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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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JUSTICIDIN B, A BIOACTIVE TRACE LIGNAN FROM THE SEEDS OF *SESBANIA DRUMMONDII*

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In an early report, the seeds of *Sesbania drummondii* (Rydb.) Cory (Fabaceae) showed in vivo 3PS (P-388) murine antileukemic and in vitro 9KB carcinoma cytotoxic activities, and these activities were not explained by a series of commonly isolated phytochemicals (1). The subsequent isolation of the novel compounds, sesbanine and drummondol, from the active extracts still failed to explain the in vivo antitumor activity (2,3). Persistent efforts, with extracts of nearly 500 kg of seeds, finally yielded sesbanimide as an exceptionally potent, novel, antitumor component (4), and this compound is undergoing further evaluation. More recently, drummondone A and B, two abscisic acid derivatives, have been isolated and characterized (5).

A re-examination of unfractionated extracts resulting from the previous large-scale isolation of sesbanimide detected potent bioactivity in the form of brine shrimp (*Artemia salina*) lethality (LC_{50} 5.1 μg/ml) (6) in a pool of column fractions eluting prior to those which yielded sesbanimide. The brine shrimp assay was then used to guide the fractionation of this pool through three successive chromatography columns and a final purification by preparative tlc to yield another trace bioactive component new to this plant and to this plant family. Spectral (uv, ir, eims, cims, hrms, and ^1H nmr) and physical (mp, mmp, and co-tlc) data subsequently identified this component as justicidin B (brine shrimp LC_{50} 1.1 μg/ml), a known phenylnaphthalene lignan (7). This compound has piscidal activity comparable to rotenone (8-10), cytotoxicities (9PS ED_{50} 3.3 μg/ml, 9KB ED_{50} 7.3×10^{-2} and 1.2×10^{-2} μg/ml) but no 3PS in vivo activity (in doses up to 200 mg/kg) (11,12).[1] The effectiveness of the brine shrimp lethality bioassay in detecting small amounts of such bioactive plant components is emphasized; the yield of justicidin B represents only 0.0000009% of the dried weight of the seeds.

[1]G.M. Cragg, National Cancer Institute, personal communication, May 2, 1986.