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COMPARATIVE CHARACTERISTICS OF THE MASS SPECTRA OF ISOMERS OF MATRINE

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The mass spectra of matrine (I) [1], leontine (II), sophoridine (III), and isosophoridine (IV) are characterized by high intensities of the peaks of the ions M^+ and $(M - 1)^+$.

In matrine, the maximum peak is that of the M^+ ion and in the others it is that of the $(M - 1)^+$ ions which are formed mainly by the detachment of $H^\cdot$ from C_6. If one connects the stability of the system only with the intensity of M^+, all the isomers have approximately the same stability with a slight increase in the case of II and IV. However, if one considers the sum of the Σ% values for the ions with m/e 248 and 247, this sum is greatest for leontine (38.7%) which is in agreement with the least strain of the (trans-AB, BC, AC, CD) system. The matrine molecule is characterized by the the lowest value (22.2%), which corresponds to the presence of a strained (cis-AC, BC) system. At the same time, the intensities of the peaks of the fragments with m/e 247, 219, 206, 205, 192, and 162, formed by the splitting off of the elements of rings A and B and, in particular, C (rupture of a C–C bond adjacent to the asymmetric centers at C_5 and C_7), are considerably greater for I than for the other isomers. However, if one sums the Σ% value of all the groups of peaks mentioned above, we obtain extremely close values for all the isomers (I, 33.3%; II, 32.4%; III, 31.4%; IV, 31.5%) (table). The combined probabilities of the expulsion of small fragments close to the center of ionization coincide for all the isomers. Almost all the fragments contained in the elimination of rings D and C pass through the stage of the $(M - 1)^+$ ion, and the rupture of the C_7–C_{11} bond is approximately equally probable, and therefore the Σ% values of the ions with m/e 150 and below are comparable for all the isomers. The only displacement is found for the ions with m/e 137 and 136 in the spectrum of I. This fact shows that the ion with m/e 137 is formed directly from M^+ by β-cleavage and the ion with m/e 136 from the $(M - 1)^+$ ion.

With the exception of the above-mentioned differences in the intensities of the M^+, $(M - 1)^+$, 137, 136 amu. peaks, the spectra of I and III are similar. This confirms the fact that matrine differs from sophoridine in the configuration at C_6 and also emphasizes that the main fragments are formed via the $(M - 1)^+$ ion. The spectra of II and IV are also similar. In the molecule of IV the A and B rings have a cis linkage, while A–C and B–C are trans-linked [2]. Since in the spectrum of IV the intensity of the ion with m/e 138 is far higher than in the other spectra, it may be concluded that this process takes place with the rupture of the C_7–C_{11} and C_5–C_{17} bonds and the migration of hydrogen from C_2 to C_5 and from C_{12} to C_7. This can take place easily with a cis-AC linkage. Experimental conditions: MKh-1303 instrument, temperature 80–100° C, ionizing voltage 40V.

Values of the Σ% in the Mass Spectra of I–IV.

Substance	248	247	219	206	205	192	177	162	150	138	137	136
(I)	12.3	9.9	1.6	2.6	5.5	2.2	1.5	1.5	4.0	1.3	3.3	1.8
(II)	14.1	24.6	0.6	0.4	1.0	0.3	8.6	0.8	6.7	0.4	1.1	2.8
(III)	11.6	15.0	1.3	1.4	3.5	1.4	2.8	1.3	6.0	1.2	1.7	2.4
(IV)	14.5	21.3	0.7	0.7	1.2	0.6	2.2	0.6	5.5	2.7	1.1	2.5

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THE STRUCTURE OF ERVAMICINE

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After the isolation of ervinceine [1], the total alkaloids from the epigeal part of *Vinca erecta* Rgl. et Schmalh. were dissolved in benzene, and the benzene solution was extracted successively with citrate-phosphate buffer solution at pH 4.5 and 2.8 and with 1 N HCl. The last fraction deposited crystals of a hydrochloride with mp 213–214° C (decomp., methanol), from which an amorphous base was obtained with R_f 0.78 in TLC on a fixed layer of silica gel (ether–chloroform, 1 : 1), $[\alpha]_D^{20}$ −274.4 (c 1.4; chloroform). The hydriodide had mp 207–208° C (decomp., methanol). The UV spectrum, $\lambda_{max}^{C_2H_5OH}$ 248, 329 mμ (lg ε 3.89, 4.00), is characteristic for α-methyleneindoline alkaloids. IR spectrum: 1670 cm^{-1} (NH), and 795, 860 cm^{-1} (1,2,4-trisubstituted benzene ring). M^+ 366 (mass spectrometry). Thus, the alkaloid has the composition and developed the formula

$$C_{19}H_{19}(=N-)(NH)(COOCH_3)(OCH_3)(=)_2.$$

The mass spectrum of the base, which we have called ervamicine, is similar to that of 16-methoxytabersonine [2].

On Adams hydrogenation in ethanol, ervamicine absorbs 1 mole of hydrogen and forms 6,7-hydroervamicine, M^+ 368 (mass spectrometry). The latter was found to be identical (R_f, UV, IR, and mass spectra) with ervinceine.

The NMR spectrum of the base taken on a JNM-4H-100/100 MHz instrument in carbon tetrachloride (τ scale) showed signals at 3.06–3.82 (aromatic protons, 3H), 6.37 (singlet, $COOCH_3$), 6.34 (singlet, OCH_3), 1.05 (NH, singlet), and 9.42 (triplet, $C-C_2H_5$).

The two olefinic protons of ring D form an AB system and give a quartet with τ_A = 4.39 and τ_B = 4.47 ppm and J_{AB} = 10.0 Hz, which shows the cis arrangement of these hydrogen atoms relative to the double bond. In a comparison of some chemical properties and the NMR spectra of ervamicine and of 16-methoxytabersonine, the signals of all the protons were found to be different. This gives grounds for assuming that these alkaloids are steroisomers [2].

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