

## Carbon-13 Fourier Transform Nuclear Magnetic Resonance Spectroscopy of the Alkaloid 1,2,3,4,6,7,12,12b-Octahydroindolo[2,3-*a*]quinolizine

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**Summary**  $^{13}\text{C}$  Chemical shift assignments are made for the fifteen carbon atoms in the alkaloid 1,2,3,4,6,7,12,12b-octahydroindolo[2,3-*a*]quinolizine.

THE ring system represented by the indole alkaloid 1,2,3,4,6,7,12,12b-octahydroindolo[2,3-*a*]quinolizine (**1**) (*Dracontium mangiferum*)<sup>1</sup> is present in many alkaloids of the general *Corynanthe-Yohimbe* type.

We now describe the  $^{13}\text{C}$  chemical shift assignments for (**1**), the simplest of this class of indole alkaloids. The fully-proton-decoupled spectrum of (**1**) shows distinct signals for all fifteen carbon atoms. Observed chemical shifts<sup>2</sup> and peak intensities<sup>3</sup> permit direct assignments to be made for most of the signals.

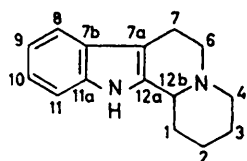
The upfield cluster of peaks observed in the spectrum were assigned, in order of increasing deshielding, to C-2, C-3, C-7, and C-1. This pattern is consistent with  $^{13}\text{C}$  data reported for nicotine<sup>4</sup> and *N*-methylpiperidine.<sup>4</sup> Three central peaks were assigned to C-6 (54.2), C-4 (56.5), and C-12b (61.3). The methylene carbon atoms C-4 and C-6 were distinguished by preparing the C-6 dideuterated

derivative (**2**) ( $\text{LiAlD}_4$  reduction of the known lactam<sup>5</sup>). The signal expected for C-6 in the deuterated material was absent in normal  $^{13}\text{C}$  Fourier Transform spectra obtained with rapid pulsing while the C-4 and C-12b signals remained. This is due to a longer  $T_1$  for the fully deuterated carbon and a resulting relative saturation of the signal.<sup>6†</sup> One also expects decreased intensity from  $^{13}\text{C}$ -D splitting, quadrupole broadening, and a decreased NOE.

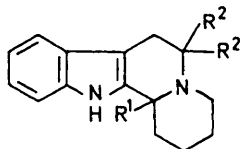
The methine C-12b absorption assignment was confirmed by preparing the known deuterated derivative (**3**).<sup>7</sup> In the spectrum of (**3**) in  $\text{CDCl}_2\text{CDCl}_2$  taken under conditions of intermediate length pulse intervals, a low intensity C-12b C-D triplet was observed near 60 p.p.m.

The four least intense signals in (**1**) were assigned to the four quaternary carbons (Table) by analogy with 2,3-dimethylindole,<sup>8</sup> although the C-11a and C-12a assignments could be reversed. The four singly-protonated benzene carbons were assigned in the chemical-shift order  $o > m > p$ , as observed in indoles,<sup>8</sup> and in contrast to dihydroindoles<sup>9</sup> and oxindoles<sup>9</sup> where  $o > p > m$  is observed. This is not surprising since the nitrogen lone pair in indoles can be

† With closely spaced pulses (e.g., 0.4–0.8 s) in FT n.m.r. the peak intensities are sensitive to differential saturation of the  $^{13}\text{C}$  nuclei. The peak intensities for non-protonated carbon atoms in (**1**) are low.



(1)

(2; R<sup>1</sup> = H, R<sup>2</sup> = D)(3; R<sup>1</sup> = D, R<sup>2</sup> = H)<sup>13</sup>C Chemical shift assignments for (1)<sup>a</sup>

Carbon	δ (p.p.m.) <sup>b</sup>	Carbon	δ (p.p.m.) <sup>b</sup>
1	30.7	8	118.2
2	22.5	9	121.2
3	25.2	10	119.2
4	56.5	11	111.6
6	54.2	11a	137.3
7	26.6	12a	136.6
7a	107.8	12b	61.3
7b	128.2		

delocalized to C-8 and C-10 as well as to C-9 and C-11. The assignments made for C-8 and C-10 could be reversed.<sup>8</sup>

The relatively clean signal separation of those carbon atoms (C-4, C-6, C-12b) adjacent to the quinolizidine nitrogen may provide a new tool for the assignment of the quinolizidine ring fusion in indole alkaloids. Studies are in progress with suitably biased *cis* and *trans* ring-fused indolo[2,3-*a*]quinolizines. For example, the C-2 *t*-butyl derivative with a strongly preferred *trans* ring fusion, shows the same C-4, C-6, C-12b <sup>13</sup>C n.m.r. pattern as (1), since in the latter a *trans* ring fusion is also preferred.

We thank Professor E. Wenkert (Indiana University)

<sup>a</sup> In (CD<sub>3</sub>)<sub>2</sub>CO. The spectrum was obtained on a Varian XL-100-15 FT NMR system. <sup>b</sup> Downfield from internal Me<sub>4</sub>Si. Accuracy ± 0.05 p.p.m.

for informing us of related studies on indole alkaloids, the National Science Foundation and the Eli Lilly Company for generous financial support (to G.W.G. and R.B.N.), and Professor L. J. Dolby (University of Oregon) for a sample of the lactam. Mr. J. D. Cargioli ran some of the spectra. G.W.G. also thanks the National Institute of General Medical Sciences for a Research Career Development Award.

(Received, 10th April 1972; Com. 606.)

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