

6-HYDROXYMETHYLDIHYDRONITIDINE FROM
FAGAROPSIS ANGOLENSIS

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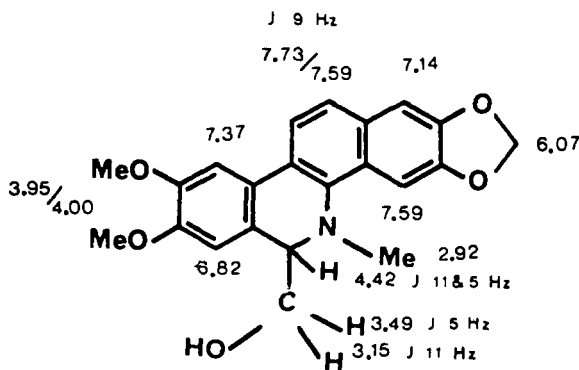
From the stem bark of *Fagaropsis angolensis* (Engl.) Dale (Rutaceae), we have reported the isolation of two limonoids and the 6-acetyl derivatives of the benzophenanthridine alkaloids dihydrochelerythrine, dihydronitidine, and dihydrosanguinarine (1). The mother liquors obtained after removal of the previously reported alkaloids from a silica gel column (1) gave, on concentration, a gummy material (15 mg) which could not be crystallized. We now wish to report the identification of this minor constituent as the novel alkaloid 6-hydroxymethyldihydronitidine (1).

This compound gave a blue fluorescence, typical of dihydrobenzophenanthridines, and a positive reaction with Dragendorff's reagent. Accurate mass measurement of the molecular ion indicated $C_{22}H_{21}NO_5$ (found: M^+ 379.1413; required 379.1420). The uv spectrum (λ max (MeOH) 231, 281, 312, 326 nm) was typical of a dihydrobenzophenanthridine (2), and bands in the ir spectrum (KCl disc) at 3450 and 1025 cm^{-1} were attributable to a pri-

mary alcohol. This compound showed no optical activity.

The ^1H -nmr spectrum of **1** (90 MHz, CDCl_3) revealed the presence of methylenedioxy, N-Me and two OMe substituents. The aromatic region of the spectrum showed six protons, four as singlets and an AB quartet for two *ortho*-coupled protons. This pattern of aromatic protons and substitution and the resonance positions of the signals agree closely with reported data for 6-acetyldihydronitidine (1). The remaining resonances, which must be attributed to C-6 and its substituent, were seen as an ABX system centered at δ 4.42, 3.49 and 3.15. This pattern, together with the ir evidence for a primary alcohol, indicates that the C-6 substituent must be a hydroxymethyl group.

Support for the proposed structure is provided by the electron impact mass spectra. It is a well-documented feature of the spectra of 6-substituted dihydrobenzophenanthridines that the base peak is formed by loss of the C-6 substituent



(3). In **1** the appearance of the base peak at m/z 348 $[M-CH_2OH]^+$ strongly supports the proposed structure.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Spectra were recorded with the following instruments: uv Unicam SP 800A; ir, Perkin-Elmer 197; 1H nmr, Perkin-Elmer R32B 90 MHz; ms AEI MS 902 instrument. Adsorbents for tlc and cc were from E. Merck.

PLANT MATERIALS.—The stem bark of *F. angolensis* was collected in the Kibale Forest, W. Uganda, in February 1978. A voucher specimen, P.G.W-998, has been deposited at the Herbarium of the Royal Botanic Garden, Edinburgh.

EXTRACTION AND ISOLATION.—Ground stem bark (300 g) was extracted with petrol (bp 40-60°) then $CHCl_3$ and finally MeOH. The MeOH extract was concentrated and the residue (17 g) was dissolved in H_2O and partitioned with EtOAc. The EtOAc fraction was chromatographed over a Si gel column (50 g). Elution with petrol containing increasing amounts of $CHCl_3$ (30%) yielded **1**.

For more details of the isolation of this compound and the previously reported alkaloid from the $CHCl_3$ extract, see Waterman and Khalid (1).

PHYSICAL AND SPECTRAL IDENTIFICATION OF **1**.—Yellow gum. Found: M 379.1413; $C_{22}H_{21}NO_5$ requires 379.1420. Uv λ max 231, 281, 312, 326 nm, ir ν max 3450 (br OH), 2900, 1500, 1450, 1240, 1025 (C-O of primary alcohol) cm^{-1} . 1H nmr (see figure with assignments). Eims m/z (rel. int.) 379 (M^+) (17), 348 $[M-CH_2OH]^+$ (100), 333 (13), 332, (20), 318 (3), 304 (5), 290 (3), 260 (3), 247 (3), 232 (1), 174 (29).

LITERATURE CITED

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Received 12 March 1984