Tetrahedron Letters,Vol.23,No.24,pp 2481-2484,1982 0040-4039/82/242481-04$03.00/0
Printed in Great Britain

STRUCTURAL CHARACTERIZATION OF VIRIDOPENTAOSES AND THEIR RELATED SACCHARIDES BY MATRIX-ASSISTED MOLECULAR SIMS[1]

Ken-ichi Harada and Makoto Suzuki*

Faculty of Pharmacy, Meijo University, Tempaku, Nagoya 468, Japan

Hideki Kambara

Central Research Labolatory, Hitachi Ltd., Kokubunji, Tokyo 185, Japan

Summary: The matrix-assisted molecular secondary ion mass spectra of viridopentaoses and their related compounds are discussed. The effective use of matrices in molecular SIMS will be a powerful method for the structural characterization of polar molecules.

Recently, sputtered type ionization methods such as plasma desorption(PD),[2] laser desorption (LD),[3] fast atom bombardment(FAB)[4] and secondary ion(SI)[5] mass spectrometry have been developed for the study of involatile and/or thermally labile compounds. These does not require heating of samples for desorption or ionization. In particular, molecular SIMS and FABMS have been worthy of notice because of their simple operation and good reproducibility.[6,7] The term FAB is used when the primary particles are neutral atoms instead of ions in SIMS.

During the structural investigation of an antibiotic sporaviridin(SVD),[8] we obtained three heteropentasaccharides, viridopentaose A(1A), B(1B) and C(1C) on hydrolysis of N-acetylsporaviridin(SVD-N-Ac) with aqueous ammonia. Their structures have been established by chemical degradations and spectroscopic studies.[9] However, their molecular weights and sequence of the constituting units could be determined with difficulty by conventional methods such as chemical ionization(CI) and field desorption(FD) mass spectrometry. In this communication we describe the application of a new potential technique, matrix-assisted molecular SIMS to the structural characterization of viridopentaoses and their derivatives.

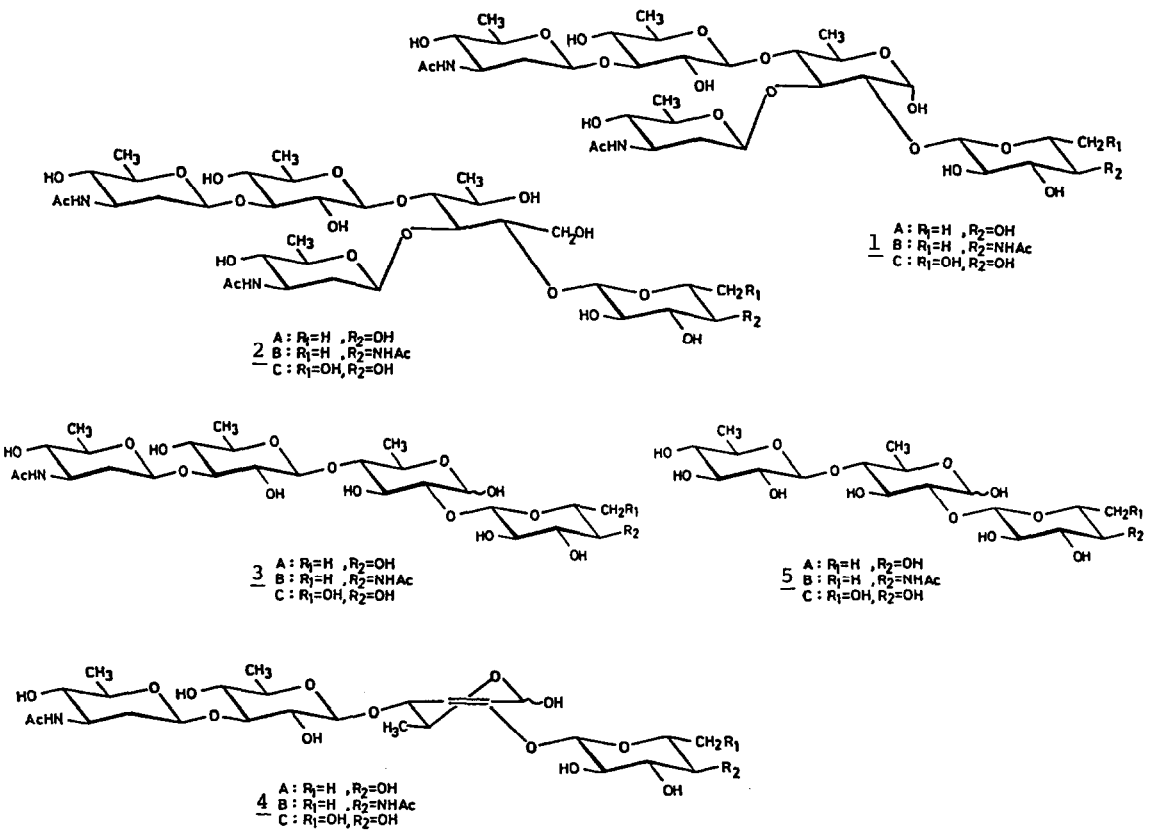
Degradative reactions of 1A, 1B and 1C were performed as follows.[9] Acidic methanolysis under appropriate conditions afforded viridotetraose A(3A), B(3B), C(3C) or viridotriose A(5A), B(5B), C(5C), respectively. Reduction with $NaBH_4$ in MeOH yielded dihydroviridopentaose A(2A), B(2B) and C(2C), respectively. Treatment with 5% NaOH(aq) in MeOH eliminated readily an N-acetylacosamine to give unsaturated tetrasaccharides, 4A, 4B and 4C, respectively.

