A New Prenylated Dehydrorotenoid from Tephrosia villosa Seeds

A. Prashant, and G. L. David Krupadanam

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A NEW PRENYLATED DEHYDROROTENOID FROM *TEPHROSIA VILLOSA* SEEDS

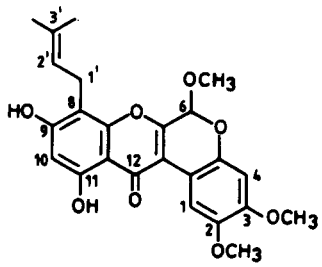
A. PRASHANT and G.L. DAVID KRUPADANAM*

Department of Chemistry, Osmania University, Hyderabad 500 007, India

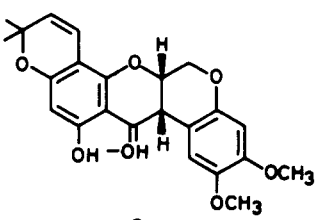
ABSTRACT.—From the seeds of *Tephrosia villosa*, a new prenylated dehydrorotenoid, identified as a 6a,12a-dehydro-2,3,6-trimethoxy-8-(3′,3′-dimethylallyl)-9,11-dihydroxyrotenone [**1**], has been isolated along with 12a-hydroxy-α-toxicarol (11-hydroxytephrosin) [**2**] and lupeol. Their structures were established on the basis of spectral evidence.

Previously, we reported the isolation and structural determination of four new, closely related, phenolic rotenoids from the pods of *Tephrosia villosa* (L.) Pers. (Leguminosae) (1). Examination of the MeOH extract of the seeds of the plant led to the isolation of two minor rotenoids identified as 6a,12a-dehydro-2,3,6-trimethoxy-8-(3′,3′-dimethylallyl)-9,11-dihydroxyrotenone [**1**] and 12a-hydroxytoxicarol [**2**], along with lupeol. The known compounds were found for the first time in *T. villosa*. Earlier, 12a-hydroxytoxicarol was reported from *Amorpha fruticosa* fruits (2,3).

Compound **1** gave $[M]^+$ *m/z* 440, $[\alpha]_D$ 0° ($CHCl_3$), pale yellow crystals, and is a new natural rotenoid, 6a,12a-dehydro-2,3,6-trimethoxy-8-(3′,3′-dimethylallyl)-9,11-dihydroxyrotenone. Its structure was determined by spectral evidence. The position and relative intensities of the peaks of the uv spectrum [λ max at 224, 277, and 325 nm] suggested a dehydrorotenoid structure, and the bathochromic shift of 10 nm (Band II) observed in the uv spectrum of **1** on addition of NaOAc indicated the presence of a 9-OH group (4). Ir bands (KBr) were seen at 3400 (br OH) and 1650 cm^{-1} (hydrogen bonded C=0). In the ^1H-nmr spectrum signals at δ 1.76, 1.86 (3H each, s, 2- and 3-MeO), 3.49 (2H, br d, $J = 7.0$ Hz, H-1′), and 5.24 (1H, br t, $J = 7.0$ Hz, H-2′) indicated the presence of a C-linked 3,3-dimethylallyl (prenyl) group. The peaks at δ 3.60, 3.91, and 3.96 (3H each, s, 2-, 3-, 6-MeO) could be attributed to three MeO's, of which one is aliphatic and the other two are aromatic in nature. The signals at δ 8.44 and 6.65 (1H each, s) are in agreement with H-1 and H-4 of the dehydrorotenoid structure (5). Signals due to a hydrogen-bonded OH group (δ 12.81, s), a free phenolic OH group (δ 6.03, br, s), and an acetal proton (δ 5.74, s) were also present. The ms exhibited the $[M]^+$ peak at *m/z* 440 and fragment ion peaks at *m/z* 419 $[M-OMe]^+$, 391 $[M-OMe-CO]^+$, 397 $[M-C_3H_7]^+$, and 385 $[M-C_4H_7]^+$. The latter two fragment ions arise due to loss of C_3H_7 and C_4H_7 units from the prenyl side chain and confirm the presence of the prenyl side chain.



