Carbon-13 Nuclear Magnetic Resonance Spectra of Veratrine Components

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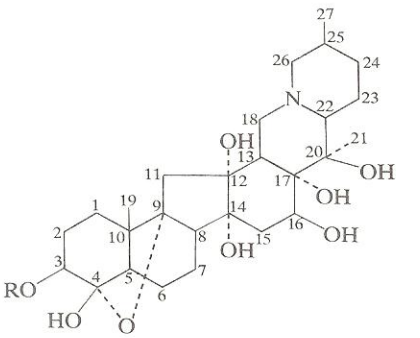
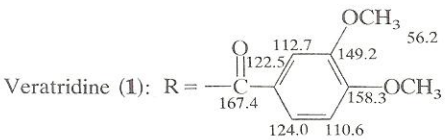
The ^{13}C NMR spectra were determined and signals assigned to the various carbons of veratridine and cevadine.

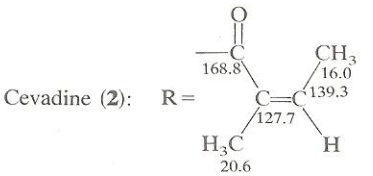
INTRODUCTION

In connection with some biological research on veratrine components we have carried out a detailed study on the ^{13}C NMR of veratridine (**1**) and cevadine (**2**). A recent report[1] on the carbon chemical shifts of this important class of molecules prompted us to publish these results in order to clarify certain ambiguities which remained in their assignments.





Veratridine (**1**): R =



Cevadine (**2**): R =

Veracevine (**3**): R = H

RESULTS AND DISCUSSION

The ^{13}C chemical shift data for compounds **1** and **2** are shown in Table 1, together with those previously reported for veracevine (**3**).[1] The assignments of the various signals are based on chemical shift correlations and the observed multiplicities in the single frequency off-resonance decoupled spectra.

Compared to alcohol **3**, the shielding of the ring A carbon atoms in esters **1** and **2** experience substituent effects comparable to those observed upon acetylation of 3β-hydroxy-5β-pregnanes.[3] As shown in Table 2, this is particularly useful in clarifying some ambiguities which remained from previous work on ceveratrum alkaloids.[1] Thus, the signals due to C-1, C-3 and C-5 can now be distinguished from those of C-15, C-16 and C-8, respectively, since the last set of carbons show chemical shifts which are unchanged within the

Table 1. Carbon-13 chemical shifts[a] for veratridine, cevadine and veracevine

Carbons	1	2	3
1	32.8	32.8	32.1
2	26.9	26.8	28.3
3	75.9	75.2	73.4
4	105.3	105.2	106.4
5	46.3	46.2	44.7
6	19.1	19.0	18.9
7	17.0	17.0	16.9
8	44.9	44.9	44.4
9	94.7	94.7	94.0
10	45.7	45.6	45.7
11	42.2	42.2	41.9
12	75.9	75.9	75.9
13	37.1	37.1	36.9
14	80.5	80.5	80.6
15	31.2	31.2	31.1
16	71.1	71.1	71.1
17	81.9	81.9	81.8
18	51.5	51.5	51.3
19	18.4	18.4	18.5
20	72.2	72.2	72.1
21	15.5	15.5	16.0
22	63.7	63.7	64.1
23	19.1	19.0	19.0
24	29.1	29.2	29.2
25	27.6	27.6	27.6
26	61.4	61.4	61.6
27	17.2	17.2	17.2

[a] In ppm downfield from TMS as internal standard.

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Table 2. Changes of chemical shifts of ring A carbon atoms upon acetylation of 3β-hydroxy-5β-steroidal skeletons

Carbon	Pregnanes[a]	Ceveratrum[b] alkaloids
1	0.9 (ppm)	0.7 (ppm)
2	−2.7	−1.4
3	3.8	2.5
4	−2.8	−1.1
5	0.8	1.6

[a] $\Delta\delta = \delta$ of 3β-OAc−δ of 3β-OH in 5β-pregnanes.
[b] $\Delta\delta = \delta$ of 3β-angelate (or veratrate)−δ of 3β-OH in ceveratrum.

series. The deshielding effect on C-5, also observed to a lesser extent for C-1, can be ascribed to a decrease of the population of that rotamer in which the OR group is *syn* to the hydrogens bonded to C-1 and C-5 as R changes from H to CO.R.

The signals of the acyl moieties were assigned on the basis of the reported values for veratric acid[4] and some angelates.[5]

EXPERIMENTAL

^{13}C NMR spectra were recorded at 20.1 MHz using a Bruker WP-80 spectrometer operating in the Fourier transform mode. Measurements were made on *c.* 0.2 M solutions in $CDCl_3$ containing 1–2% of TMS as internal standard, and maintained at a probe temperature of *c.* 35 °C. Pulses of 60° width were applied at a repetition rate of 2 s. 8K Data points were used for a spectral width of 5000 Hz.

Veratridine and cevadine were obtained from a commercial sample of veratrine following the method described by Kupchan *et al.*[2]

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