MASS SPECTRA OF PLATYPHYLLINE, SENECIONINE, AND SENECIPHYLLINE

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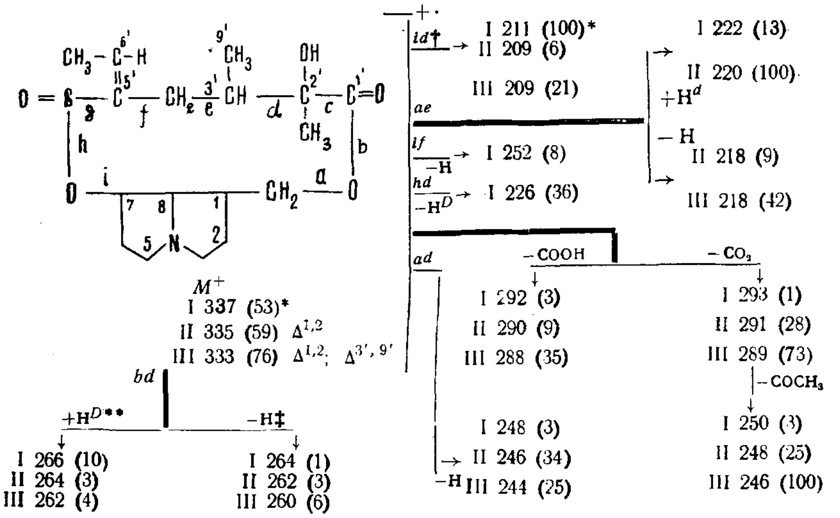
Continuing a study of the mass spectra of pyrrolizidine alkaloids [1, 2], we have obtained the spectra of the macrocyclic base platyphylline (I), senecionine (II), and seneciphylline (III) [3]. Mass spectra have been used previously mainly for the identification of these alkaloids [4, 5]. In characterizing their decomposition, the main attention has been directed to the fragments of the retronecine nucleus. The scheme shows the direction of decomposition of the macrocyclic rings of bases (I-III).

Scheme



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* The maximum peak in the range between M^+ and 200 m/e is taken as 100%.

† Cleavage of the corresponding bond.

‡ (+H) – migration of hydrogen to the charged fragment; (−H) to the neutral fragment.

** (H^D) – migration of active hydrogen.

Following the ejection of CO_2 by the cleavage *a*c, the fragment CH_3CO is expelled with the migration of active hydrogen to the charged fragment. In the cleavage *a*d with the opposite migration of hydrogen, ions with m/e values less than 2 units are produced. A $\Delta^{1,2}$ bond favors the cleavage of bond *a* and a $\Delta^{5',6'}$bond induces cleavage e particularly in the absence of a $\Delta^{3',9'}$ bond. Correspondingly, the ions obtained in the cleavage e are the strongest in the spectrum of (II) (220 m/e, 100%).

We have established that the ester group at C_7 participates in the fragmentation of (I-III). In the case of platyphylline (I), in which cleavage *a* is uncharacteristic in view of the absence of a $\Delta^{1,2}$ double bond, the cleavage of bond i leads to the appearance of the strongest ion with m/e 211. The formation of ions with m/e 226 and 252 in the spectrum of (I) is also caused by the cleavage of the bonds of the COO group at C_7.

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The ions with m/e 209 (II and III) are of low intensity, but their origin is confirmed by the presence of an ion of the same mass in the spectrum of trichodesmine [2] having the same chain of bonds from *a* to d.

The ions formed by cleavages at bd are similar to the ions with m/e 266 and 264 in the spectrum of incanine [2]. Thus, the main pathways of the fragmentation of compounds (II-III) depend on the positions of the double bonds. The proposed scheme is confirmed by the spectra of the OD-analogs of (I-III).

Samples of (I-III) were isolated in the alkaloid chemistry laboratory of IKhRV (Institute of the Chemistry of Plant Substances).

LITERATURE CITED

1. U. A. Abdullaev, Ya. V. Rashkes, Kh. Shakhidoyatov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 634 (1972).
2. Ya. V. Rashkes, U. A. Abdullaev, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 40 (1974).
3. A. P. Orekhov, The Chemistry of Plant Alkaloids of the USSR [in Russian] (1965), pp. 247, 248, 259.
4. C. K. Atal, K. K. Kapur, C. C. J. Culvenor, and L. W. Smith, Tetrahedron Lett., 537 (1966).
5. C. C. J. Culvenor, N. J. Koretskaya, L. W. Smith, and L. M. Utkin, Austr. J. Chem., 21, 1671 (1968).