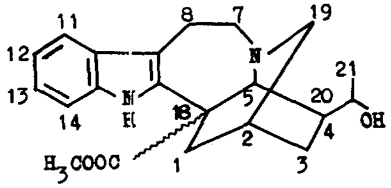
Tetrahedron Letters No. 43, pp. 3873-3878. 1965 Pergamon Press Ltd.
Printed in Great Britain.

THE STRUCTURE OF HEYNEANINE

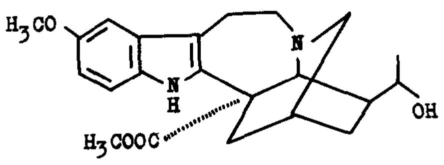
T.R. Govindachari, B.S. Joshi, A.K. Saksena,
S.S. Sathe and N. Viswanathan
CIBA Research Centre, Goregaon, Bombay 62.

(Received 1 September 1965)

The isolation of lupeol and some unidentified triterpenes from the bark of Tabernaemontana heyneana Wall (fam. Apocyanaceae) has been reported earlier[1]. We have re-examined the roots and bark of this plant. The defatted bark was submitted to the gradient elution technique of Svoboda[2] and the crude alkaloid mixture from the benzene extract on countercurrent distribution between ethyl acetate and citric acid-disodium hydrogen phosphate buffer (p_H4) gave an amorphous alkaloid (TLC-Silica gel, Rf 0.77, ethyl acetate). Further chromatography on alumina gave a crystalline alkaloid named heyneanine, m.p. 105-107° and 160-162°. The alkaloid gave a molecular ion peak at 354, confirming the molecular formula $C_{21}H_{26}N_2O_3$ assigned on the basis of elementary analysis. No degradation experiments have been carried out, but purely on the basis of the physical evidence presented, we ascribe structure (I) to heyneanine.



I



II

The U.V. spectrum (λ_{max} 225, 286, 293 mμ; ε_{max} 31600, 8130, 7240; λ_{min} 251, 290 mμ; ε_{min} 2510, 6920) is typical of an indole unsubstituted in the benzene ring. The I.R. spectrum has bands at 3600 and 3670 cm^{-1} (OH), 3440 cm^{-1} (indole NH) and 1720 cm^{-1} (COOMe). The NMR spectrum* of heyneanine is instructive and closely resembles that of voacristine (II). (Fig.1). Voacristine shows the $\rangle$NH proton signal at 7.9 δ and the typical 1,2,4-aromatic proton pattern between 6.75 δ and 7.35 δ. The aromatic methoxyl signal in voacristine appears at 3.85 δ, but this is absent in the spectrum of heyneanine. Instead signals for four protons appear in the aromatic region between 7 δ and 7.5 δ, indicating that the indole ring is unsubstituted and the signal for the $\rangle$NH proton appears at 8.3 δ. The spectra of voacristine and heyneanine are almost identical in the other regions. Thus, the ester methoxyl appears at 3.8 δ and the C_{21} secondary methyl group appears as a doublet at 1.1 δ (J = 6.5 cps) in both.

---

* Determined in $CDCl_3$ at 60 MC/sec with $Si(CH_3)_4$ as internal standard.

