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ELECTRON-IMPACT MASS SPECTROMETRY OF METHYL 2,3,5,6-TETRA-*O*-METHYL-D-GLUCOFURANOSIDE

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ABSTRACT

The fragmentation of methyl 2,3,5,6-tetra-*O*-methyl-D-glucofuranoside under electron impact is described using data for labelled analogues and metastable measurements. Although the fragmentation showed features of that of hexopyranosides and pentofuranosides, there were characteristic differences. Mass-spectral data that are useful for identification of pentoses and hexoses as pyranosides or furanosides are tabulated.

INTRODUCTION

The mass spectrometry of monosaccharides is well documented[1–4] but, apparently, a detailed study of the fragmentation of methylated methyl hexofuranosides has not been described. Heyns *et al.*[3] suggested that the fragmentation of methyl 2,3,5,6-tetra-*O*-methyl-D-galactofuranoside is analogous to that of the methylated pentofuranosides. The relative intensities of the most important ions of 2,3,5,6-tetra-*O*-methyl-D-glucofuranose[5] and methyl 2,3,5,6-tetra-*O*-methyl-D-galactofuranoside[3] have been published. We now present the spectra of methyl 2,3,5,6-tetra-*O*-methyl-D-glucofuranoside and ten specifically labelled trideuteriomethyl analogues, together with the fragmentation pattern and ion structures deduced therefrom.

EXPERIMENTAL

Mass spectra were recorded with an AEI MS902 mass spectrometer. Samples were introduced using the all-glass heated-inlet system at 180°. The ion source was operated at 160–180° with an ionizing current of 500 μA, an electron energy of 60 eV, an accelerating voltage of 6 kV, and an ion-source pressure of 2.0×10^{-6} Torr.

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Metastable measurements in the first field-free region were carried out by the refocusing technique of Barber and Eliott[6].

Monosaccharide derivatives were methylated by the Kuhn procedure[7], using MeI or CD_3I (99% D, Merck) as appropriate. Isolation of the anomers was effected by t.l. c. on Silica Gel G (Fertigplatten, Merck) with hexane–acetone (3:2), and detection with u.v. light after spraying with 1% morin in methanol. The products were extracted from the silica gel with chloroform. The upper band represented the β anomer, the lower band the α anomer.

^{1}H-N.m.r. spectra were recorded at 25° with a Varian HA-100 (Organic Chemical Institute T.N.O., Utrecht) or HR-220 spectrometer (T.N.O. Central Laboratories, Delft) for solutions in acetonitrile-d_3. N.m.r. spectra of intermediate compounds were recorded at 60 MHz and 25°. Chemical shifts are given relative to that of internal Me_4Si on the δ scale. By comparison of the chemical shifts of the methoxyl singlets in the spectra of a methylated glucofuranoside with those of the analogues having trideuteriomethyl groups at specific positions, these singlets could be assigned unequivocally.

Methyl 2,3,5,6-tetra-O-*methyl*-α-(**1a**) *and* β-D-*glucofuranoside* (**1b**) *and methyl 3,5,6-tri*-O-*methyl-2*-O-*trideuteriomethyl*-α-(**3a**) *and* β-D-*glucofuranoside* (**3b**). — 1,2-*O*-Isopropylidene-α-D-glucofuranose[8] was methylated, and the 3,5,6-tri-*O*-methyl derivative was purified by distillation at 110° (bath)/0.1 mmHg. N.m.r. data ($CDCl_3$): δ 5.83 (d, $J_{1,2}$ 3.8 Hz, H-1), 4.54 (d, $J_{2,1}$ 3.8 Hz, H-2), 3.76 (d, $J_{3,4}$ 3.1 Hz, H-3), 4.11 (dd, $J_{4,3}$ 3.1, $J_{4,5}$ 8.7 Hz, H-4), 3.38–3.42 (3 s, MeO-3,5,6), 1.30 and 1.46 (2 s, CMe_2), and 3.4–3.7 (other protons).

