

## SECONDARY-ION MASS SPECTROMETRY OF SOME CATALPOL AND MUSSAENOSIDE DERIVATIVES

U. A. Abdullaev, M. S. Maksudov, and Z. Saatov

UDC 543.51+547.918:547.912

*The iridoid glycosides catalpol, veronicoside, catalposide, mussaenoside, and 8-epiloganin have been investigated by secondary-ion mass spectrometry (SIMS). A tendency of these compounds to give cationized form of the molecular ions in the SIMS regime has been shown. In the SIMS spectra of veronicoside and catalposide the maximum peaks were those of acyl cations, and in the cases of mussaenoside and 8-epiloganin they were the peaks of ions formed by the elimination of a glucose molecule.*

Because of the presence of sugar residues and other polar groups in iridoid molecules, the electron-impact mass spectra of the iridoids do not give valuable information on the molecular masses and, all the more, on the structures of the molecules [1]. At the same time, in this regime the peracetates and permethylated derivatives of the iridoids mainly show the peaks of stable ions relating to the sugar moieties of the molecules and to their fragments [2]. The development of mild methods of ionization, such as fast-atom bombardment (FAB) and field desorption (FD), has promoted the introduction of mass spectrometry for the direct investigation of iridoids [3-5]. For this reason, we have set ourselves the aim of considering the behavior of iridoids under the conditions of secondary-ion mass spectrometry (SIMS) using glycerol as the liquid matrix.

In the SIMS regime, catalpol (1) did not show the  $MH^+$  peak with  $m/z$  363, and in its place there were the peaks of cationized forms of the molecular ion  $(M + Na)^+$  with  $m/z$  385,  $(M + 2Na - H)^+$  with  $m/z$  407, and  $(M + 3Na - 2H)^+$  with  $m/z$  429. Among these, the strongest was the peak of the  $(M + Na)^+$  ion. Although the (1) molecule has an appreciable number of easily eliminable groupings, its SIMS spectrum lacked the peaks of fragmentary ions. It is known that the cationized forms of molecules possess a high stability and undergo practically no fragmentation [3, 6]. Thus, in a report [5] of an investigation in which the FAB and FD regimes were used for the ionization of iridoid molecules, only the peaks of the  $(M + Na)^+$  ions are mentioned and there is no information on fragmentary ions.

In the SIMS spectra of veronicoside (2) and catalposide (3), together with the peaks of the  $(M + Na)^+$  ions, there were the peaks of the  $MH^+$  ions and of cluster ions with glycerol (Table 1). The formation of a considerable number of  $MH^+$  ions in this case is the reason for the appearance of a number of primary and secondary fragmentary ions both of the iridoid series and of the side-chains. For the spectra of (2) and (3) the maximum peaks were those of benzoyl and *p*-hydroxybenzoyl cations, peaks of  $(MH - Acyl)^+$  ions being absent. The peaks of ions formed as a result of the elimination of glycosyl fragments,  $(MH - 162)^+$  and  $(MH - 180)^+$ , possessed a high intensity, and this showed that the protonation of the molecules in the SIMS regime took place through the oxygen atoms of the pyran rings.