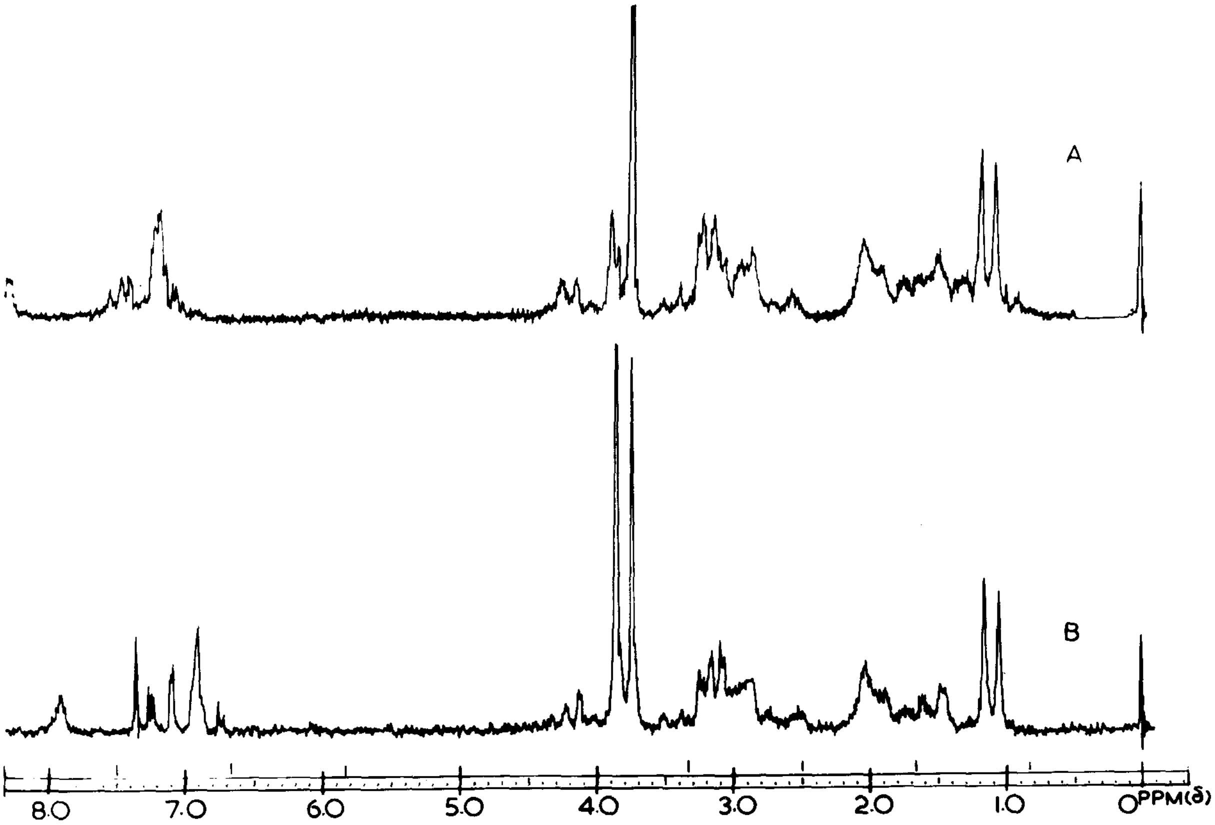
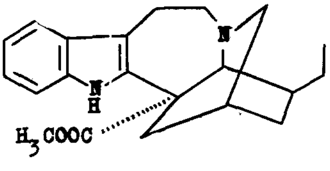


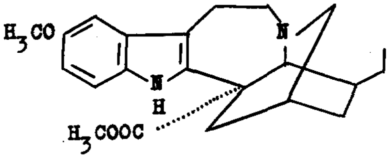
FIG. 1

NMR Spectra (A) of heyneanine (I) and (B) of voacristine (II).

Biemann[3] and Budzikiewicz *et al*[4] have shown that the mass spectra of coronaridine (desmethoxyvoacangine) (III) and voacangine (IV) show fragmentation ions differing in the aromatic part of the fragmentation by thirty mass units. A study of the mass spectra of heyneanine and voacristine (Fig. 2) brings

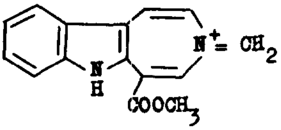


III

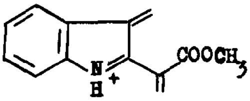


IV

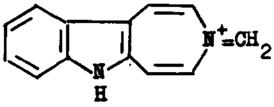
to light a similar relationship. It can be seen that there are over twenty fragmentation ions in the higher mass range which differ by thirty mass units. Some of the important fragments of heyneanine are depicted in structures a-f.