The foregoing compound was treated with methanolic M HCl (24 h, 85°) to remove the isopropylidene group. After neutralisation (Ag_2CO_3), centrifugation, and drying, the resulting mixture of methyl glycosides was methylated with MeI to give **1a** and **1b**, or with CD_3I to give **3a** and **3b**; the α and β anomers were obtained in a 1:1 ratio. N.m.r. data (CD_3CN) **1a**: δ 3.30 (s, MeO-1), 3.33 (s, MeO-2), 3.35 (s, MeO-3), 3.34 (s, MeO-5), 3.29 (s, MeO-6), for skeleton protons see **2a**; **1b**: δ 3.27 (s, MeO-1), 3.36 (s, MeO-2), 3.34 (s, MeO-3), 3.35 (s, MeO-5), 3.30 (s, MeO-6), for skeleton protons see **2b**; **3a** and **3b**: the data were identical to those of **1a** and **1b**, respectively, except that the signals for MeO-2 (δ 3.33 and 3.36, respectively) are missing.

Trideuteriomethyl 2,3,5,6-tetra-O-*trideuteriomethyl*-α-(**2a**) *and* β-D-*glucofuranoside* (**2b**). — A procedure was followed similar to that for the preparation of **1a** and **1b**, except that the 1,2-*O*-isopropylidene group was removed by boiling a solution in methanol-d_4 for 5 h with Amberlite IR-120 (H^+) resin as catalyst. N.m.r. data (220 MHz, CD_3CN) **2a**: δ 4.90 (d, H-1), 3.69 (dd, H-2), 3.75 (dd, H-3), 4.02 (dd, H-4), 3.48 (m, H-5), 3.61 (dd, H-6), and 3.39 (dd, H-6′); $J_{1,2}$ 4.1, $J_{2,3}$ 3.9, $J_{3,4}$ 5.6, $J_{4,5}$ 7.1, $J_{5,6}$ 1.6, $J_{5,6'}$ 5.9, and $J_{6,6'}$ −10.3 Hz; **2b**: δ 4.75 (d, H-1), 3.65 (m, H-2,3), 3.95 (dd, H-4), 3.52 (m, H-5), 3.66 (dd, H-6), and 3.42 (dd, H-6′); $J_{1,2}$ ~1.0, $J_{2,3}$ not determined, $J_{3,4}$ 4.7, $J_{4,5}$ 8.8, $J_{5,6}$ 1.7, $J_{5,6'}$ 5.3, $J_{6,6'}$ −10.5 Hz.

Methyl 5-O-*methyl-2,3,6-tri*-O-*trideuteriomethyl*-α- (**4a**) *and* -β-D-*glucofurano-*

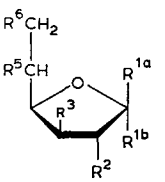
side (**4b**). — 1,2-*O*-Isopropylidene-5-*O*-methyl-α-D-glucofuranose[9] was treated with methanolic M HCl, the acid was neutralized, and the product was methylated with CD_3I. N.m.r. data (CD_3CN) **4a**: δ 3.30 (s, MeO-1), 3.34 (s, MeO-5), for skeleton protons see **2a**; **4b**: δ 3.27 (s, MeO-1), 3.35 (s, MeO-5), for skeleton protons see **2b**.

