THE STRUCTURE OF ERVINE

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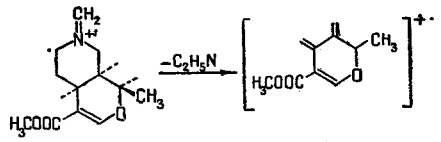
Previously, on the basis of the IR and UV spectra and chemical properties of ervine and its derivatives, the structure of $3\alpha, 15\alpha, 19\alpha, 20\alpha$-heteroyohimbine was proposed for it [1]. However, its NMR and mass spectra have not been studied.

The mass spectra of ervine were compared with the spectra of ajmalicine and reserpinine. We see from the figures given in the table that the fragmentation of ervine is similar to that of the alkaloids ajmalicine and reserpinine, but a difference is observed in the intensities of some peaks. In the spectrum of ervine, as in those of ajmalicine and reserpinine, the molecular peak is the maximum one. The peak with m/e $(M - 1)^+$ amounts to more than 50% of the maximum peak [2].

Relative intensity, %	Ervine	Ajmalicine	Reserpinine	Hydroxyindole-ervine
M+	352 (100)	352 (100)	382 (100)	368 (100)
(M–1)+	351 (65)	351 (60)	381 (50)	367 (6)
$(M-CH_3)^+$	337 (20)	337 (5)	367 (11)	353 (6)
$(M-OCH_3)^+$	321 (4)	321 (5)	351 (3)	337 (6)
Indole fragments	156 (13)	156 (63)	186 (20)	130 (6)
	169 (6)	169 (16)	199 (11)	144 (4)
	170 (4)	170 (10)	200 (10)	145 (4)
	225 (2)	225 (8)	255 (4)	159 (4)
Nonindole fragments	223 (8)	223 (3)	223 (1)	223 (34)
	208 (2)	208 (4)	—	208 (12)
				69 (19)

The results of the comparison of the mass spectra of reserpinine and ervine show that they differ only in the fragments of the indole moiety of the molecule, by 30 m/e. The mass spectrum of ajmalicine is distinguished by the intensity of the indole ions with m/e 156, 184, and 222 compared with the corresponding ions in the mass spectra of ervine and reserpinine. This is apparently due to the nature of the fusion of the C/D and D/E rings in the molecules of these alkaloids.

In the mass spectrum of hydroxyindole-ervine, apart from the peaks shown in the table, there are the peaks of ions with m/e $(M - OH)^+$ (6%) and 180 (8%). The formation of an ion with m/e 180 from an ion with m/e 223 shows that hydroxyindole-ervine has retained the cis linkage of rings D/E and the β-orientation of the methyl group at C_{19} [3].



m/e 223 m/e 180

These facts and the NMR spectra (C-19 CH_3, δ 1.20 ppm, C-19 H, δ 4.25 ppm, $COOCH_3$, δ 3.46 ppm) allow us to assume that hydroxyindole-ervine has the stereochemistry IV-A or IV-B [4].

The NMR spectrum of ervine has a three-proton doublet at δ 1.33 ppm, J = 7 Hz (C-19 CH_3), a one-proton multiplet with a center at δ 4.41 ppm, J = 11 Hz (C-19 H), and a singlet from an olefinic proton with δ 7.50 ppm. In addition, there are the signals of a $COOCH_3$ group, (δ 3.68 ppm, singlet), an NH group (δ 7.92 ppm, singlet), and four aromatic protons.

The results of a comparison of the chemical shifts and the spin-spin coupling constants of the C-19 H, C-20 H,

and C-19 CH_3 protons in the NMR spectrum of ervine with those of alkaloids of analogous structure [5] shows that ervine must have the cis linkage of rings D/E.

On the basis of what has been said above, ervine may be assigned to the heteroyohimbine alkaloids in which rings C/D have trans linkage, rings D/E cis linkage, and the CH_3 group at C_{19} has the β-axial configuration.

EXPERIMENTAL

The mass spectra were recorded on a MKh-1303 mass spectrometer (stabilized temperature of the internal inlet tube 90–130° C and ionizing voltage 40–50 V), and the NMR spectra on a JNM-4H-100/100 MHz instrument (with HMDS as internal standard and $CDCl_3$ as the solvent).

CONCLUSIONS

Results of a comparative study of the NMR and mass spectra of ervine and hydroxyindole-ervine have shown that ervine belongs to the heteroyohimbine alkaloids in which the C/D rings have a trans linkage and the D/E rings a cis linkage and the CH_3 group at C_{19} has the β-axial configuration.

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