

Study of Acetylated Methyl 2-Deoxy-D-erythro-pentosides by Electron Impact and Chemical Ionization Mass Spectrometry

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Anomeric pairs of methyl 3,5-di-O-acetyl-2-deoxy-D-erythro-pentofuranosides and methyl 3,4-di-O-acetyl-2-deoxy-D-erythro-pentopyranosides have been studied by electron impact and chemical ionization mass spectrometry. Electron impact fragmentation was verified by measurements of metastable transitions, as well as using collision-induced spectra, obtained after collision with helium atoms. The ring size can be unambiguously determined from electron impact spectra. Metastable and collision spectra of $[M - OCH_3]^+$ ions, as well as of $[M + NH_4]^+$ cluster ions, also reflect the ring size of the compounds under study. Configuration of the anomeric pairs cannot be determined unambiguously from the quantitative differences found in their spectra.

Acetylated saccharides and their derivatives, due to their relatively high volatility, are suitable for electron impact (EI) and chemical ionization (CI) mass spectrometric measurements [1, 2]. Techniques developed for measurements of metastable transitions or collision processes are excellent tools for the elucidation of EI and CI processes [3, 4]. For this purpose, instruments with reversed geometry as well as MS-MS or MS-MS-MS sequential arrangements are most suitable. The application of modern techniques of tandem spectrometry in metastable and collision experiments allows to obtain new structural information from minute quantities of complex samples. For example, the techniques mentioned above, in combination with fast atom bombardment ionization, were applied in studies of acetylated stereoisomers of hexoses and aminohexoses [5-7].

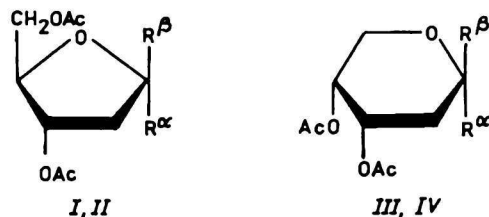
Here we present the results of mass spectrometric study of peracetylated methyl 2-deoxy-D-erythro-pentosides I-IV. Spectra of selected ions,

obtained after electron and chemical ionization, were compared with the spectra obtained by unimolecular (MIKE) and collisionally induced dissociation (CID), formed in a spectrometer with reversed geometry. The results are interpreted from the viewpoint of the differences in ring size and the configuration at the anomeric centre of the compounds investigated.

2-Deoxy-D-erythro-pentose as a component of deoxyribonucleic acids plays an important role in biochemistry of saccharides [8].

EXPERIMENTAL

Preparation of compounds I-IV has been described in [8]. The EI spectra were obtained with a CH-5 instrument, using a direct inlet of the sample at the ion source temperature of 180 °C. The spectra were normalized with the on-line computer. The peak intensities presented in Tables 1-4 represent average values of three measurements. Under the same conditions, the EI ions were produced also in a VG ZAB-2F mass spectrometer. The studied ions, obtained at 70 eV or 12 eV, were magnetically focused into the second field-free region of the instrument. The MIKE spectra were obtained by scanning the deflection voltage of the electrostatic analyzer. CID spectra were obtained by the same technique using helium as the collision gas, introduced into the collisional chamber in the second field-free region, until the intensity of the parent peak was reduced to 50%. In the measurements of the CI spectra, ammonia was introduced until the pressure reading at the ion source housing reached 10^{-3} - 10^{-4} Pa.



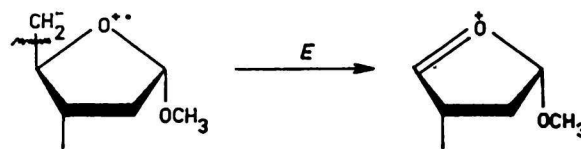
I, II

III, IV

	R ^α	R ^β
I	OCH ₃	H
II	H	OCH ₃
III	OCH ₃	H
IV	H	OCH ₃

RESULTS AND DISCUSSION

The conventional 70 eV spectra of methyl 3,5-di-*O*-acetyl-2-deoxy-*D*-erythro-pentofuranosides (*I* and *II*) and methyl 3,4-di-*O*-acetyl-2-deoxy-*D*-erythro-pentopyranosides (*III* and *IV*) are presented in Table 1. In analogy to per-*O*-acetyl methyl glyco-



