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AN ALKALOID FROM TWO *RAUWOLFIA* SPP.

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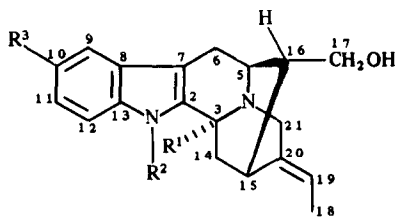
Key Word Index—*Rauwolfia tetraphylla*; *R. cubana*; Apocynaceae; *N*(*a*)-demethylaccedine.

Abstract—*N*(*a*)-Demethylaccedine, a new sarpagine-type alkaloid was isolated from *Rauwolfia tetraphylla and R. cubana* and its structure elucidated through chemical and spectroscopic studies.

The alkaloid fraction of the stem bark of the two *Rauwolfia* species growing in Cuba, namely, *R. tetraphylla* L. and *R. cubana* A. DC. gave, among several known bases, a new alkaloid: *N*(*a*)-demethylaccedine.

N(*a*)-Demethylaccedine (**1**), mp 183–184°, $[\alpha]_D^{20}$ +67° (MeOH; *c* 0.95). The UV spectrum λ_{max}^{EtOH} nm (log ε): 226 (4.33), 284 (3.81), 291 (3.76) and 314 (3.48) indicated the superimposition of 2,3-dimethylindole and 2-acylindole chromophores [1]. The IR spectrum (KBr) showed absorptions at 3320 *s* (NH/OH), 1635 *m* (conj. C=O) and 750 *s* cm^{-1}. The mass spectrum showed $[M]^+$ at *m/z* 310 corresponding to the formula $C_{19}H_{22}O_2N_2$. Other major peaks were at *m/z* 293, 292, 279, 185, 184, 138, 130 and 129, suggesting the existence of a primary alcoholic function and a sarpagan nucleus hydroxylated in the β-carboline portion of the molecule [2, 3]. The structure of the alkaloid was determined mainly by analysis of the ^1H and ^{13}C NMR spectra and after comparing them with some earlier NMR data for accedine (**2**) [2], *N*(*a*)-demethyl-16-*epi*-accedine (**3**) [4] and related alkaloids [5]. The ^1H NMR spectrum of compound **1** showed signals (80°, δ, TMS) of the indolic proton (10.8 and 10.6, *br s*, 1 H), four aromatic hydrogens (6.65 to 7.69, complex), an ethylidenic side chain (5.25, *q*, 1H and 1.53, *d*, 3H; $J = 7$ Hz) and a CH–CH_2–O function (3.3, *brd*, 2H). In addition there were two protons which were exchangeable with D_2O (5.9 and 4.3, *br s* in the spectrum registered at 30°).



	R¹	R²	R³	
1	OH	H	H	
2	OH	Me	H	
3	OH	H	H	inverted configuration at C-16
4	H	H	OH	

The analysis of the ^{13}C NMR spectrum of compound **1** was partially based on the results recorded for the alkaloid sarpagine (**4**) (Table 1) and other sarpagine-type alkaloids [6]. These data clearly showed that the new alkaloid (**1**) had the 16*R*-configuration as the alkaloids of this series show signals of C-6, C-14 and C-17 deshielded in relation to those of the 16S-series. On the contrary, the

Table 1. ^{13}C NMR Spectral data of *N*(*a*)-demethylaccedine (**1**) and sarpagine (**4**)

C	1	4
2	137.6a	136.4
3	81.1	50.2a
5	57.2	54.5a
6	26.0	26.9
7	104.6	102.3
8	126.9	128.0
9	118.1	102.0
10	118.1	150.1
11	120.4	110.0
12	111.3	111.0
13	136.5a	130.7
14	41.3	33.6
15	29.9	27.4
16	43.2	44.3
17	63.2	63.6
18	12.5	12.6
19	114.0	115.2
20	140.5	139.9
21	48.5	55.8

The spectra were recorded in DMSO-d_6 (compound **1**) or in DMSO-d_6/$CDCl_3$ 1:1 (compound **4**). The δ values are in ppm downfield from TMS. Signals with the same symbol may be interchanged.

C-20 signal shields proportionally when compared in the same way. A supplementary proof for the proposed structure for the alkaloid **(1)** was obtained after methylation under controlled conditions with methyl iodide, to give 16-*epi*-affinine **(5)** identical with an authentic sample [7].

EXPERIMENTAL

The UV spectrum was obtained on a Pye-Unicam SP-1800 recording spectrophotometer and the IR spectrum was determined on a Pye-Unicam SP-1000 apparatus. NMR spectra were recorded in DMSO-d_6 solution on a Jeol FX-900 spectrometer (^{1}H NMR: 90 MHz; ^{13}C NMR: 22.5 MHz) with TMS as internal standard. The mass spectrum was taken with a JMS DX-300 mass spectrometer fitted with a direct inlet system (70 eV).

REFERENCES

1. Sangster, A. and Stuart, K. L. (1965) *Chem. Rev.* **65**, 69.
2. Achenbach, H. and Schaller, E. (1975) *Chem. Ber.* **108**, 3842.
3. Budzikiewicz, H. Djerassi, C. and Williams, D. H. (1964) *Structure Elucidation of Natural Products by Mass Spectrometry*, Vol. I. Alkaloids. Holden-Day.
4. Achenbach, H. and Schaller, E. (1976) *Tetrahedron Letters*, 351.
5. Kingston, D. G. I. and Ekundayo, O. (1981) *J. Nat. Prod.*, **44**, 509.
6. Koskinen, A. and Lounasmaa, M. (1983). *Progress in the Chemistry of Organic Natural Products*, (Herz, W., Grisenbach, H. and Kirby, G. W., eds) Vol. 43, p. 326. Springer, Vienna.
7. Gómez, C. *et al.*, (1988). *Rev. Cub. Farm.*, (in press).