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PRESENCE OF BORNYL *p*-COUMARATE IN THE ROOTS OF *EUPATORIUM DELTOIDEUM*

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Previous chemical work on the aerial parts of *Eupatorium deltoideum* Jacq. (Compositae) revealed the presence of sesquiterpene lactones of the guainolide, germacranolide, and heliangolide types (1). We report here the isolation and identification of bornyl *p*-coumarate from the roots of *E. deltoideum*.

This seems the first time that bornyl *p*-coumarate has been isolated from a *Eupatorium* species, although it was previously found in *Verbesina rupestris* (2). The structure became evident by comparing its ^{13}C-nmr spectrum with those of bornyl acetate (3) and *p*-coumaric acid (4).

EXPERIMENTAL

PLANT MATERIAL.—*E. deltoideum* was collected in September 1985 along the México-Puebla Highway (33 km). A voucher specimen (1) (Quijano 26) was deposited at Herbario Nacional del Instituto de Biología, Universidad Nacional Autónoma de México.

EXTRACTION, SEPARATION, AND IDENTIFICATION.—Powdered, dried roots of *E. deltoideum* (2 kg) were extracted with EtOAc (4 liters). The extract was concentrated under reduced pressure and chromatographed over Si gel. The fractions eluted with hexane-EtOAc (8:2) were recrystallized from $CHCl_3$/hexane to afford 125 mg of bornyl *p*-coumarate, mp 146-148° [lit. (2) mp 153-154° (MeOH/H_2O)]; $[\alpha]^{25}D - 33.2°$ (*c*, 5 $CHCl_3$); uv (MeOH) λ max nm (log ε) 213 (4.00), 228 (4.02), 313 (4.32); ir ($CHCl_3$) ν max cm^{-1} 3590, 3380, 3015, 1694, 1635, 1606; ^{1}H·nmr (60 MHz, C_6D_6) δ 0.76 (s, 3H, Me), 0.80 (s, 3H, Me), 0.92 (s, 3H, Me), 5.30 (dd, J=10, 4 Hz, 1H, H-2), 6.43 (d, J=16 Hz, 1H, H-2′), 6.80 (d, J=8 Hz, 2H, H-5′, and H-9′), 7.16 (d, J=8 Hz, 2H, H-6′, and H-8′), 7.93 (d, J=16 Hz, 1H, H-3′); ^{13}C nmr (25.2 MHz, $CDCl_3$) δ 168.7 (s, C-1′), 158.5 (s, C-7′), 144.8 (d, C-3′), 129.9 (d, C-5′, and C-9′), 126.4 (s, C-4′), 115.8 (d, C-6′, and C-8′), 115.1 (d, C-2′), 80.4 (d, C-2), 48.9 (s, C-1), 47.8 (s, C-7), 44.9 (d, C-4), 36.8 (t, C-3), 28.0 (t, C-5), 27.2 (t, C-6), 19.7 (q, C-8), 18.8 (q, C-9), 13.6 (q, C-10).

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TILIROSIDE FROM THE SEEDS OF *EREMOCARPUS SETIGERUS*

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An initial EtOH extract of the defatted seeds of *Eremocarpus setigerus* (Hook.) Benth. (Euphorbiaceae) was active in several bioassays (3PS, 9PS, crown gall tumors, and brine shrimp) (1, 2). Extracts of a subsequent seed collection failed to repeat these bioactivities, but, when extracted sequentially with hexane, C_6H_6, $CHCl_3$, and EtOH, an insoluble material precipitated from the EtOH extract. Column chromatography of a portion of the precipitate yielded yellow crystals of a major component. This compound was surprisely quite active in inhibiting crown gall tumors (1) but was inactive in other bioassays [9KB, 9ASK, 9PS, brine shrimp, and 3PS (in doses up to 30 mg/kg)]. Extracts of the whole plant have previously yielded the diterpenes, eremone and hautriwaic acid, neither of which are responsible for antitumor activity (3).

Upon acidic hydrolysis, the yellow crystals furnished kaempferol, and the compound was subsequently identified (uv, ir, ^1H nmr, ^{13}C nmr, fabms, and mp) as tiliroside [kaempferol-3-β-D-(6″-*O*-*p*-coumaroyl)-glucoside] (4). Kaempferol-3-β-D-glucoside (astragalin) is reported to have 3PS antileukemic activity (T/C 122 and 130% at 12.5 mg/kg) (5, 6). Tiliroside is a feeding deterrent to insects (7), and has been found in members of several plant families (8, 9), but this is apparently the first report of its occurrence in the Euphorbiaceae.

EXPERIMENTAL

PLANT MATERIAL.—Seeds of *E. setigerus* were obtained commerically. Collection was made in the wild near Sacramento, California, and authenticated by Charles Edson, World Botanical Associates, 7776 Thurston Rd. Springfield, Oregon 97478.

EXTRACTION AND ISOLATION.—The powdered seeds (1.5 kg) were defatted with hexane using Soxhlet extraction. The marc was then extracted sequentially via percolation with C_6H_6, $CHCl_3$, and EtOH. Brine shrimp lethality (LC_{50} 496, 774, and 1264 ppm, respectively) (2) was exhibited by the residues. A portion (300 mg) of an EtOH insoluble material (1.5 g), from the EtOH residue (36.5 g) was chromatographed over 12 g of Si gel ($CHCl_3$/MeOH gradient); 30 mg of yellow compound (crystallized from $CHCl_3$/MeOH), which was active in the potato disc assay (−59%, −47%, −40%) (1), was obtained from the 10% MeOH in $CHCl_3$ eluates. Acidic hydrolysis of this compound yielded kaempferol (co-tlc, uv, ir, eims).

IDENTIFICATION OF TILIROSIDE.—Mp 257-260°, reported mp 253-256° (10), fabms *m/z* 595 (MH^+); uv, ir, ^1H nmr, and ^1C nmr were all comparable to published spectral data (4, 10, 11). Details of the isolation and identification are available from the major author.

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