Scheme 2

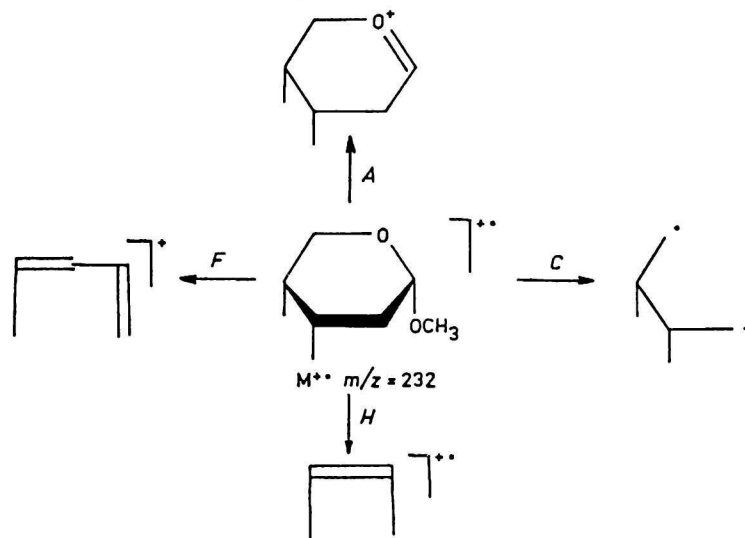
Table 1. Conventional (70 eV) Mass Spectral Data of Compounds *I*–*IV*

<i>m/z</i>	<i>I_r</i> /%				Characteristic ions
	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	
231	0.3	0.2		1.2	M–H
201	1.2	2.4	2.2	1.8	A ₁
172	2.0	2.2	14.2	10.8	C ₁
159	28.2	34.2			E ₁
144			6.5	5.5	H ₁
141			17.6	9.5	A ₂
140	4.0	4.0	4.0	6.2	
130	7.1	18.2	4.2	4.8	
129			4.0	3.0	
113			36.2	30.3	C ₂
112			86.5	91.8	C ₂
103	6.2	7.0	12.2	12.4	
102	1.0	1.0	36.5	30.3	H ₂
100	3.0	3.0	38.5	30.0	
99	100.0	100.0	38.7	37.6	E ₂ , F ₁
87	24.3	64.0	18.2	13.2	F ₂
86			10.0	8.6	H ₁
85	3.0	3.0	4.0	4.4	
84	3.2	3.2	3.2	3.6	
81	34.5	65.2	100.0	70.0	A ₃
73	2.0	3.0	6.2	6.8	
71	24.4	28.0	36.3	36.5	
70	6.0	12.2	80.5	100.0	C ₃
69	5.0	6.0	12.6	12.4	
59	16.0	36.3	20.6	20.5	
58	3.2	4.0	16.5	19.2	
57	2.5	3.0	4.0	5.4	
55	2.0	3.3	10.2	11.2	
45	3.0	4.5	6.0	6.2	
43	160.5	180.2	185.3	190.4	

sides [1, 3, 4], molecular ions of the compounds under study decompose in five different ways (Scheme 1). Four (A, C, H, F) of these are characteristic both of pyranoid and furanoid structures. The pathway E, characteristic of furanoid structures, is illustrated in Scheme 2. The designation by capitals is in accordance with the commonly used terminology [3, 4] of the fragmentation of saccharides. The primary ions, A₁, C₁, H₁, F₁, and E₁, provide secondary and tertiary products after elimination of the molecules of acetic acid or ketene (Table 1). The course of the fragmentation series was confirmed by measuring the MIKE spectra of the primary ions.

The fragmentation differences due to different ring size are significant. They are characterized mainly by the presence of the E series in the case of furanosides and the C series in the case of pyranosides. The differences in peak intensities in the spectra of the pair *III* and *IV* are reflected mainly in the ratio of the intense A₃ and C₃ peaks (*m/z* = 81/70). While in the case of the α -derivative the ratio of these intensities is greater than 1, in the case of the β -anomer it is smaller than 1. The aforementioned differences are somewhat more significant in the spectra obtained after ionization with low-energy (12 eV) electrons.

The step-by-step elimination of the two molecules of acetic acid represents the spontaneous decomposition of metastable A₁ ions of *m/z* = 201 (Fig. 1,



Scheme 1

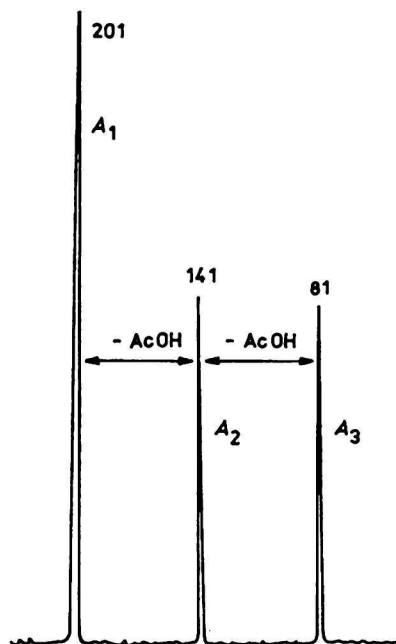


Fig. 1. MIKE spectrum of A_1 ions of methyl 3,4-di-O-acetyl-2-deoxy- β -D-erythro-pentopyranoside (IV).

Table 2). The quantitative differences observed in the spectra of isomers are very small. A higher proportion of A_2 ions can be achieved also after decreasing the energy of ionizing electrons from conventional 70 eV to 12 eV (Table 2).