a : m/e 253



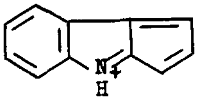
b : m/e 214



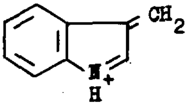
c : m/e 195

(a)-$COOCH_3$

d : m/e 194



e : m/e 154



f : m/e 130

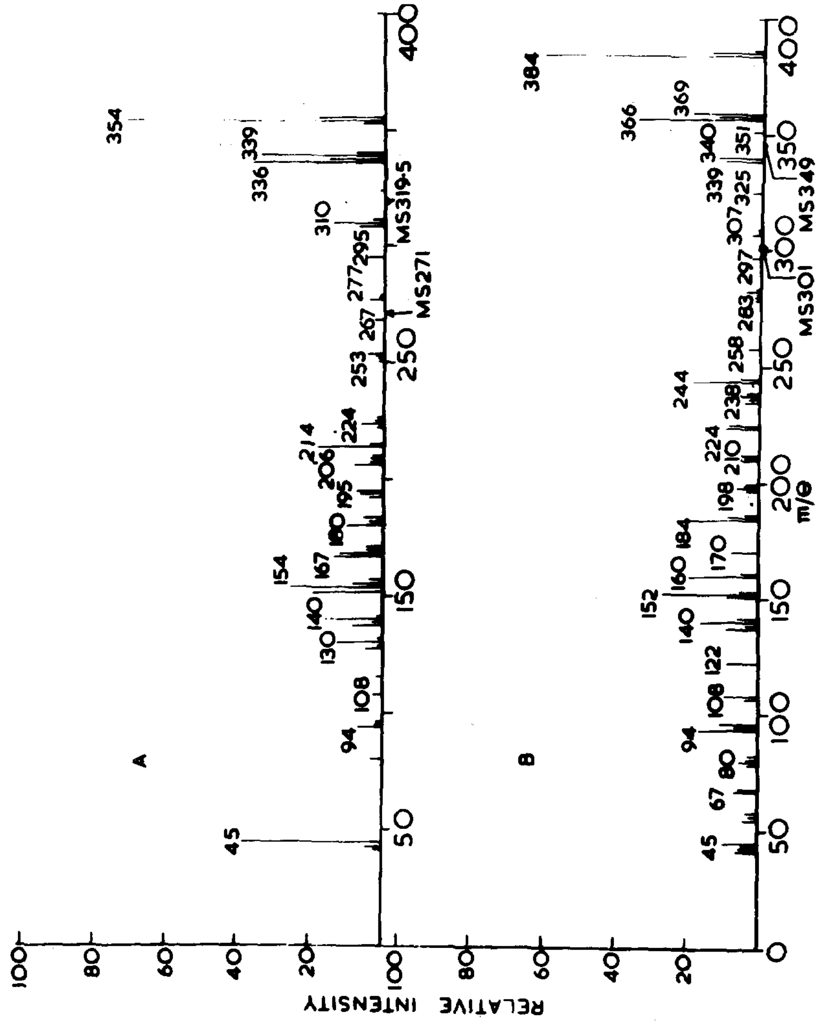


FIG. 2

Mass Spectra (A) of heyneanine (I) and (B) of voacristine (II).

Taken in conjunction with the U.V., I.R. and N.M.R. spectra, there can be little doubt that heyneanine is correctly represented by (I). Efforts to confirm this structure chemically are currently in progress.

Acknowledgement : Our thanks are due to Dr. H. Hürzeler for the mass spectra, Dr. Marvin Gorman and Dr. A. Hofmann for samples of coronaridine and voacristine.

REFERENCES

1. A.V. Subbaratnam, *J. Sci. Ind. Res. India*, *14B*, 424 (1955)
2. G.H. Svoboda, *Lloydia*, *27*, 299 (1964)
3. K. Biemann, *Mass Spectrometry*, McGraw-Hill, New York, (1962), p.323
4. H. Budzikiewicz, C. Djerassi, F. Pusieux, F. Percheran and J. Poisson, *Bull. Soc. Chim. France*, 1899 (1963)