*Methyl 2,3-di-*O*-methyl-5,6-di-*O*-trideuteriomethyl-α-* (**6a**) *and β-*D*-glucofuranoside* (**6b**) *and trideuteriomethyl 2,3-di-*O*-methyl-5,6-di-*O*-trideuteriomethyl-α-* (**5a**) *and β-*D*-glucofuranoside* (**5b**). — 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose was methylated with MeI, and the 3-*O*-methyl derivative was purified by distillation at 130° (bath)/0.005 mmHg. N.m.r. data ($CDCl_3$): δ 5.80 (d, $J_{1,2}$ 3.7 Hz, H-1), 4.51 (d, $J_{2,1}$ 3.7 Hz, H-2), 3.72 (d, $J_{3,4}$ 2.8 Hz, H-3), 3.41 (s, MeO-3), 1.31, 1.34, 1.43 and 1.48 (4 s, 2 CMe_2), and 3.9–4.4 (other protons). The 5,6-*O*-isopropylidene group was removed by acid hydrolysis[8], and the resulting 1,2-*O*-isopropylidene-3-*O*-methyl derivative was purified by elution from silica gel with ether. N.m.r. data ($CDCl_3$): δ 5.86 (d, $J_{1,2}$ 3.7 Hz, H-1), 4.55 (d, $J_{1,2}$ 3.7 Hz, H-2), 3.44 (s, MeO-3), 2.97 (s, 2 OH), 1.32 and 1.48 (2s, CMe_2), and 3.7–4.2 (other protons). Methylation with CD_3I yielded the corresponding 5,6-*O*-trideuteriomethyl derivative, the n.m.r. data of which were identical to those of the 3,5,6-tri-*O*-methyl analogue, except for the presence of only one methoxyl singlet (δ 3.42). Treatment with methanolic M HCl and subsequent methylation with MeI yielded **6a** and **6b**, from which **5a** and **5b** were prepared by hydrolysis [Amberlite IR-120 (H^+) resin, 5 h, 100°] and subsequent methylation with CD_3I. N.m.r. data (CD_3CN) **6a**: δ 3.30 (s, MeO-1), 3.33 (s, MeO-2), 3.35 (s, MeO-3), for skeleton protons see **2a**; **6b**: δ 3.27 (s, MeO-1), 3.36 (s, MeO-2), 3.34 (s, MeO-3), for skeleton protons see **2b**; **5a** and **5b**: the data were identical to those of **6a** and **6b**, respectively, except that the signals for MeO-1 (δ 3.30 and 3.27, respectively) were missing.

RESULTS AND DISCUSSION

The mass spectra for compounds **1–6** are compiled in Table I; the fragment ions and the corresponding ions of the labelled analogues are presented in one block. The main fragmentation pathways of methyl 2,3,5,6-tetra-*O*-methyl-D-glucofuranoside, derived from metastable ion measurements, are presented in Fig. 1.

1a,b $R^2 = R^3 = R^5 = R^6 = OMe$
2a,b $R^2 = R^3 = R^5 = R^6 = OCD_3$
3a,b $R^2 = OCD_3$, $R^3 = R^5 = R^6 = OMe$
4a,b $R^2 = R^3 = R^6 = OCD_3$, $R^5 = OMe$
5a,b $R^5 = R^6 = OCD_3$, $R^2 = R^3 = OMe$
6a,b $R^5 = R^6 = OCD_3$, $R^2 = R^3 = OMe$
Series **a**: $R^{1a} = H$, $R^{1b} = OMe$ (for **2a** and **5a** $R^{1b} = OCD_3$)
Series **b**: $R^{1b} = H$, $R^{1a} = OMe$ (for **2b** and **5b** $R^{1a} = OCD_3$)



From the data presented in Table I, the elemental compositions of the major fragment ions and the most plausible structures were deduced (Table II). Primary

TABLE I

MASS SPECTRA OF METHYLATED METHYL D-GLUCOFURANOSIDE AND LABELLED ANALOGUES[a]

