THE STRUCTURE AND CONFIGURATION OF KORSEVININE

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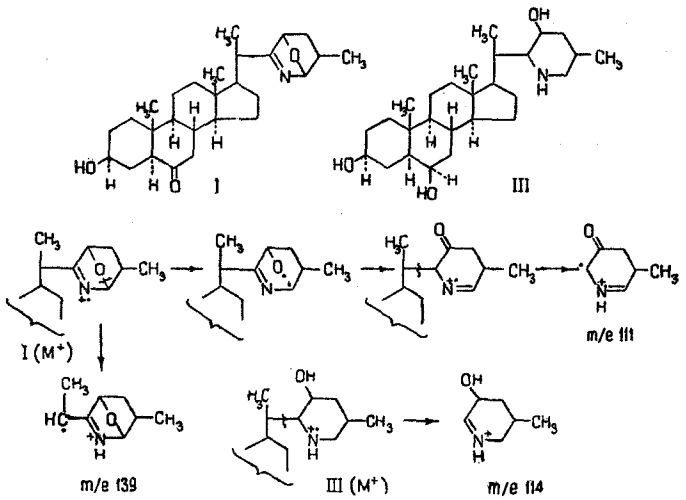
From the total ether-soluble alkaloids of Korolkowia sewerzowii Rgl. we have isolated a new base, korsevinine (I), $C_{27}H_{41}O_3N$, with mp 224–225° C (from acetone), $[\alpha]_D$ −16.04°, R_f 0.65 in a thin layer of Al_2O_3 and $CaSO_4$ (9 : 1) in the ethyl acetate–chloroform–methanol (30 : 20 : 3) (a) system [1]. The IR spectrum of substance I has absorption bands at (cm^{-1}): 3400, 1070 (OH), 2940, 1460–1440(—CH_3), 1700 (CO), and 1620 (C=N). Under the action of acetic anhydride in pyridine, I forms monoacetylkorsevinine (II), with mp 154–155° C (from methanol), R_f 0.88 (a). The IR spectrum of II has absorption bands at (cm^{-1}): 1710 (CO), 1723, 1245 (—$COOCH_3$), 2950 and 1450 (—CH_3), and 1620 (C=N). The reduction of I with sodium borohydride leads to hexahydrokorsevinine (III), with mp 220–221° C. This substance possesses strongly basic properties; IR spectrum (cm^{-1}): 3400, 1040, 1070 (OH), 2940, 2870, 1450 (—CH_3); the absorption band of the secondary nitrogen atom is masked by the absorption bands of the hydroxyl groups. The acetylation of III with acetic anhydride in pyridine yielded triacetylhexahydrokorsevinine (IV). IR spectrum (cm^{-1}): 3400 (OH), (OH), 2950, 2870, 1435 (—CH_3), 1740, 1725, 1265–1240, 1050, 1028 ($COOCH_3$), 1640 (N—$COCH_3$).

Substance	Chemical shifts, τ								
	s, 3H; 19–CH_3	s, 3H; 18–CH_3	d, 3H; 21–CH_3	d, 3H 26–CH_3	s, 3H; $COOCH_3$ (a)	s, 3H; $COOCH_3$ (e)	s, 3H; N–$COCH_3$	m, H (a) HCOCOCH$_3$	m, H (e) HCOCOCH$_3$
I	9.31	9.31	9.02	9.00	—	—	—	—	—
II	9.29	9.31	9.01	9.00	—	8.04	—	5.40	—
III	9.03	9.33	9.21	9.17	—	—	—	—	—
IV	9.04	9.32	9.12	9.08	8.04	8.03	7.93	5.40	5.12

The characteristics of the NMR spectra of I–IV are given in the table.

The mass spectrum of I has peaks of ions with m/e 110 (27%), 111 (81%), 139 (10%), $(M - 43)^+$, $(M - 28)^+$, $(M - 18)^+$ (M − 15), and 427 $(M)^+$, and in the mass spectrum of III there are the peaks of the ions 98 (13%), 114 (100%), 124 (3%), $(M - 33)^+$, $(M - 18)^+$, $(M - 15)^+$, and 433 (M^+).

The chemical properties described, and the IR, mass, and NMR spectra enabled the following structural formulas and partial configurations to be put forward for I and III [1–4]:



The NMR spectra were taken on a JNM-4-H-100 instrument ($CDCl_3$ with hexamethyldisiloxane as internal standard), the IR spectrum on a UR-20 instrument (KBr), and the mass spectrum on a MKh-1303 instrument with a glass inlet system.

REFERENCES

1. R. N. Nuriddinov and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], 4, 258, 333, 334, 1968.
2. R. F. Zurcher, Helv. Chim. Acta, 46, 2054, 1963.
3. T. Masamune, N. Sato, K. Kobayashi, and Y. Mori, Tetrah., 23, 1591, 1967.
4. H. Budzikiewicz, Tetrah., 20, 2267, 1964.

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