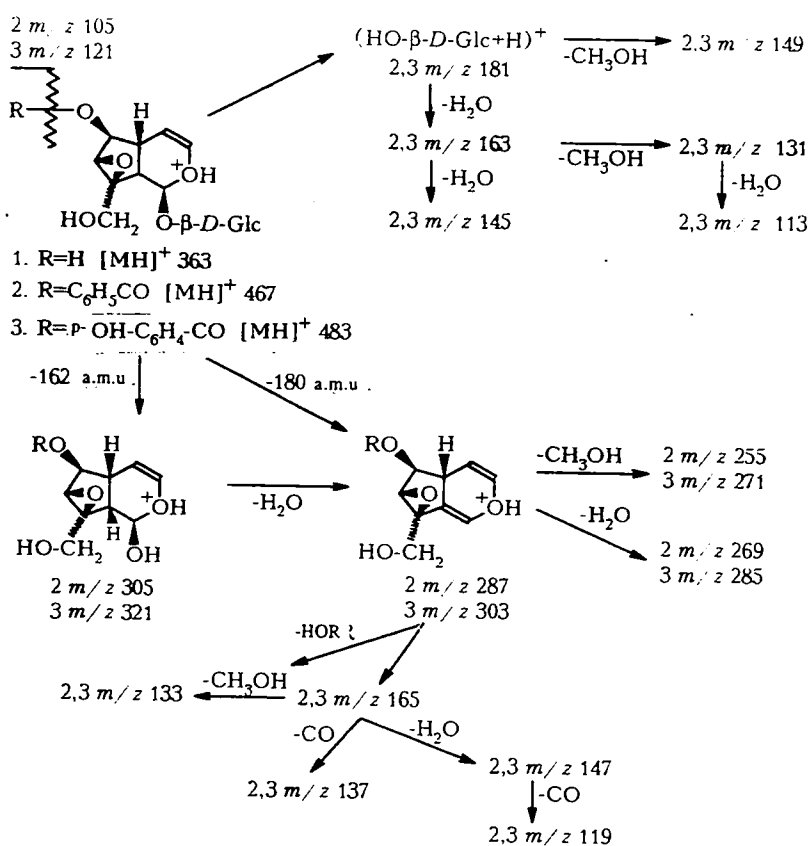
The further fragmentation of the ions obtained,  $(MH - 162)$  and  $(MH - 180)^+$ , took place through the alternative ejection of side-chain residues (scheme 1), the elimination of an AcylOH grouping leading to the formation of intense peaks of ions with  $m/z$  165. (See Scheme 1 on following page.)

Definite interest is presented by a comparative analysis of the SIMS spectra of the isomeric iridoids mussaenoside (4) and 8-epiloganin (5), differing by the position of a hydroxy group in the five-membered ring of the molecule. The appearance of cationized forms of the molecular ions and of dimeric and trimeric cluster ions is characteristic of both compounds (see Table 1). The peaks of the  $(M + Na)^+$  ions were almost 4 times more intense than those of  $MH^+$ . However, in this case the formation of the latter ions served as the source of number of fragmentary ions. It must be mentioned that here the elimination of a glucose molecule from  $MH^+$  acquired a dominating character, in contrast to (2) and (3). So far as concerns the participation of the 3-methoxycarbonyl group in the fragmentation of  $MH^+$ , it is ejected in the form of  $CH_3OH$  from ions with  $m/z$  229, 211, and 193. As can be seen from the given spectra of (4) and (5) and Scheme 2, the fragmentation of  $MH^+$  takes

---

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (3712) 89 14 75. Translated from *Khimiya Prirodnykh Soedinenii*, No. 1, pp. 62-65, January-February, 1996. Original article submitted Spetemebr 17, 1995.

Scheme 1



place similarly for (4) and (5), and at this stage of the investigation there is still no possibility of revealing any mass-spectral differences whatever between the SIMS spectra of these compounds.

Scheme 2

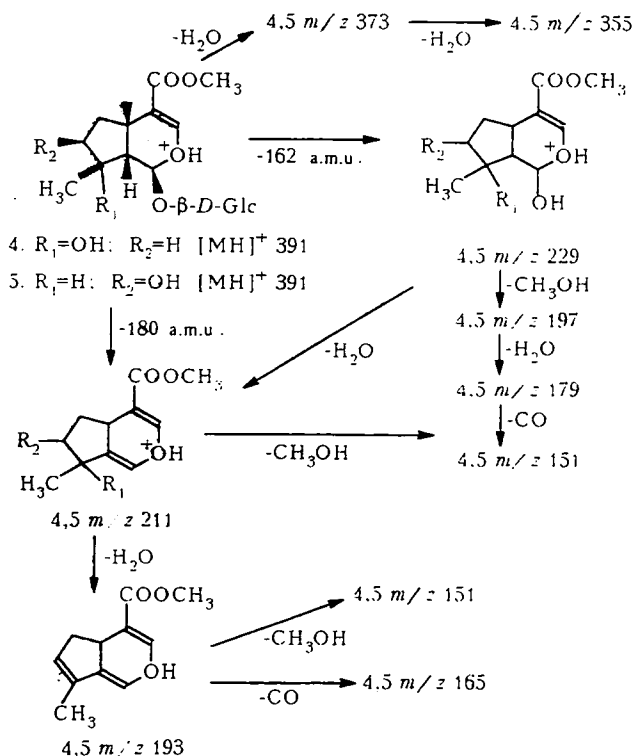


TABLE 1. Cluster Ions in the SIMS of Compounds (1-5) [ $m/z$  (I, %)]