m/e	*Compound number (Positions of OCD_3 groups)*											
	1a —	**1b** —	**2a** *(All)*	**2b** *(All)*	**3a** *(2)*	**3b** *(2)*	**4a** *(2,3,6)*	**4b** *(2,3,6)*	**5a** *(1,5,6)*	**5b** *(1,5,6)*	**6a** *(5,6)*	**6b** *(5,6)*
228	.	.	.	.	.	.	0.2	0.1	.	.	.	.
225	.	.	.	.	.	.	.	.	.	0.1	0.1	.
222	.	.	.	.	0.1	0.1	.	.	.	.	.	.
219	.	0.1	.	.	.	.	.	.	.	.	.	.
217	.	.	0.6	1.6	.	.	.	.	.	.	.	.
214	.	.	.	.	.	.	.	.	.	.	.	.
211	.	.	.	.	.	.	0.7	1.4	0.5	1.6	.	.
208	.	.	.	.	0.8	1.3	.	.	.	.	0.5	1.2
205	0.5	1.7	.	.	.	.	.	.	.	.	.	.
196	.	.	0.4	0.3	.	.	.	.	.	.	.	.
193	.	.	.	.	.	.	0.3	0.2	0.1	0.1	0.2	0.2
190	.	.	.	.	0.2	0.1	.	.	0.1	0.1	0.1	0.1
187	0.3	0.3	.	.	0.2	0.1	.	.	.	.	.	0.1
182	.	.	1.7	3.2	.	.	.	.	.	.	.	.
179	.	.	.	.	.	.	0.3	0.4	1.0	2.8	.	.
176	.	.	.	.	2.2	3.0	1.9	3.0	0.2	0.5	1.4	2.5
173	1.7	3.8	.	.	0.1	0.2	.	.	.	.	0.1	0.2
170	.	.	13.0	17.2	.	.	.	.	.	.	.	.
167	.	.	.	.	.	.	14.4	16.3	.	.	.	.
164	.	.	.	.	13.4	12.7	.	.	7.0	18.0	.	.
161	11.9	22.2	.	.	.	.	.	.	.	.	11.7	20.6
168	.	.	0.3	0.1	.	.	.	.	.	.	.	.
165	.	.	.	.	.	.	0.3	0.8	0.2	0.9	0.1	0.1
162	.	.	.	.	0.3	0.6	.	.	0.1	0.1	0.6	1.1
159	0.3	1.0	.	.	0.1	0.4	.	.	.	.	.	.
161	.	.	2.7	2.1	.	.	3.5	2.3	0.3	0.4	.	.
158	.	.	.	.	3.0	2.2	0.2	0.2	1.9	1.8	2.5	2.3
155	3.0	2.6	.	.	0.2	0.2	0.8	0.4	0.2	0.1	0.1	0.3
154	.	.	5.0	6.0	.	.	.	.	.	.	.	.
151	.	.	.	.	.	.	4.5	4.3	1.5	2.3	0.1	0.1
148	.	.	.	.	5.4	5.5	1.6	2.1	3.8	4.2	4.5	5.6
145	5.0	6.5	.	.	0.5	0.8	.	.	.	.	0.1	0.1
140	.	.	1.2	1.7	.	.	.	.	.	.	.	.
137	.	.	.	.	.	.	1.5	1.7	0.2	0.2	.	.
134	.	.	.	.	1.6	1.9	0.3	0.3	1.1	1.7	0.2	0.5
131	1.3	2.0	.	.	0.1	0.3	.	.	.	.	1.0	1.7

