzyl-benzofuran (**4**). The unexpected product **4** could be formed through **3** (the most probably intermediary) which suffers a ring contraction to yield the furan ring under acidic conditions [5].

Confirmation of the structure and relative configuration of tepicanol A (**1**) was achieved by a single X-ray analysis (see Fig. 1).

EXPERIMENTAL

Plant material. Tephrosia tepicana was collected in Jalisco, México, Ca. 10.5 km NW road of Station of

* Part 8 in the Series 'Flavonoids from Tephrosia species' For part 7 see reference [1]. Contribution no. 1554 of Instituto de Química, UNAM.

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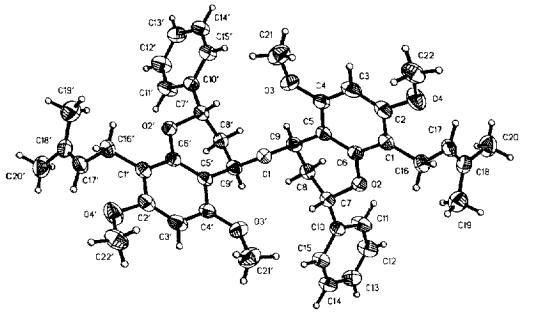

Fig. 1. ORTEP drawing of compound **1**.

Microondas of Cerro Boludo, March 1987. A voucher specimen is deposited in the Herbarium of Instituto de Biología (UNAM), México.

Extraction and separation. The air-dried plant material, leaves and flowers (119 g) was extracted successively with petrol, EtOAc and MeOH. After evapn of solvents, green syrups A (1.92 g), B (1.95 g) and C (4.3 g) respectively, were obtained. In the same way, from the air-dried roots (206.8 g), green syrups D (2.36 g), E (2.67 g) and F (11.17 g) were obtained. The petrol extract A (1.92 g) was chromatographed on a column of silica gel (20 g) eluting with petrol and mixts of petrol–CH_2Cl_2. From the frs eluted with petrol 20.4 mg of sitosterol and 16.5 mg of α-amyrin (mp. 159–161°) were obtained. The EtOAc extract B (1.95 g) was fractionated on silica gel (20 g) using petrol and mixts of petrol–CH_2Cl_2 (8:2) and gave sitosterol and 11.7 mg of α-toxicarol (mp 120–122°), identified by IR, ^{1}H NMR, EM and by comparison with an authentic sample.

The MeOH extract C (4.3 g) was chromatographed on a column of silica gel (40 g), eluting with CH_2Cl_2 and mixts of EtOAc–MeOH. From frs eluted with EtOAc–MeOH (1:1) 27.7 mg of D(+)-pinitol (mp 177–180°) were obtained. In the same way, extract D (2.36 g) afforded 5-hydroxy-7-methoxy-8-prenyflavanone [2] (53.3 mg) (mp 122–123°), tephrowatsin A (**2a**) (12.3 mg), tephrowatsin B (**3**) (15.7 mg), quercetol B (**2b**) (10.9 mg), 5,7 dimethoxy-8-prenylflavanone (**3b**) (47.9 mg), and tepicanol A (**1**) (6.4 mg), (mp 138–140°). From extract E (2.67 g) 5-hydroxy-7-methoxy-8-prenylflavanone (21 mg), 5,7-dimethoxy-8-prenylflavanone (12.6 mg) [2], tephrowatsin A (**2a**) (17.3 mg), tephrowatsin B (**3**) (9.5 mg), quercetol B (**2b**) (50.9 mg) and tepicanol A (1) (15.7 mg) were obtained. Finally, from extract F (11.17 g), 5-hydroxy-7-methoxy-8-prenyl flavanone (8.6 mg), tephrowatsin A (**2a**) (9.7 mg), and tephrowatsin B (**3**) (7.6 mg) were obtained.

