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ALKALOIDS OF *Arundo donax*.
V. MASS SPECTROMETRY OF THE ALKALOIDS OF *Arundo donax*

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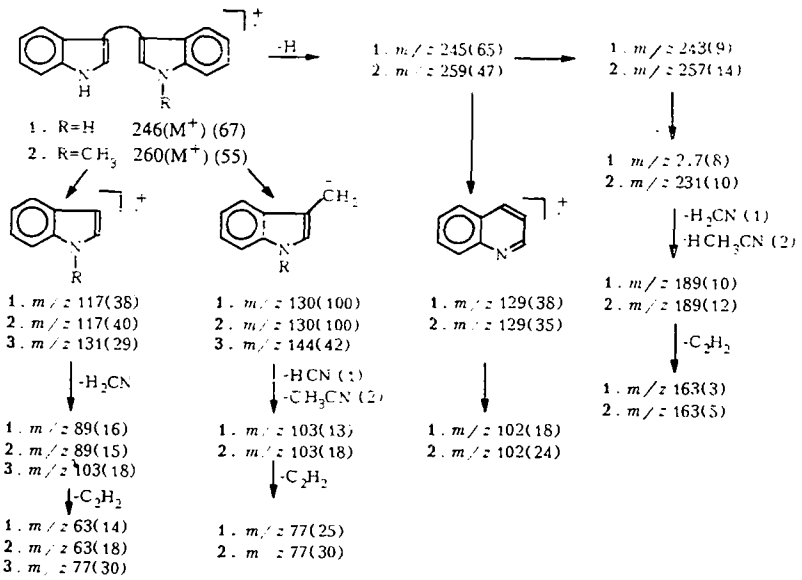
The mass spectra of alkaloids isolated from the epigeal part of the plant Arundo donax *L. have been investigated. The main pathways of fragmentation under electron impact have been determined for arundine, ardine, donaxaridine, donaxarine, and donaxinine. An analogy has been found in the fragmentation of the M^+ ions of donaxarine and donaxinine, the main pathway of their fragmentation consisting in the elimination of the elements of the N-methylpyrrolidone ring.*

It is known [1-3] that the alkaloids of *Arundo* L. are mainly indole and pyrrolidone derivatives. Information on the mass spectrum of donaxine, belonging to the indole type, was first given in [1]. The spectrum of donaxine is characterized by an intense peak of the M^+ ion and by peaks with *m/z* 174 and 130, 102, and 44, which are characteristic for indole derivatives [4]. Similar intense ion peaks are present in the spectrum of 3,3′-bis(N-methylindolinium hydroxide) [1]. In this case, because of thermal decomposition in the ionization chamber, the molecule of the quaternary base is converted into an ion with *m/z* 174.

The above-mentioned indole fragments are also characteristic for the mass spectra of the alkaloids arundine (**1**) [2] and ardine (**2**) [5], except for the peak of the ion with *m/z* 44, which does not appear in these spectra. Scheme 1 shows pathways for the formation of the main fragmentary ions. We may note that the peaks of the $(M - 1)^+$ ions and of the M^+ ions have



Scheme 1. Mass-spectrometric fragmentation of arundine (**1**) and of ardine (**2**).

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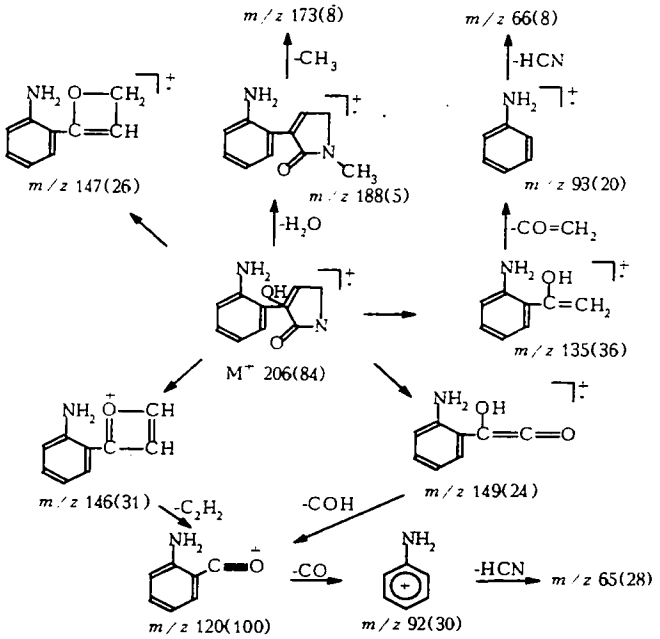
almost equal intensities, while in the case of ardine, because of the presence of an additional methyl group in one half of the molecule, a parallelism is observed in the appearance of fragmentary indole ions. The results of measurements of the elementary compositions of the key ions are given in the Experimental part.

