

C-13 NMR of Hecubine and Voaphylline, and a Study of Mass Spectral Fragmentation of Hecubine by Linked Scan Measurements

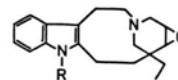
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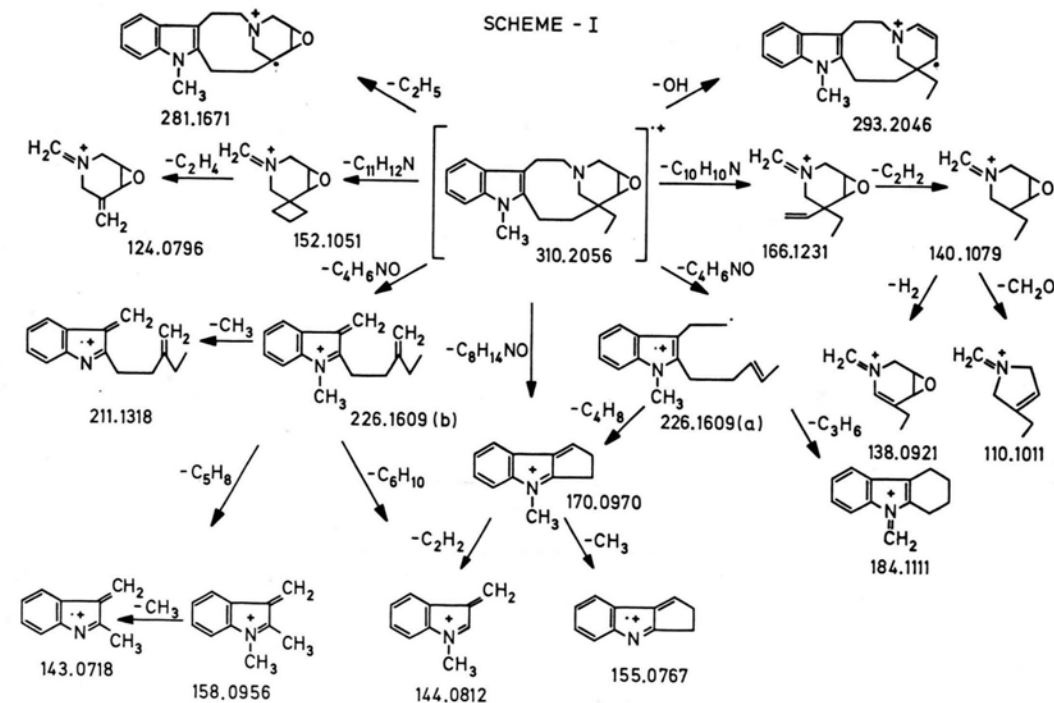
¹³C NMR Spectra, Hecubine, Voaphylline

The C-13 NMR of hecubine and voaphylline are reported. The mass spectrum of hecubine has been studied by high resolution mass measurements, and the fragmentation patterns followed by a study of metastable ion transitions as determined by linked scan measurements.



I R = H
II R = CH₃

Metastable ion transitions were measured on Finigan MAT 312 mass spectrometer both by focussing on parent ions and looking for daughter ions (Ua/B Scan) and by focussing on selected daughter ions and searching for parent ions (Ua/B² Scan). The formulae of the ions were established by computer monitored high resolution mass measurements, and confirmed by peak matching experiments on important ions. As a result of these studies, the structures of some of the fragment ions have been



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m/z	Formula	Proposed structure	Parent ion
A. Some indole bearing ions			
i) 226.1609 (39%)	C ₁₆ H ₂₀ N		310
ii) 184.1111 (17%)	C ₁₃ H ₁₄ N		226
iii) 170.0970 (75%)	C ₁₂ H ₁₂ N		310, 226
iv) 158.0956 (72%)	C ₁₁ H ₁₂ N		226
v) 144.0812 (28%)	C ₁₀ H ₁₀ N		226, 170
B. Piperidine unit bearing ions			
i) 166.1231 (8.3%)	C ₁₀ H ₁₆ NO		310
ii) 152.1051 (12%)	C ₉ H ₁₄ NO		310
iii) 140.1079 (100%)	C ₈ H ₁₄ NO		166
iv) 138.0921 (10%)	C ₈ H ₁₂ NO		140
v) 124.0796 (9%)	C ₇ H ₁₀ NO		152

Table I. m/z, formula, structure and parent ion of two groups of fragment ions.

Table II. ¹³C NMR of hecubine and voaphylline.

Carbon No.	Chemical shift		Multiplicity	Carbon No.	Chemical shift		Multiplicity
	hecubine	voaphylline			hecubine	voaphylline	
2	140.79	139.33	s	13	136.84	135.59	s
3	58.05	58.53	t	14	52.37	52.30	d
5	53.51	53.51	t*	15	59.36	59.34	d
6	26.28	26.02	t	16	20.92	23.25	t
7	108.47	109.68	s	17	32.4	32.32	t
8	127.71	128.55	s	18	7.43	7.37	q
9	117.58	117.68	d	19	35.17	36.52	t
10	118.46	118.74	d	20	33.74	33.64	s
11	120.2	120.58	d	21	53.75	53.80	t*
12	109.22	110.05	d	N-CH ₃	29.98	-	q

* These assignments may be interchanged.

identified. The fragment ions may be considered in two groups *i.e.* (a) those bearing the indole moiety and (b) those bearing the oxygenated piperidine moiety. The exact masses of the ions, intensities, formulae, proposed structures and the parent ions from which they were derived, as proved by metastable ion transition, are shown in Table I.

Scheme 1 shows the transformations of various ions as established by linked scan studies of the metastable ion transitions. The molecular formulae were established in each case by accurate mass measurements.

The C-13 NMR of hecubine and voaphylline have been recorded in $CDCl_3$. The assignments to various carbon atoms are shown in Table II. It is notable that the presence of an N-methyl group on the indole nitrogen atom of hecubine causes upfield shifts of 1.21, 0.84, 0.83 and 2.33 ppm at C-7, C-8, C-12 and C-16 respectively, and downfield shifts of 1.46 and 1.25 ppm at C-2 and C-13 respectively as compared to voaphylline. The upfield shifts at C-16 and C-19 in hecubine may reflect differences in optimum conformations adopted by the two substances in solution.

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