As expected [2, 4], ammonium ions, originating from ammonia at the conditions of chemical ionization, provide significant cluster ions $[M + NH_4]^+$, appearing with compounds I–IV at $m/z = 250$. This phenomenon allows direct determination of their molecular mass. Cluster ions $[M + NH_4]^+$ were

Table 2. MIKE and CID Spectral Data of A_1 Ions of Compounds I–IV with $m/z = 201$

E/eV	m/z	MIKE $I_r/\%$				CID $I_r/\%$			
		I	II	III	IV	I	II	III	IV
70	141	45	51	49	90	9	14	25	37
70	81	100	100	100	100	100	100	100	100
12	141	72	37	100	100	22	23	54	85
12	81	100	100	100	100	100	100	100	100

Table 3. MIKE Spectral Data of $[M + NH_4]^+$ Ions of Compounds I–IV

m/z	$I_r/\%$				Characteristic ions
	I	II	III	IV	
233	100	100	100	100	$[M + H]^+$
218	2	1	6	8	$[A_1 + NH_4]^+$
201	80	32	20	43	A_1

Table 4. CID Spectral Data of $[M + NH_4]^+$ Ions of Compounds I–IV

m/z	$I_r/\%$				Characteristic ions
	I	II	III	IV	
233	20	87	29	6	$[M + H]^+$
218	4	2	6	2	$[A_1 + NH_3]^+$
201	100	100	68	47	A_1
141	6	2	84	70	A_2
99	9	5	8	6	A_3
81	76	50	100	100	A_3
43	34	14	42	52	CH_3CO^+
18	14	7	16	20	NH_4^+

isolated in the magnetic field and subjected to MIKE and CID experiments. Fig. 2 shows a representative CID spectrum.

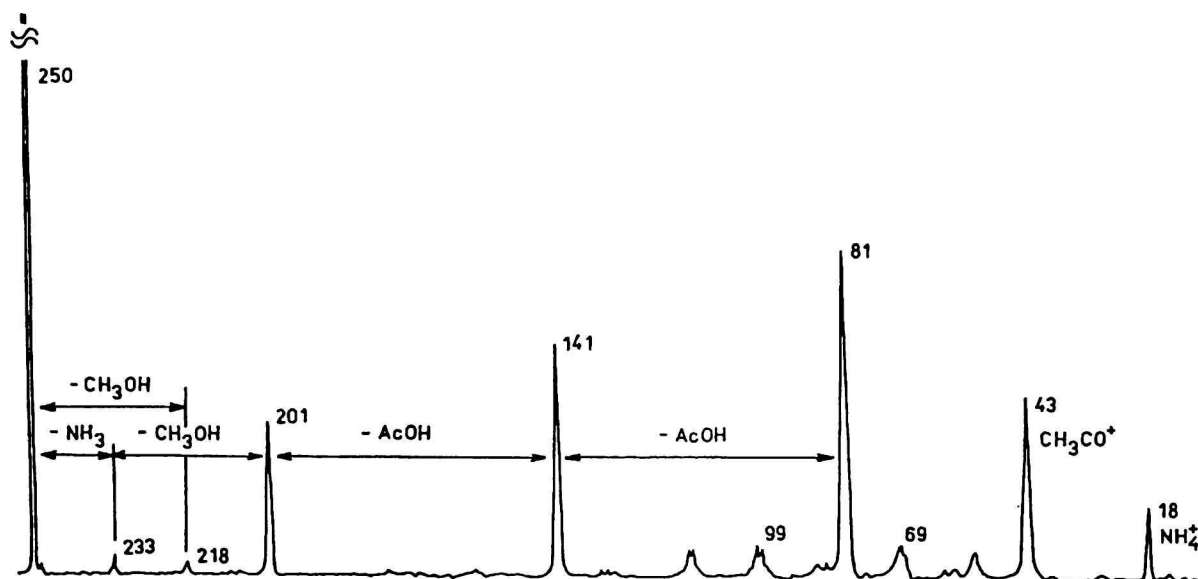


Fig. 2. CID spectrum of $[M + NH_4]^+$ ions of methyl 3,4-di-O-acetyl-2-deoxy- β -D-erythro-pentopyranoside (IV).

Two reactions were observed in the MIKE spectrum (Table 3). The first one was the loss of the molecule of ammonia to give the protonated methyl glycoside $[M + H]^+$. The elimination of the molecule of methanol from the $[M + NH_4]^+$ adduct was less pronounced. The formation of $[A_1 + NH_3]^+$ ions, having probably the structure of a protonated *N*-glycoside, was observed with permethylated saccharides [9]. The elimination of the aglycon provides A_1 ions with $m/z = 201$.

CID spectra of $[M + NH_4]^+$ cluster ions (Table 4) document also processes of deeper decomposition during the formation of A_2 and A_3 ions. It is evident from the comparison of MIKE and CID spectra of cluster ions of isomeric compounds I–IV (Tables 3 and 4) that the MIKE spectra are not informative regarding either the ring size or anomeric configuration.

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