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CARYOCAR MICROCARPUM: AN ANT REPELLENT AND FISH POISON OF THE NORTHWEST AMAZON

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The genus *Caryocar*, one of two genera in the small, tropical, New World family Caryocaraceae, has had little chemical investigation beyond characterization of its seed oils which furnish edible fats of potential commercial value. The ethnobotany of the family has been reviewed (1). Our interest in *Caryocar microcarpum* Ducke arose through an observation by one of us (RFR) that its leaves were repellent, if not toxic, to leaf-cutting ants known to cause extensive damage to tropical crops and from its use by tribes of Tukanoan and Kubeo Indians of the northwest Amazon as a fish poison. A related species, *Caryocar brasiliense*, was found by De Oliveira and co-workers to have some activity against Sarcoma 180 in animals by reason of its content of oleanolic acid (2).

The leaves of *C. microcarpum* were found to contain large quantities of gallitannin along with ellagic acid, gallic acid, and methyl gallate as well as glycosides of oleanolic acid and its hydroxylated derivatives, 2β-hydroxyoleanolic acid, hederagenin, and bayogenin.

Saponins are known to be ichthyotoxic; tannins and saponins are known to be repellent to herbivores (3). Hydroxyoleanolic acid derivatives have been found repellent to termites (4), and related friedooleanan-12-ene-27-oic acids are repellent to the leaf-cutting ant *Atta cephalotes* (5,6). Our findings are thus consonant with the observation of atticidal activity and with the widespread use of *C. microcarpum* as a fish poison among the Indian peoples of the northwest Amazon. Examination of the light petroleum ether extracts of the leaves is in progress and will be reported at a later date.

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EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were taken on a Gallenkamp apparatus and are uncorrected. Column chromatography was done on Si gel or Al_2O_3 (Merck), tlc on Si gel plates for triterpenes and on cellulose plates for phenolic compounds. Spectral data were obtained on the following instruments: Beckman DB-G (uv), Perkin-Elmer 599B and 700 (ir), Varian T-60 (^{1}H nmr), and Nuclide 12-90-G (ms).

PLANT MATERIAL.—The leaves of *C. microcarpum* were collected in the area of Mitu, Comisaría de Vaupés, Colombia; a voucher specimen (Schultes et Raffauf, 24390) has been deposited in the Economic Botany Herbarium, Harvard University, Cambridge MA, 02138.

EXTRACTION AND ISOLATION.—A sample of dried leaf (4.8 kg) previously milled, defatted with hexane, and air dried was extracted with EtOH at room temperature. The extract was concentrated to 3 liters from which ellagic acid (20 g) was removed by filtration. the filtrate was concentrated to a thick syrup which was partitioned between $CHCl_3$ and H_2O containing 10% MeOH. The aqueous phase was concentrated and lyophilized to give a brown powder (165 g).

A portion of this (16.5 g) was hydrolyzed by heating for 4 h under reflux with 125 ml of 3 N HCl in 50% MeOH. The resulting solution yielded an additional quantity of ellagic acid (2.4 g) along with gallic acid (128 mg) and methyl gallate (280 mg).

A second portion (50 g) was dissolved in MeOH, tannins were precipitated with aqueous lead acetate solution, and from the filtrate a mixture of saponins was obtained which was hydrolyzed as described above to give the sapogenins (1.6 g). These were converted to their methyl esters which were chromatographed on Al_2O_3 to give the esters of the following acids in order of their elution: oleanolic, 2β-hydroxyoleanolic, hederagenin, and bayogenin.

All compounds were characterized by comparison of melting points, tlc behavior, and standard spectral data with those of authentic samples or, in the case of 2β-hydroxyoleanolic acid ester, with data given in the literature (7).

Full details of the isolation and characterization of the compounds are available on request to the senior author.

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