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DECARINE FROM THE BARK OF *ZANTHOXYLUM VIRIDE*

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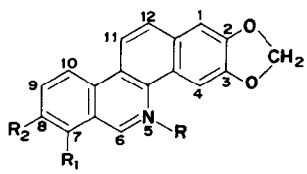
Key Word Index—*Zanthoxylum viride*; Rutaceae; benzophenanthridine alkaloid; decarine.

Plant. Zanthoxylum viride Waterm [1]. (syn. *Fagara viridis* A. Chev.) [2]. *Voucher specimen.* FF 9, deposited at the Herbarium of the Pharmaceutical Society, University of Bradford, England. *Source.* Collected for the Tropical Products Institute in secondary forest near Ibadan, Nigeria. *Previous work.* Paris and Moyse-Mignon [3] reported the presence of the lignan sesamin and several uncharacterized alkaloids. Recently the alkaloids canthin-6-one, chelerythrine, nitidine and magnoflorine have been identified in the root bark [4, 5]. *Plant part.* Stem bark.

Present work. Investigation of the material FF 9 revealed, in addition to those bases already reported, a further alkaloid [6]. This compound, isolated as the hydrochloride by shaking the $CHCl_3$ extract of FF 9 with N HCl and purifying the resulting precipitate over alumina, gave orange needles (78 mg from 1 kg of bark) mp 244–246° from MeOH/N HCl. The UV, λ_{max}^{EtOH} 247, 253, 277, 326, 384 nm, was indicative of a benzophenanthridine nucleus [7] and, on the addition of N NaOH underwent a bathochromic shift, suggesting the occurrence of a phenolic hydroxyl function. Accurate mass measurement gave M^+ 319·0848; $C_{19}H_{13}NO_4$ requires 319·0844. The 60 MHz PMR spectrum (CF_3COOH) gave signals for methoxy (δ 4·33) and methylene-dioxy (δ 6·22) substituents but lacked any indication of an *N*-methyl group and the observed pattern for the seven aromatic protons, with two AB quartets (J = 9 Hz) for H-9, H-10 and H-11, H-12, suggested that substitution occurred at C-2, C-3, C-7 and C-8 of the benzophenanthridine nucleus [8, 9]. The MS fragmentation pattern was compatible with that anticipated for an *N*-demethyl benzophenanthridine with methylene-dioxy, methoxy and hydroxy substituents [8].

Recently two phenolic benzophenanthridines with similar substitution pattern have been reported from other African species of *Zanthoxylum*: the *N*-methylated fagaridine (**1**) from *Z. senegalense* DC (syn. *Fagara xanthoxyloides* Lam.) [8] and decarine (**2**) from *Z. decaryi* H. Perr [10].



	R	R_1	R_2
(1)	Me	OH	OMe
(2)		OMe	OH

To establish the relationship of the substitution pattern of the isolated alkaloid to that of fagaridine it was reacted with excess MeI and the resulting quaternary methiodide recrystallized from EtOH–N HCl to give yellow needles mp 137–139°. Accurate mass measurement gave M^+-1 333·1000; $C_{20}H_{15}NO_4$ requires 333·1001. Neither the mp nor the UV (λ_{max}^{EtOH} 223, 256, 276, 289, 325 nm) and IR (ν_{max} 3300, 1460, 1360, 1237, 1205, 830, 755 cm^{-1}) spectra of the quaternized material were in accord with the data published for fagaridine [8], thus indicating the substitution pattern (**1**) to be untenable. As, in all other benzophenanthridines recorded from the Rutaceae, the methylene-dioxy group occurs at C-2, C-3, it seemed likely that the compound had structure (**2**). Subsequent to this, the alkaloid (**2**) was identified unambiguously by Vaquette *et al.* [10] and given the trivial name decarine. Direct comparison of our alkaloid and an authentic sample of decarine (mmp, UV, IR, TLC-3 systems) has now proved them to be identical.

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