TABLE I *(continued)*

m/e	*Compound number (Positions of OCD_3 groups)*											
	1a —	**1b** —	**2a** *(All)*	**2b** *(All)*	**3a** *(2)*	**3b** *(2)*	**4a** *(2,3,6)*	**4b** *(2,3,6)*	**5a** *(1,5,6)*	**5b** *(1,5,6)*	**6a** *(5,6)*	**6b** *(5,6)*
135	.	.	1.7	2.8	.	.	0.4	0.4	0.4	0.4	0.1	0.2
132	.	.	.	.	2.2	2.8	1.8	2.8	1.4	2.6	0.4	0.9
129	1.6	3.0	.	.	0.2	0.5	.	.	0.2	0.4	1.2	2.8
133	.	.	1.2	1.6	.	.	1.2	2.6	0.5	2.5	0.2	0.4
130	.	.	.	.	1.2	0.8	0.3	0.4	0.8	0.9	1.0	3.8
127	1.2	1.1	.	.	0.6	0.4	.	.	0.5	0.5	0.4	0.7
123	.	.	7.6	9.2	.	.	0.5	0.4	4.8	4.6	.	.
120	.	.	.	.	1.4	0.9	3.2	4.0	3.4	4.1	6.4	7.6
117	7.4	10.1	.	.	8.9	9.2	5.5	5.7	1.6	1.2	1.6	1.8
107	.	.	100.0	100.0	.	.	73.9	69.3	.	.	.	.
104	.	.	.	.	80.1	76.5	26.1	30.7	28.9	28.4	5.0	8.0
101	100.0	100.0	.	.	19.9	23.5	.	.	71.1	71.6	95.0	92.0
95	.	.	10.1	15.4	.	.	1.0	1.7	6.4	7.1	6.1	7.9
92	.	.	.	.	2.3	2.7	8.1	12.0	3.7	5.7	2.5	4.2
89	9.7	10.7	.	.	10.7	11.2	0.6	1.1	0.9	3.7	3.9	3.1
94	.	.	12.6	15.4	.	.	6.7	4.6	1.8	3.3	1.6	3.5
91	.	.	.	.	13.2	7.8	5.1	8.2	3.4	4.1	0.4	0.2
88	11.6	7.8	.	.	3.0	4.4	1.0	1.8	3.6	3.1	6.8	7.3
81	.	.	76.9	76.2	.	.	3.4	3.5	2.7	3.4	.	.
78	.	.	.	.	7.0	5.2	60.6	63.2	56.4	59.1	6.2	8.9
75	69.2	60.1	.	.	65.9	76.5	4.5	10.0	1.9	2.0	46.2	64.9
76	.	.	3.8	5.5	.	1.0	2.7	3.4	1.3	.	1.1	0.8
73	3.8	3.0	.	3.7	.	4.2	0.9	3.2	3.7	3.4	3.5	4.5
74	1.4	1.3	4.8	5.5	3.4	2.4	2.9	3.3	4.1	2.5	2.9	3.2
71	5.2	3.2	.	.	4.9	3.5	1.8	2.4	2.9	2.6	3.0	2.1
63	.	.	6.4	8.1	.	.	0.2	0.2	6.3	0.1	4.8	6.5
62	.	.	0.7	1.1	0.6	0.5	3.4	4.9	1.9	1.6	1.2	1.6
60	.	.	.	.	0.7	0.2	2.7	3.8	2.9	2.2	1.6	1.9
59	8.3	5.6	.	.	9.1	9.8	0.6	0.9	0.5	0.6	0.8	0.3
48	.	.	15.8	19.1	7.5	6.2	9.5	17.3	21.6	15.6	8.8	9.8
45	20.3	13.0	.	.	21.3	19.8	3.7	7.9	12.6	9.4	10.6	13.8

[a]The relative intensities (with respect to the sum of the intensities of the ions *m/e* 101, 104, and 107) are corrected for isotopic contributions.

fragmentation reactions involve the loss of the substituents at C-1 and C-4, each of which is adjacent to the ring oxygen atom, resulting in the formation of the ions

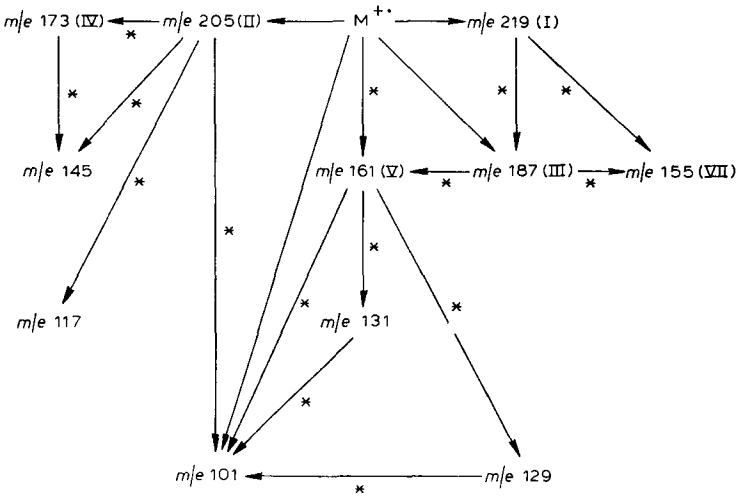


Fig. 1. Fragmentation scheme of methyl 2,3,5,6-tetra-*O*-methyl-D-glucofuranoside; *signifies observed metastable transitions.