Tepicanol A (**1**). Colourless crystals, mp 138–140°, $[\alpha]_D = -260°$ ($CHCl_3$; *c*, 0.27), UV λ_{max}^{MeOH}, nm (log ε): 208 (5.24), 270 (3,51) IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3034, 3015, 3920, 1606, 1119. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55 (6H, *br s*, H10′, H10‴), 1.59 (6H, *br s*, H11′, H11‴), 1.89 (2H, *ddd*, *J* = 2.3, 12.5, 13.5 Hz, H3ax, H3″ax), 2.84 (2H, *dt*, 2.3, 13.5 Hz, H3eq, H3″eq), 3.22 (4H, *br d*, *J* = 7.3 Hz, H-7′, H-7‴), 3.61 (6H, *s*, 2 × OMe), 3.80 (6H, *s*, 2 × OMe), 4.95 (2H, *t*, *J* = 2.3 Hz, H-4, H-4″), 5.15 (2H, *br t*, *J* = 7.3 Hz, H-8′, H-8‴), 5.36 (2H, *dd*, *J* = 2.3, 12.5 Hz, H-2, H-2″), 6.08 (2H, *s*, H-6, H-6″), 7.30–7.43 (6H, *m*, H-3′, H-3‴, H-4′, H-4‴, H-5′, H-5‴), 7.53 (4H, *br d*, *J* = 7.0 Hz, H-2′, H-2‴, H-6′, H-6‴).

EIMS (70 eV) *m/z* (rel. int.): 690 $[M]^+$ (7), 354 $[M\text{-}C_{22}H_{24}O_3]^+$ (30), 336 $[M\text{-}C_{22}H_{26}O_4]^+$ (76), 332 $[M\text{-}C_{23}H_{28}O_4]^+$ (29), 321 $[M\text{-}C_{23}H_{29}O_4]^+$ (100), 249 (16), 104 (28).

4,6-Dimethoxy-7-prenyl-2,benzyl-benzofuran (**4**). A soln of tepicanol A (**1**) (30 mg) in Ac_2O (2 ml) and HOAc (1 ml) was refluxed for 4 hr, the reaction being monitored by TLC. H_2O was added and the soln extracted with EtOAc. The organic layer was washed with 10% K_2CO_3 twice, filtered and evapd to dryness. The residue was purified by prep. TLC (petrol–Me_2CO, 9:1) to give 8 mg of **4** as colourless crystals, mp 73–75°. UV λ_{max}^{MeOH}, nm (log ε): 213 (5.7), 272 (3.7). IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 2925, 1610, 1111. ^{1}H NMR (80 MHz, C_6D_6) δ 1.65 (3H, *br s*, H11′), 1.86 (3H, *br s*, H12′). 3.40 (3H, *s*, OMe), 3.45 (3H, *s*, OMe), 3.50 (2H, *d*, *J* = 3 Hz, H-1′), 3.76 (2H, *d*, *J* = 7 Hz, H-8′), 5.32 (1H, *t*, *J* = 3 Hz, H-3), 5.6 (1H, *t*, *J* = 7 Hz, H-9′), 5.95 (1H, *s*, H-5), 7.15 (5H, *m*, phenyl). EIMS 70 eV *m/z* (rel. int.): 336 $[M]^+$ (100). 335 $[M\text{-}H]^+$ (87), 281 $[M\text{-}C_4H_7]^+$ (14), 245 $[M\text{-}C_7H_7]^+$ (38), 91 $[C_7H_7]^+$ (23).

X-ray crystal data of tepicanol A (**1**). $C_{44}H_{50}O_7$ MW = 690, orthorhomic, space group $P2_12_12_1$, with unit cell dimensions: *a* = 15.4744 (4), *b* = 5.5939 (7), *c* = 21.7935 (4) Å, *V* = 188.49 (0.6) Å^3, *Z* = 2, D_X = 1.21 g cm^{-1}, μ = 6.44 cm^{-1}. Intensity data of colourless crystal (0.12 × 0.42 × 0.1 mm) were collected on a Nicolet P_3/F four circle diffractometer using CuKα Ni-filtered radiation (λ = 1.54178). Among them were 2056 reflections unique with $F \geqslant 3\sigma F$ in the range $3° \leqslant 2\theta \leqslant 100°$. The structure was solved by direct methods software provided by the diffractometer manufacture. The non-hydrogen atoms were anisotropically refined by the block-diagonal least-squares method. Hydrogen atoms were located from a difference Fourier synthesis. The structure was finally refined to *R* = 0.0547 (*wR* = 0.0641). List of atomic coordinates, thermal parameters, bond lengths and angles, the torsion angles and the calcd and observed structure factors have been deposited at the Cambridge Crystallographic Data Centre, U.K.

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