1



2

The 3,3-dimethylallyl group present in **1** may be placed at either the 8 or 10 position. In 5,7-dihydroxyisoflavones having a C-linked 3,3-dimethylallyl group, its position at 6 or 8 is determined by the chemical shift value of H-6 or H-8 (6–8). H-6 appears in the region δ 6.35–6.29, while H-8 appears in the region δ 6.50–6.41 (ca. 6.4). In **1** H-10 (equivalent to H-6 of isoflavone) appeared at δ 6.30, indicating the position of 3,3-dimethylallyl at the 8 position. The placement of the prenyl group at the 8 position is also supported on biogenetic grounds (9). Thus, on the basis of the above spectral evidence and literature data, structure **1** was assigned. Prenylated rotenoids have been shown to be intermediates on the biosynthetic pathway to other rotenoids (9). Recently, two prenylated rotenoids, rot-2′-enoic acid and 12a-hydroxyrot-2′-enoic acid, have also been isolated from *Millettia pachycarpa* (10). Thus, the isolation of the new prenylated dehydrorotenoid from *T. villosa* is further evidence for the natural occurrence of prenylated rotenoids and their role as intermediates for other rotenoids in the biosynthesis of rotenoids.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—^{1}H-nmr spectra were recorded at 220 MHz using TMS as internal standard.

EXTRACTION AND SEPARATION.—Pods of *T. villosa* were collected on the Osmania University Campus in October 1988. A voucher specimen, BM186, has been kept at the Osmania University Herbarium, Department of Botany, Osmania University. The air-dried seeds (2 kg) were powdered, and the material was extracted with MeOH in a Soxhlet. The residue after evaporation of solvent (15 g) was chromatographed on Si gel using $CHCl_3$ and a $CHCl_3$/EtOAc gradient. The fractions eluted with $CHCl_3$ yielded pure lupeol (500 mg). The fractions eluted with $CHCl_3$-EtOAc (3:1) afforded **2** (60 mg) and **1** (50 mg). Compounds **2** and **1** were further purified by preparative tlc on Si gel using $CHCl_3$-EtOAc (3:1).

Compound **1**.—Amorphous powder: $[\alpha]_D$ 0° ($c = 0.5$, $CHCl_3$); uv λ max (MeOH) nm (log ε) 224 (4.20), 277 (4.07), 325 (3.85), +NaOAc 224, 287, 346; Ir max (KBr) cm^{-1} 3400, 1650; ^{1}H nmr (200 MHz, $CDCl_3$) δ 8.44 (1H, s, H-1), 6.65 (1H, s, H-4), 5.74 (1H, s, H-6), 6.30 (1H, s, H-10), 3.49 (2H, br d, H-1′), 5.24 (1H, br t, H-2′), 1.86 (3H, s, 3′-Me), 1.76 (3H, s, 3′-Me), 3.60 (3H, s, 6-OMe), 3.96 (3H, s, 2-OMe), 3.91 (3H, s, 3-OMe), 6.03 (1H, br s, 9-OH), 12.81 (1H, s, 11-OH); ms *m/z* (rel. int.) 440 $[M]^+$ (18%), 419 $[M-OMe]^+$ (4), 391 $[M-OMe-CO]^+$ (3), 397 $[M-C_3H_7]^+$ (20), 385 $[M-C_4H_7]^+$ (28), [rDA fragment (AB ring) 220-OMe]$^+$ (10). Elemental analysis: found C 65.15, H 5.03; $C_{24}H_{24}O_8$ requires C 65.45, H 5.54.

2a-Hydroxytoxicarol [**2**].—Light yellow powder: $[\alpha]_D$ −1.7° ($c = 0.5$, $CHCl_3$); mp 226° [lit. (2) mp non-crystallizable oil]; spectral data as in Lester *et al.* (2).

Lupeol.—White crystals: $[\alpha]_D$ +25° ($c = 0.60$, $CHCl_3$); mp 212°; spectral data as in Reynolds *et al.* (11).

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