m/e 219 (I) and 161 (V). A third primary fragmentation is the fission of the C-5–C-6 bond, resulting in the formation of the ion *m/e* 205 (II).

Elimination of methanol from I yields the ions at *m/e* 187 (III). Kochetkov *et al.*[5] stated that 75% of the peak intensity of the ion *m/e* 187 in methyl 2,3,4,6-tetra-*O*-methylglucopyranosides originates from loss of methanol at C-1 and C-3. In contrast, we find that the major contributor to the ion *m/e* 187 is IIIa, which still contains MeO-3,5,6. Consequently, MeO-1 and MeO-2 have been eliminated. Conjugation of the double bonds in IIIa might be responsible for its larger contribution in comparison with IIIb (elimination from C-1 and C-6) and IIIc (elimination from C-5 and C-6). The occurrence of IIIb and IIIc means that the ion *m/e* 187 can also be generated directly from the molecular ion.

The ion *m/e* 187 can lose another methanol molecule to give the ion *m/e* 155. Kochetkov *et al.*[5] concluded from labeling experiments that each of the remaining methoxyl groups in the ion *m/e* 187 could be lost to give the ion *m/e* 155. We conclude that only 12% of the peak intensity of the ion *m/e* 155 (VIIc and VIId) originates from that having *m/e* 187 (IIIb and IIIc), and that the major contributor is VIIa. This ion, with three conjugated double bonds, arises from the ion *m/e* 219, as it still contains MeO-2 and MeO-6. This observation is supported by the detection of a metastable peak for the transition 219 → 155. The mode of formation of VIIb (13%) containing MeO-1 and MeO-5 is not clear, but it is probably derived directly from the molecular ion.

The elimination of methanol from the ion *m/e* 205 yields the ion *m/e* 173 with the major contribution from IVa (elimination from C-3). Less important contributors are IVb (elimination from C-2) and IVc (elimination from C-1). In the spectra of glucofuranosides, a peak was detected at *m/e* 145 with a relative intensity of ~5%.

TABLE II

STRUCTURES FOR THE MAJOR FRAGMENT IONS[a]

Mass	Structure	K	Mass	Structure	K	Mass	Structure	K	Mass	Structure	K
219	 I	100	205	 II	100	187	 IIIa	59			
187	IIIb	30	187	 IIIc	11	173	 IVa	81			
173	 IVb	6	173	 IVc	13	161	 V	100			
159	 VIa	9	159	 VIb	72	159	 VIc	19	159	 VId	19
155	 VIIa	75	155	 VIIb	13	155	 VIIc	7			
155	 VIId	5	145	 VIIIa	61	145	 VIIIb	30			
131	 IX	84	129	 Xa	11	129	 Xb	62			
127	 XIa	43	127	same as XIa, with OCH_3-groups left on: C2 + C3 24; C3 + C6 17; C5 + C6 13							
117	 XIIa	53	117	 XIIb	13	117	 XIIc	31			
101	 XIIIa	71	101	 XIIIb	21						

[a]The encircled numbers refer to the number of the carbon atom from which the methoxyl group stems, and *K* is the relative contribution to the intensity.

