

FURTHER NOVEL CONSTITUENTS OF *ZANTHOXYLUM ZANTHOXYLOIDES*
ROOT AND PERICARP

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The roots of *Zanthoxylum zanthoxyloides* (Lam.) Waterm. are available commercially for use as chewing sticks and are highly pungent when chewed. Previous studies (1-11) of the plant showed it to be a rich source of chemicals of phytochemical and pharmaceutical interest. That the plant may contain minor constituents of chemotaxonomic and therapeutic potentials has further stimulated research on this plant and, hence, the present analysis of the root and pericarp by gc, gc/ms, and cc monitored by tlc.

EXPERIMENTAL

PLANT MATERIALS.—The plant materials used were collected in Ipetumodu and identified (O.A. Olatunji, Department of Botany, University of Ife, Ile-Ife, Nigeria). Voucher specimens (Olat. 360) are deposited at the departmental Herbarium.

EXTRACTION AND IDENTIFICATION OF CHEMICALS.—Air-dried pericarps (31.7 g) and roots (42 g) were separately covered with A.R. grade *n*-hexane or CH₂Cl₂ with occasional shaking during 7 days. These extracts were analyzed directly by gc, tlc, and gc/ms. The CHCl₃ extracts of these plant materials were obtained for analysis by cc and tlc. Chemicals were identified by direct gc comparison, gc/ms, and, where possible, mmp and other spectral comparisons with authentic samples. The relative quantities of volatile chemicals were obtained from integrated values.

Terpene hydrocarbons and terpenoids constitute about 3% of the root volatile fraction and were identified as α -pinene, camphene, sabinene, myrcene, longifolene, caryophyllene, aromadendrene, alloaromadendrene, γ -elemene, muurolene, cadina-3,9-diene, β -elemene, ledol, and β -cadin-4-en-10-ol which occur in trace amounts and α -copaene (0.80%) and guaia-1(5),7(11)-diene (1.21%), which were the major terpenes identified. The major volatile constituents were identified as the amides: (2*E*, 4*E*)-*N*-isobutyl-2,4-decadienamide (pellitorine) (31.13%), fagaramide (33.19%), and (2*E*, 4*E*, 8*Z*, 10*E*, 12*E*)-*N*-isobutyl-2,4,8,10,12-tetradecapentaenamide- γ -sanshoöl (6.63%) and are responsible for the insecticidal properties and pungency of the root. Other constituents were (–) asarinin (8.48%), dihydrochelyerythrine (6.42%), sitosterol and stimasta-5, 22-dien-3 β -Ol (8.56%), hydroxymethyl benzoic acid (0.16%), *n*-hexadecanoate, 9,12-octadecadienoate, *n*-octadecanoate, squalene, lupeol, skimmianine, and fagaridine. This represents a first report of the terpenes, (–) asarinin and γ -sanshoöl, in *Z. zanthoxyloides*, though γ -sanshoöl has been reported before in many Japanese *Zanthoxylum* species (12).

The pericarps furnished scoparone (7 mg), imperatorin (4 mg), scopoletin (8.7 mg), xanthoxin (12.3 mg), bergapten (2.2 mg), marmesin (12 mg), umbelliferone (13.2 mg), and psoralen (6.2 mg). Pericarp volatile constituents include *n*-nonane, (1.06%), α -pinene (1.73%), 2(10)-pinene (0.01%), myrcene (0.20%), γ -terpinene (tr.), β -ocimene (2.47%), Δ -3-carene (14.12%), 3-pinanone (8.32%), *n*-decyl aldehyde (0.84%), decyl alcohol, guaia-1(5),7(11)-diene (0.61%), α -copaene (0.73%), γ -cadinene (0.31%), undecyl alcohol (tr.), *n*-dec-1-ene (1.92%), tridecanone (1.22%), caryophyllene (tr.), α -bergamotene (tr.), humulene (tr.), (–)- β -cubebene, α -farnesene (1.48%), hepty-1-yl ketone (0.34%), heptadecene (1.00%), *n*-tetradecanoate, 2-methylhexadecane (0.47), *trans*-farnesol (0.27%), *n*-hexadecanoate, ethyl hexadecanoate, methyl octadecanoate, 9-octadecenoate, methyl linoleate, and octadecanoate.

These volatile constituents are responsible for the characteristic sweet smell of the pericarp. The identification of alcohols, aldehydes, and ketones, particularly 3-pinanone and 3-tridecanone, is significant biochemically as derivatives of these chemicals are implicated (13) in many areas of insect behavior, especially as attractants.

Full details of isolation are available from the author.

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ISOLATION OF GRIFFONILIDE FROM THE STEM BARK OF *BAUHINIA THONNINGII*

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The bark of *Bauhinia 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 γ -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 (143.6 g) 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 co-occurrence 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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