The results of a detailed study of the mass spectra of donaxarine and donaxaridine, the fragmentation of which was described in [6], have proved interesting. The structures of these compounds were determined from their PMR, mass, IR, and UV spectra. These spectra were interpreted mainly with respect to functional groups, on the basis of which these substances were erroneously assigned to the indole derivatives. The x-ray structural analyses [2] of donaxarine (**3**) and donaxaridine (**4**) that we have performed have shown that they are pyrrolidone derivatives, and because of this it has been necessary to reconsider the mass-spectrometric fragmentation of donaxarine and donaxaridine on the basis of the new structures that we have established for these alkaloids. Although in the fragmentation schemes for donaxarine and donaxaridine proposed previously the accurate masses did correspond to the suggested structures of the fragmentary ions, in the case of donaxaridine the peak of the ion with *m/z* 148 should be one of the most intense fragments, being favored, on the one hand by the −OH group and, on the other hand, by the aromatic system of the molecule. In addition to this, an ion with *m/z* 130 should be a fragment of a donaxine impurity.

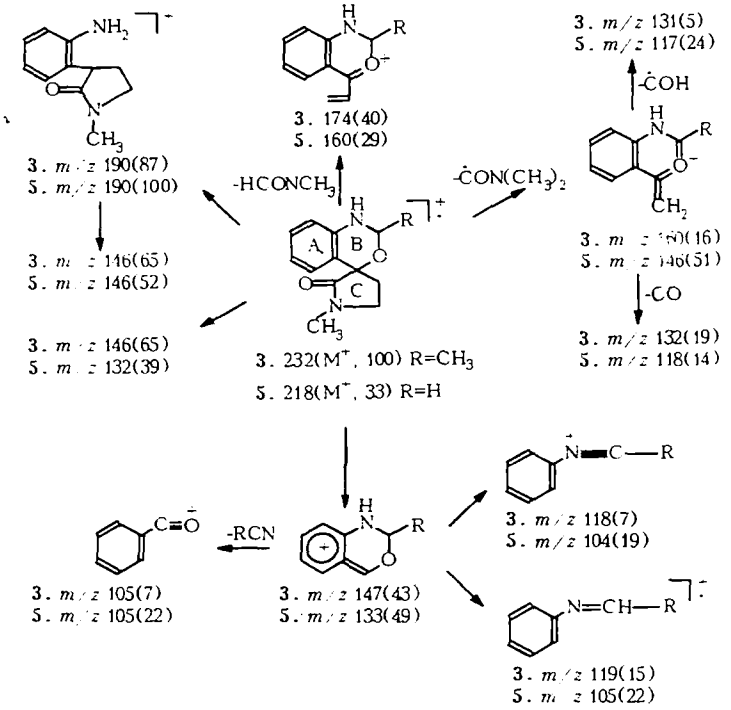
As can be seen from our proposed scheme 2, for donaxaridine the breakdown of the pyrrolidone ring takes place in different directions with the formation of fragmentary ions containing an aminophenyl grouping. Such a fragmentation mechanism has been described in detail in [7].



Scheme 2. Mass-spectrometric fragmentation of donaxaridine (**4**).

The appearance of a spiro-linked ring in the structure of donaxarine substantially changes the direction of fragmentation of this compound in comparison with the spectrum of donaxaridine. Scheme 3 shows the routes of formation of the main ions in the mass spectrum of donaxarine. An important point in the fragmentation of donaxarine is the formation of an ion with *m/z* 190 as the result of the ejection of a ketene molecule from the elements of ring *B*. In addition to this, the appearance in the spectra of ions with *m/z* 118 and 119, having the compositions C_8H_9N and C_8H_8N, is possible only in the case of the corrected structures of the above-mentioned alkaloids.