The SI mass spectra of viridopentaoses and their derivatives were investigated and the SI mass spectra of 1B as a typical example are shown in Fig. 1.[10] The mass spectrum of 1B without matrix, so-called dry surface, presents three cationized molecular ion species, $(M+Na)^+$, $(M+K)^+$ and $(M+Ag)^+$ in the high mass region and they indicated accurately the molecular weight(Fig. 1a). Because Ag-containing ions appear as doublet peaks due to the presence of Ag-isotopes(107, 109), the argentated molecules, $(M+Ag)^+$ are valuable in the mass spectra supported on silver. The chief fragment ions are observed at m/z 172 and m/z 188 as oxonium type ions derived from the

amino sugars. The molecular ion species of other related compounds, 1, 3 and 5 series are summarized in Table 1.

Fig. 1b shows the SI mass spectrum of 1B using glycerol as a matrix. The protonated molecule(MH^+) appears at m/z 840 with considerable intensity together with the weak sodiated molecule,$(M+Na)^+$. The principal fragmentations are considered to be due to the cleavages of the glycosidic bonds(Fig. 2). The resulting fragment ions are observed as oxonium or protonated type derived from mono-, di-, tri- and tetrasaccharide moieties. These sequence ions of 1B together with those of 1, 2 and 4 series are summarized in Table 2. These ions are available for the determination of sequence of the constituting monosaccharides. The fragmentations are closely similar to those of CIMS.

When basic matrices such as 3-amino-1,2-propanediol, mono-, di- and triethanolamine are used, adduct ions result from reaction of substrate with the amine. In the case of 1B with dietanolamine(DEA), the adduct ion$(M+DEAH)^+$ occurs at m/z 945, which is significant for the molecular weight information(Fig. 1c). The diethamolamine matrix mass spectra are freqently accompanied by a series of ions at m/z 106, 150, 211, 255.....702, which are derived from only the matrix. The occurrence of these ions will be discussed elsewhere.[11] The fragmentations are analogous to



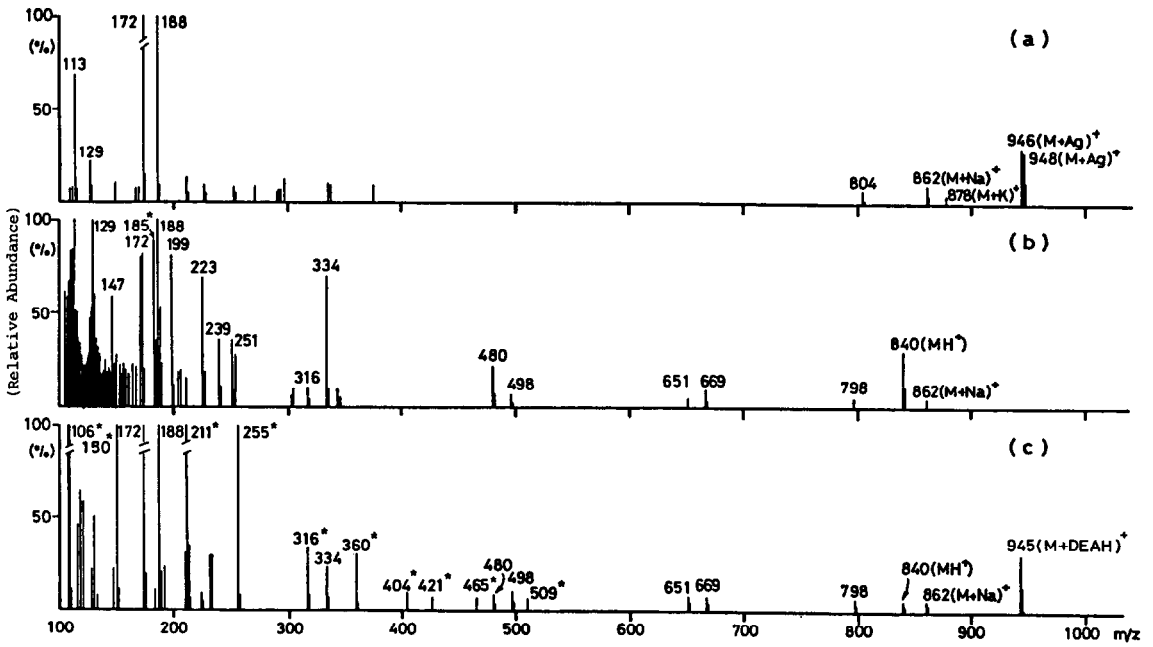


Fig. 1. Secondary ion mass spectra of 1B (a)dry surface (b)glycerol matrix (c)diethanolamine matrix. [* Matrix derived ions]