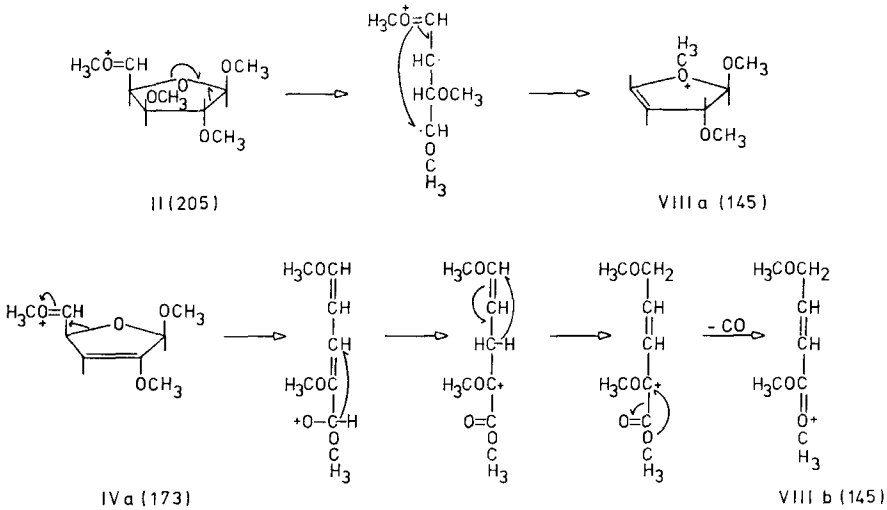


Fig. 2. Formation of the ion *m/e* 145.

Kochetkov *et al.*[5] stated that, for hexopyranosides, this ion results by the loss of a methoxyl radical from the ion *m/e* 176. The ion *m/e* 176 is not found in the spectra of the hexofuranosides. Metastable measurements indicate that the ions *m/e* 173 and 205 are precursors of the ion *m/e* 145. The formation of the ion *m/e* 145 (VIIIa) requires the elimination of a CH_3O–CHO molecule from the ion *m/e* 205. The formation of VIIIb proceeds *via* elimination of CO from the ion *m/e* 173 (IVa). The proposed fragmentation mechanisms are rationalized in Fig. 2.

The ion at *m/e* 161 can be generated from the molecular ion, but might also arise from the ion *m/e* 187 as shown by metastable measurements. This fragmentation involves the elimination of a C_2H_2 molecule from IIIc.

The most intense peak in the spectra of glucofuranosides is at *m/e* 101. This ion is also encountered in the spectra of hexopyranosides, pentofuranosides, and pentopyranosides[10–12]. Two mechanisms have been suggested for the formation of this ion, resulting in cyclopropane and acyclic structures, respectively. Glycosides could be distinguished by differences in the relative contributions of the possible isomers to the abundance of this ion[10,11].

The ion at *m/e* 101 is supposed[12] to originate from precursor ions at *m/e* 250, 176, and 161, but, for glucofuranosides, the ion *m/e* 176 is not present. Metastable measurements indicate as precursors the ions *m/e* 129, 131 (both originating from the ion *m/e* 161), 161, and 205. In spite of the absence of a detectable metastable transition from the molecular ion, which is absent from the mass spectrum, M^+ cannot be excluded as a precursor of the ion *m/e* 101, plausible mechanisms for the formation of which are given in Fig. 3.

The analogues used in this study did not allow discrimination between the presence of C-1 or C-4 in XIIIa. Labelling with ^{13}C at C-1 should answer this problem.

