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ISOLATION OF GRIFFONILIDE FROM THE STEM BARK OF BAUHINIA THONNINGII

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The bark of Baubinia thonningii (Schum) Milne Redh. (Caesalpiniaceae) is used in many parts of Africa in the treatment of a number of inflammatory conditions (1,2). Previous phytochemical investigation of the bark collected from Portuguese Guinea led to the isolation of some aliphatic acids, rhamnetin, a carotenoid, and an unidentified sterol (3). We now wish to report the isolation of a y-lactone from the bark collected near Kano, Nigeria.

EXPERIMENTAL

GENERAL PROCEDURES .--- The stem bark of B. thonningii was collected in June 1982, from Kano, Nigeria. Vouchers of the plant were confirmed and deposited in the Herbarium, Biological Sciences Department, Ahmadu Bello University, Zaria, Nigeria.

Spectra were recorded with the following instruments: uv, Hitachi 220; ir, Hitachi 260-10; ¹H nmr, Hitachi R-900 (90 and 22-6 MHz); ms, Direct Inlet Hitachi M-003 (E1 at 70 eV). Florisil for column chromatography was from BDH (100-200 ml); Si gel for tlc was pre-coated Merck grade.

EXTRACTION AND ISOLATION OF GRIFFONILIDE. - Dried pulverized bark (5.0 kg) was defatted and then percolated with 95% EtOH. The residue from the EtOH extract (143.6g) gave an EtOAc soluble fraction (120.5 g), which on column chromatography (Florisil, 20% EtOH in CHCl₃) afforded griffonilide (42.5 mg).

Griffonilide has previously been reported as the modified aglycone from the acid or enzymatic hydrolysis of lithospermoside (4,5) or griffonin (6). However, it was first recorded as a free natural product in cooccurrence with griffonin from the root of Griffonia simplicifolia Baill (Caesalpiniaceae) (6). Detailed spectral analyses, including ¹³C-nmr, ord, and cd, the preparation and spectral characterization of its diacetate, direct comparison of spectra, mmp [182-183, lit (6) 183-185°], and Co-tlc with an authentic standard led to its identification. However, in our hands the diacetate melted at 167-170° [lit (6), mp 155°] while the cd spectrum and the mp of griffonilide differed very significantly from those recorded for the diastereomer, dasycarponilide [lit (5), mp 164-165°].

Full details of the isolation and identification of griffonilide are available on request to the senior author.

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ALKALOIDS FROM ROLLINIA EMARGINATA

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As part of an investigation of the Argentinian species of the genus *Rollinia* (Annonaceae) (1) that grow in Argentina, the major alkaloids of *Rollinia emarginata* Schlecht are reported here.

R. emarginata is a shrub widely distributed in the northeast of Argentina. The plant is claimed to be a remedy for tumors in their early stages and for other human diseases. In this communication, we describe the isolation and identification of three alkaloids: (-)-anonaine, (-)-asimilobine, and (+)-reticuline.

EXPERIMENTAL

PLANT MATERIAL.—Aerial parts of *R. emarginata* were collected near Resistencia, Chaco province, Argentina. The plant was authenticated by the "Miguel Lillo" Botanical Institute of San Miguel de Tucumán, Argentina, where a voucher specimen (No. 6193) has been deposited.

EXTRACTION AND ISOLATION OF ALKALOIDS.—Air-dried and powdered stem bark of the plant (1.1 kg) was extracted in a Soxhlet apparatus with CHCl₃-MeOH (9:1) until the extract gave a negative test for alkaloids with Mayer's reagent. The organic solution was concentrated under reduced pressure to a syrup: a dark green, semisolid residue was obtained, which was fractionated in a silica gel column (MN 60 H, for tlc) using CHCl₃-MeOH (94:6) as eluant. Two aporphines were obtained, (-)-anonaine (60 mg) (2) and (-)-asimilobine (43 mg) (3), and one benzyltetrahydroisoquinoline, (+)-reticuline (52 mg) (4). All alkaloids were identified on the basis of their spectral data (ir, ms, ¹H nmr), which were identical with those reported in the literature (2-4). (+)-Reticuline was also compared with an authentic sample.

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