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PYRROLIZIDINE ALKALOIDS FROM *SENECIO BRASILIENSIS* POPULATIONS

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Senecio brasiliensis (Spreng.) Less. (Compositae) has been associated with cattle poisoning in countries bordering the Rio de La Plata (1,2). We report here the pyrrolizidine alkaloids of three *S. brasiliensis* populations growing on rangelands in Paraguay. The pyrrolizidine alkaloid content and composition based on dried material and variation in different organs and collection sites are summarized in Table 1.

EXPERIMENTAL

PLANT MATERIAL.—Collections were made on November 10, 1985, along Ruta 2 in Department Alto Paraná, Paraguay. Voucher specimens have been filed with the Smithsonian Institution (US), Washington, DC (Schmeda 742-744).

EXTRACTION AND ISOLATION.—Freshly collected samples were separated into flowering tops, leaves, stems, and roots and extracted with 95% EtOH at room temperature for 48 h. After filtration, the plant material was dried, ground, and re-extracted twice with 95% EtOH at room temperature. The combined extracts were evaporated under reduced pressure and processed by standard procedures (3-5). The free base and *N*-oxide pyrrolizidine-alkaloid content were determined for each sample by the ^{1}H-nmr method (5) using a Varian EM 390 spectrometer. Small amounts of each plant part were air-dried in the shade to determine the ratio of fresh to dry weight.

All crude alkaloid bases and *N*-oxides (ca. 4 g) were chromatographed on Si gel with $CHCl_3$/EtOH gradient with increasing amounts of EtOH, affording after tlc (Si gel; $CHCl_3$-EtOH, 85:15; Dragendorff reagent) and recrystallization, integerrimine, retrorsine, and its 20-21 *E*-isomer. Compounds were identified by ^{1}H-nmr (6), ms, mp (7), and authentic sample comparisons.

Details of the identification are available upon request to the senior author.

TABLE 1. Pyrrolizidine Alkaloid (PA) Content and Composition in Three *Senecio brasiliensis* Populations (mg/100 g dry weight)

Location	Plant part	Free Bases					*N*-oxide					Total	Bases (%)	*N*-oxide (%)
		Integerrimine	Retrorsine	Total	Integerrimine[a]	Retrorsine[a]	Integerrimine	Retrorsine	Total	Integerrimine[a]	Retrorsine[a]			
Km 295;	Flowering tops	165.6	34.1	199.7	83	17	391.3	—	391.3	100	—	591.0	33.8	66.2
Ruta 2	Leaves	115.1	7.9	123.0	93.6	6.4	189.1	31.2	220.3	85.8	14.2	343.3	36.0	64.0
(Schmeda	Stems	13.5	—	13.5	100	—	30.1	—	30.1	100	—	43.6	30.9	69.1
742, US)	Roots	30.8	—	30.8	100	—	0.4	—	0.4	100	—	31.2	98.6	1.4
Km 231;	Flowering tops	714.0	—	714.0	100	—	135.4	52.0	187.4	72.3	27.7	901.4	79.2	20.8
Ruta 2	Leaves	124.2	8.4	132.6	93.7	6.3	175.2	73.1	248.3	70.6	29.4	380.9	35.1	64.9
(Schmeda	Stems	37.8	—	37.8	100	—	7.9	—	7.9	100	—	45.7	82.6	17.4
743, US)	Roots	13.4	—	13.4	100	—	6.4	0.4	6.8	94.3	5.7	20.2	66.3	33.7
Km 231.5	Flowering Tops	273.6	—	273.6	100	—	599.3	96.8	696.1	86.1	13.9	969.7	28.2	71.8
Ruta 2	Leaves	79.3	40.6	119.9	66.1	33.9	88.1	—	88.1	100	—	208.0	58.0	42.0
(Schmeda	Stems	2.9	—	2.9	100	—	17.6	—	17.6	100	—	20.5	14.0	86.0
744, US)	Roots	16.0	5.6	21.6	74.1	25.9	10.9	3.8	14.7	74.2	25.8	36.3	59.6	40.4

[a]Individual PAs, %.

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α- AND β-PELTATIN FROM *ERIOPE MACROSTACHYA*[1]

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Eriope macrostachya Mart. (Labiatae) is one of 28 species of the genus native to tropical and subtropical South America. It has no recorded reputation in the ethnobotanical literature as an anticancer drug (1). However, fractionation for antitumor constituents yielded a total extract showing strong cytotoxicity [ED_{50} 10^{-1} g/ml vs. KB and 3.1×10^{-2} vs. PS (P-388 lymphocytic leukemia)] according to standard National Cancer Institute protocols (2). A MeOH-H_2O (9:1)-soluble portion of the EtOH extract of the stems of the plant was chromatographed on Si gel to yield α- and β-peltatin, identified by mp, $[\alpha]_D$, ir, ^1H nmr, and tlc. These compounds are well-known cytotoxic constituents of *Podopohyllum peltatum* (3). To our knowledge, β-peltatin has been isolated from but one other member of the mint family, *Hyptis verticellata* (4).

The initial collection of plant material was made by Dr. Aparacio Pereira-Duarte (no. 12188) in the State of Minas Gerais, Brazil; the bulk collection was made and authenticated by the Economic Botany Laboratory, USDA, Beltsville, Maryland. Voucher specimens have been deposited in the herbaria of the Jardim Botanico, Rio de Janeiro, and Beltsville, respectively.

Full experimental details are available on request to either senior author.

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[1]Part XIII in the series "Antitumor Plants." For part XII, see *J. Org. Chem.*, **47**, 1519 (1982). The use of the word *antitumor* in this title signifies no more than the fact that this plant has been deemed of sufficient interest in this respect by the National Cancer Institute to warrant investigation.