

## MASS-SPECTROMETRIC FRAGMENTATION OF THE ALKALOID ARUNDININE

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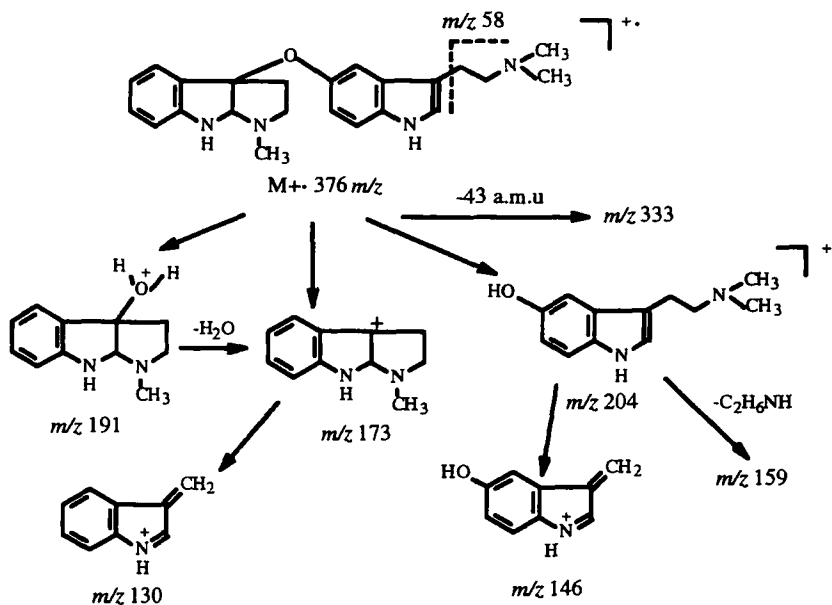
UDC 543.51+547.944/945

The dimeric alkaloid arundinine has been isolated from the perennial giant grass *Arundo donax* (fam. Gramineae), and its structure has been established on the basis of  $^1\text{H}$  and  $^{13}\text{C}$  NMR results and x-ray structural analysis [1, 2].

We have made an investigation of the mass-spectrometric fragmentation of arundinine using high-resolution regimes. The mass spectrum was taken on a Kratos MS 25 RF spectrometer and on a MKh-1310 instrument with the use of a system for the direct injection of the specimen into the ion source at an energy of 50 eV and an evaporator temperature of 180–190°C. The mass spectrum of arundinine is characterized by the presence of a peak of the molecular ion with  $m/z$  376, and peaks of fragmentary ions with  $m/z$  333, 204, 191, 190, 173, 159, 146, and 130. The elementary compositions of all these ions were determined on the high-resolution mass spectrometer (Table 1).

The ion peaks with  $m/z$  173 and 130 are diagnostic and are present in the mass spectra of all types of 3-alkyl derivatives of indole alkaloids.

By comparing the accurate mass and elementary composition of the molecular ion of arundinine with those of the above-mentioned fragmentary ions, the mass-spectrometric fragmentation of arundinine can be represented in the following way:



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TABLE 1

$m/z$ values of the ions	Accurate masses		Composition
	experimental	theoretical	
376 ( $M^+$ )	376.2273	376.2263	$C_{23}H_{28}N_4O$
333	333.1822	333.1841	$C_{21}H_{23}N_3O$
204	204.1274	204.1262	$C_{12}H_{16}N_2O$
191	191.1192	190.1184	$C_{11}H_{15}N_2O$
190	190.1116	190.1106	$C_{11}H_{14}N_2O$
173	173.1080	173.1078	$C_{11}H_{13}N_2$
159	159.0689	159.0684	$C_{10}H_9NO$
146	146.0603	146.0606	$C_9H_8NO$
130	130.0657	130.0657	$C_9H_6N$

The main direction of the mass-spectrometric fragmentation of arundinine is the breakdown of the molecular ion at the ether bridge into two halves. An ion with  $m/z$  204 is formed from the alkylindole half, while the tricyclic half gives rise to the intense fragments in the spectrum with  $m/z$  191 and 173. The ions with  $m/z$  204 and 173 are direct components of the  $M^+$  ion.

The ion with  $m/z$  191 includes the oxygen atom of the ether bridge. Although its formation takes place through a complex rearrangement mechanism, we give its simplified structure, passing as the result of ejection of an  $H_2O$  molecule into an ion with  $m/z$  173. The further breakdown of the above-mentioned fragments leads to the characteristic indole ions described in the literature.

We may note that the ion peak with  $m/z$  58 observed in the low-mass region is characteristic for an N-alkyl chain.

## REFERENCES

1. *Second International Symposium on the Chemistry of Natural Compounds*, Eskishehir, Turkey, October 22—24, 1996, p. 19.
2. I. Zh. Zhalolov, V. U. Khuzhaev, B. Tashkhodzhaev, M. G. Levkovich, S. F. Aripova, and N. D. Abdullaev, *Khim. Prir. Soedin.*, 790 (1998).