Table 1. Molecular ion species (m/z) in the mass spectra (dry surface) of 1, 3 and 5 series

	1A	1B	1C	3A	3B	3C	5A	5B	5C
MH^+	799	—	—	—	—	—	—	—	—
$[M+Na]^+$	821	862	837	650	691	666	479	520	495
$[M+K]^+$	837	878	853	—	—	—	—	536	—
$[M+Ag]^+$	905 907	946 948	921 923	734 736	775 777	750 752	563 565	604 606	579 581

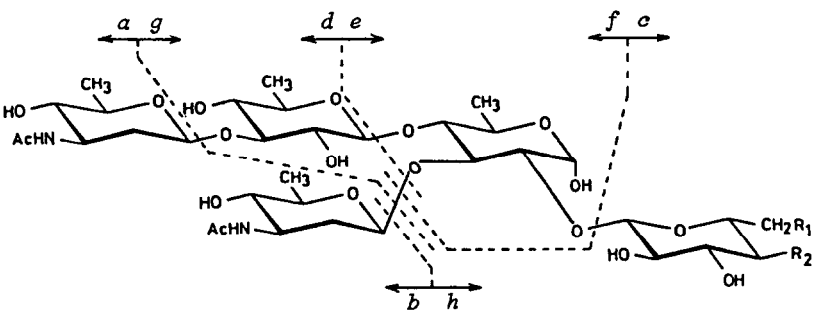


Fig. 2. Diagnostic sequence ions in the mass spectra with glycerol matrix.

Table 2. Sequence ions (m/z) in the mass spectra with glycerol matrix of 1, 2 and 4 series

	1A	1B	1C	2A	2B	2C	4A	4B	4C
MH^+	799	840	815	801	842	817	610	651	626
a	172	172	172	172	172	172	172	172	172
b	172	172	172	172	172	172			
c	—	188	—	—	188	—	—	188	—
d	318	—	318	318	—	318	318	—	318
e+3H	—	334*	—	—	354	—	—	316*	—
f+3H	482	—	482	484	—	484	464	—	464
g+3H	—	498	—	—	500	—	—	462*	—
h+2H	628	669	644	630	671	646			

* Dehydrated sequence ions.

those of 1B with glycerol. However, these fragment ions seem to be dissociated from the MH^+, since the adduct ion is considerably stable.

As mentioned above, the effective use of matrices in molecular SIMS will be a powerful technique for the structural characterization of polar compounds.

References and notes

1. Structural investigation of an antibiotic sporaviridin, part V. Part IV: see ref. 9.
2. R. D. Macfarlane and D. F. Torgerson, Science, 191, 920(1976).
3. M. A. Posthunus, P. G. Kistemaker and H. L. C. Meuzelaar, Anal. Chem,. 50 985(1978).
4. M. Barber, R. S. Bordoli, R. D. Sedgwivk and A. N. Tyler, J. C. S. Chem. Commun., 324(1981).
5. A. Benninghoven and W. K. Sichtermann, Anal. Chem,. 50, 1180(1978).
6. H. Kambara and S. Hishida, Org. Mass Spectrom., 16, 167(1981); Anal. Chem., 53, 2340(1981); K. I. Harada, M. Suzuki, N. Takeda, A. Tatematsu and H. Kambara, J. Antibiotics, 53, 104 (1982).
7. D. H. Wlliams, C. Bradley, G. Bojesen, S. Santikarm and L. C. E. Tayler, J.Am. Chem. Soc., 103, 5700(1981).
8. T. Okuda, Y. Ito, T. Yamaguchi, T. Furumai, M. Suzuki and M. Tsuruoka, J. Antibiotics, Ser. A., 19, 85(1966).
9. K. I. Harada, S. Ito and M. Suzuki, Tetrahedron Letters, preceding communication.
10. Operating conditions are as follows: A double focusing mass spectrometer Hitachi M-80 equipped with an additional electron impact(EI) ion source to produce primary ions was used. The primary ions were Xe^+ ions. A side entry, direct inlet prove was used to introduce samples on a silver substrate into the ion source chamber. The acceleration voltages of the primary and secondary ions were 7 kV and 3kV, respectively, which gave an impact energy of 4 keV.
11. K. I. Harada, M. Suzuki and H. Kambara, Org. Mass Spectrom., to be submitted.

(Received in Japan 5 March 1982)