Tetrahedron Letters No.55, pp. 4773-4774, 1970. Pergamon Press. Printed in Great Britain.

4-METHYL-2, 6-NAPHTHYRIDINE, A NEW PLANT CONSTITUENT FROM ANTIRRHINUM MAJUS.

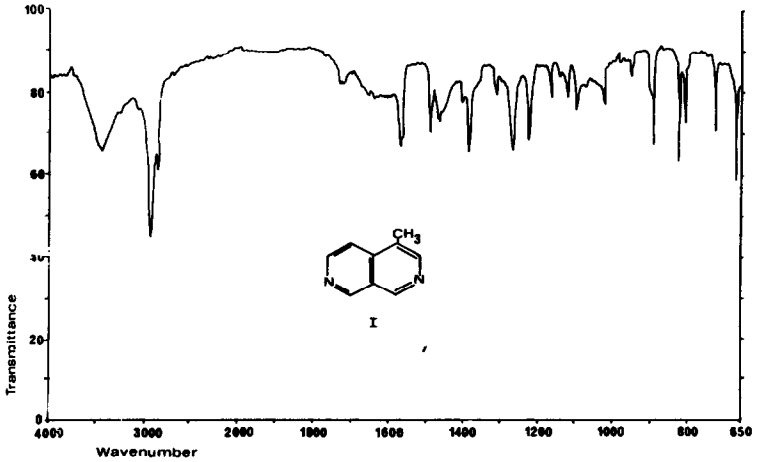
K.J. Harkiss and D. Swift,
Postgraduate Schools of Pharmacy and Pharmaceutical Chemistry,
University of Bradford,
Bradford, 7,
Yorkshire.

(Received in UK 19 October 1970; accepted for publication 28 October 1970)

The synthesis of 2,6-naphthyridine has been described (1, 3), but its methyl derivatives have not yet been prepared. The natural occurrence of simple naphthyridines has hitherto been unrecorded. We wish, therefore, to report the isolation from Antirrhinum majus of a base which we believe to be 4 -methyl-2,6-naphthyridine (I). Other bases were also obtained, but in quantities insufficient for characterisation. Thin-layer chromatography of alcoholic extracts from the dried aerial parts of A. majus showed the presence of five compounds which react with Dragendorff's reagent. The major product (I), after isolation by chromatography and recrystallisation from ethanol, formed colourless needles, m.p.78°. By means of high resolution mass spectrometry the formula $C_9H_8N_2$ was assigned to the molecular ion ($^m/_e$ 144). The NMR spectrum showed singlets at τ 1.45, 0.80 and 0.49, doublets centred on τ 1.26 and 2.23 (J 5.5 Hz) each arising from single protons, and a methyl singlet at τ 7.25.

The ultra violet absorption in ethanol was as follows :

λ max (log e) 215 nm(4.16) 260 nm (3.7) 337.6 nm (3.7), the latter two showing some fine structure.



I

The above observations indicated a methyl benzdiazine or naphthyridine. The simplicity of the NMR spectrum (in which only one pair of protons showed measurable spin-spin coupling) eliminated the methyl 1,5, 1,6, 1,7, and 1,8-naphthyridines and certain of the methyl cinnolines, phthalazines, quinazolines and quinoxalines. The remainder of these benzdiazines were also eliminated after a comparison of infra-red and NMR data; notably they showed a band between 1600-1700 cm^{-1} in the infra-red. Of possible methyl 2,6 and 2,7-naphthyridines, the 2,7 were discounted since the NMR of (I) did not show the two singlets of similar chemical shifts that would be expected from the H_1 and H_8 protons. In 2,6-naphthyridine the chemical shift values are as follows : H_1, H_5, τ 0.61, H_3 H_7, τ 1.25, H_4, H_8, τ 2.22. Comparison of these values with those of (I) leads to the conclusion that the methyl group is at position 4 rather than 3.

Published UV data for 2,6 and 2,7-naphthyridines are wholly consistent with this conclusion; 2,7-naphthyridine has no band at wavelengths greater than 305 nm (2), whereas in 2,6-naphthyridine the band of longest wavelength lies at 330 nm (I).

Experimental

Mass spectra were obtained on an A.E.I. MS902 mass spectrometer; infra-red spectra were obtained as KCl microdiscs on a Unicam SP200 spectrophotometer and UV on a Unicam SP800 spectrophotometer. The NMR spectra were obtained as CCl_4 solutions with TMS internal standard on a Perkin Elmer R12 spectrometer. (I) was isolated and purified by column (alumina/benzene) and preparative layer (aluminium oxide/chloroform) chromatography. Purity was confirmed by TLC (aluminium oxide/chloroform, hRf 55; silica gel/chloroform: ethanol: ether (85:10:5), hRf 60).

Acknowledgments

The authors wish to thank Professor W.W. Paudler for unpublished NMR data for 2,7-naphthyridine,

Professor F.M. Riccieri for infra-red spectra of 2,6-naphthyridine,

Dr. B. Blessington and Mr. R Nettleton for mass spectra determination and

Dr. W.L.F. Armarego for samples of methyl quinazolines.

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