The mass spectrum of donaxinine (**5**) [8] is characterized by complete parallelism with the spectrum of donaxarine, as shown in Scheme 3; however, the elements of both spiro rings may participate in the formation of ions with *m/z* 190. In addition to this, a homologous fragment of the ion with *m/z* 119 is observed at 105 *m/z* in the composition of the doublet [C_7H_5O (**1**) + C_7H_7N (**2**)].



Scheme 3. Mass-spectrometric fragmentation of of donaxarine (**3**) and donaxinine (**5**).

Such identity of the mass spectra of the two compounds has permitted us to propose for donaxinine the structure of spiro[(N-methylpyrrolidin-2-one)-3,4′-(3′,1′-benzoxazine), and this has been confirmed by PMR spectroscopy and synthesis.

EXPERIMENTAL

Mass spectra were taken on a MKh-1310 mass spectrometer using a SVP5 system for the direct injection of the sample, at a temperature of the ionization chamber of 150°C and of the evaporator bulb of 70-80°C, with an ionizing energy of 70 eV.

Arundine: M^+ 246(246.1157, $C_{17}H_{14}N_2$); 245(245.1078, $C_{17}H_{13}N_2$), 130(130.0656, C_9H_8N); 129(129.0576, C_9H_7N); 117(117.0577, C_8H_7N); 102(102.0469, C_8H_6).

Ardine: M^+ 260(260.1312, $C_{18}H_{16}N_2$); 259(259.1232, $C_{18}H_{15}N_2$); 144(144.0813, $C_{10}H_{10}N$); 131(131.0744, C_9H_9N); 130(130.0655, C_9H_8N); 129(129.0577, C_9H_7N); 117(117.0576, C_8H_7N); 102(102.0468, C_8H_6).

Donaxaridine: M^+ 206(206.1054, $C_{11}H_{14}N_2O_2$); 149(149.0475, $C_8H_7NO_2$); 147(147.0684, C_9H_9NO); 135(135.0683, C_8H_9NO); 120(120.0448, C_7H_6NO); 92(92.0499, C_6H_6N).

Donaxarine: M^+ 232(232.1211, $C_{13}H_{16}N_2O_2$); 190(190.1080, $C_{11}H_{14}N_2O$); 174(174.0918, $C_{11}H_{12}NO$); 160(160.0761, $C_{10}H_{10}NO$); 147(147.0684, C_9H_9NO); 146(146.0605, C_9H_8NO); 119(119.0734, C_8H_9N); 118(118.0656, C_8H_8N); 105(105.0340, C_7H_5O).

Donaxanine: M^+ 218(218.1054, $C_{12}H_{14}N_2O_2$); 190(190.1106, $C_{11}H_{14}N_2O$); 160(160.0763, $C_{10}H_{10}NO$); 146(146.0606, C_9H_8NO), 133(133.0522, C_8H_7NO); 105(105.0577, C_7H_7N (2)); (105.0335, C_7H_5O (1)); 104(104.0498, C_7H_6N).

REFERENCES

1. S. Ghosal, R. K. Chaudhuri, S. K. Dutta, and S. K. Bhattacharya, Planta Med., **21**, 22 (1971).
2. V. U. Khuzhaev, S. F. Aripova, and R. Sh. Shakirov, Khim. Prir. Soedin., 685 (1994).
3. V. U. Khuzhaev, B. Tashkhodzhaeva, and S. F. Aripova, Khim. Prir. Soedin., 730 (1995).

4. H. Budzikiewicz, C. Djerassi, and D. Williams, Interpretation of Mass Spectra of Organic Compounds, Holden-Day, San Francisco (1964).
5. V. U. Khuzhaev, S. F. Aripova, and R. Sh. Shakirov, Khim. Prir. Soedin., 328 (1995).
6. K. A. Ubaidullaev, S. F. Aripova, and R. Sh. Shakirov, Khim. Prir. Soedin., 553 (1976).
7. K. L. Lutfullin, M. Tadzhibaev, U. A. Abdullaev, V. M. Malikov, and S. Yu. Yunusov, Khim. Prir. Soedin., 625 (1976).
8. V. U. Khuzhaev, S. F. Aripova, and U. A. Abdullaev, Khim. Prir. Soedin., 738 (1995).