Ions	Compound				
	1	2	3	4	5
MH <sup>+</sup>	363(0)	467(7)	483(5)	391(2.2)	391(1.8)
(M+Na) <sup>+</sup>	385(100)	489(13)	505(8)	413(8)	413(8.5)
(M+2Na-H) <sup>+</sup>	407(20)	-	-	-	-
(M+3Na-2H) <sup>+</sup>	429(17)	-	-	-	-
(MH+Glyc) <sup>+</sup>	-	559(8)	575(10)	-	-
(MH+2Glyc) <sup>+</sup>	-	651(0.6)	667(1)	-	-
(2M+H) <sup>-</sup>	-	933(4)	-	781(1)	781(0.8)
(2M+Na) <sup>-</sup>	-	955(0.6)	-	803(0.5)	803(0.3)
(3M+H) <sup>-</sup>	-	-	-	1171(0.05)	1171(0.02)

## EXPERIMENTAL

The secondary-ion mass spectra of the iridoids under consideration were obtained by the use of glycerol as matrix in a MKh-1310 instrument by the procedure described in [7].

**Veronicoside (2)**,  $m/z$  (I, %): 955 (0.6), 933 (4), 651 (0.6), 559 (8), 489 (M + Na)<sup>+</sup> (13), 467 MH<sup>+</sup> (7), 465 (2), 449 (6), 431 (2), 345 (1), 305 (60), 287 (62), 269 (24), 255 (6), 181 (7), 165 (45), 163 (14), 149 (19), 147 (29), 145 (32), 137 (35), 135 (24), 127 (17), 119 (14), 117 (6), 105 (100).

**Catalposide (3)**,  $m/z$  (I, %): 667 (1), 575 (10), 505 (M + Na)<sup>+</sup> (8), 483 MH<sup>+</sup> (5), 465 (3), 321 (25), 303 (11), 285 (3), 181 (4), 165 (23), 163 (10), 149 (16), 147 (8), 145 (11), 137 (11), 135 (11), 127 (6), 121 (100), 119 (7), 117 (6).

**Mussaenoside (4)**,  $m/z$  (I, %): 1171 (0.05), 803 (0.5), 781 (1), 413 (M + Na)<sup>+</sup> (8), 411 (0.6), 391 MH<sup>+</sup> (2.2), 389 (3.5), 373 (1.9), 371 (0.5), 355 (0.9), 341 (0.8), 229 (77), 227 (4), 211 (100), 209 (23), 197 (8), 193 (55), 181 (6), 179 (66), 165 (15), 163 (15), 161 (13), 151 (15), 149 (16), 145 (14), 131 (3), 113 (2.2).

**8-Epiloganin (5)**,  $m/z$  (I, %): 1171 (0.02), 803 (0.3), 781 (0.8), 413 (M + Na)<sup>+</sup> (8.5), 411 (1.1), 391 MH<sup>+</sup> (2), 389 (0.7), 373 (2), 371 (0.7), 355 (0.7), 341 (1), 229 (60.0), 211 (100), 209 (25), 197 (25), 193 (50), 181 (15), 179 (55), 165 (15), 163 (12), 161 (40), 151 (32), 149 (20), 145 (20), 131 (8), 113 (3.5).

## REFERENCES

1. W. Bentley, R. A. W. Johnstone, and I. Grimshaw, *J. Chem. Soc.*, No. 21, 2234 (1967).
2. V. A. Mnatskanyan, *Iridoid Glycosides* [in Russian], *Izd-vo Akad. Nauk Armyanskoi SSR*, Erevan (1986), p. 68.
3. J. Chapman, *Practical Organic Mass Spectrometry*, Wiley, Chichester (1985).
4. T. Iwaga, T. Hamada, S. Kurogi, T. Hase, T. Okubo, and M. Kim, *Phytochemistry*, **30**, 4057 (1991).
5. Chongen Yang and Zhendan He, *Yunnan Zhiwu Yanjiu*, **15**, 413 (1993).
6. L. M. Teesch, R. C. Orlando, and J. Adams, *J. Am. Chem. Soc.*, **113**, 3668 (1991).
7. Ya. V. Rashkes, G. G. Mil'grom, and Yu. M. Mil'grom, *Khim. Prir. Soedin.*, 385 (1993).