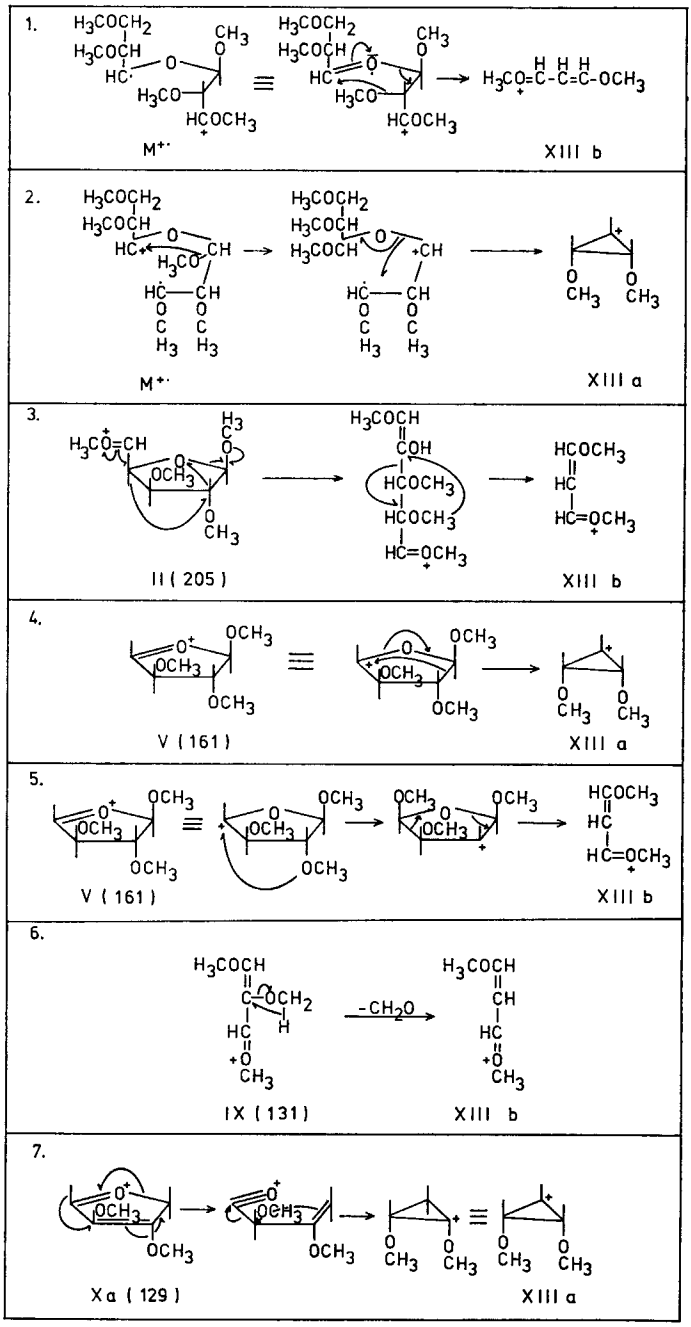


Fig. 3. Formation of the ion *m/e* 101.

In the spectra of the methylated methyl glucofuranosides, a hitherto unexplained peak with an intensity of 7–10% is found at *m/e* 117. Metastable measure-

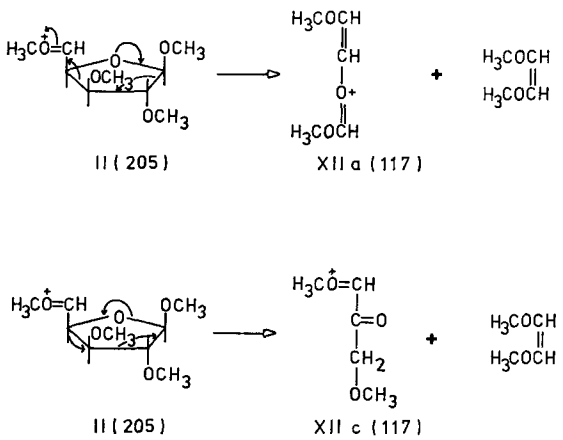


Fig. 4. Formation of the ion *m/e* 117.

ments indicated the ion *m/e* 132 (not found in the spectrum) to be a possible precursor which can give the ion *m/e* 117 by loss of $CH_3^{\cdot}$. The major fraction of the ion *m/e* 117 (XIIa and XIIc) still contains the MeO-1,5 or MeO-3,5, indicating that the ion

TABLE III

CHARACTERISTIC DIFFERENCES IN THE MASS SPECTRA OF METHYLATED METHYL GLYCOSIDES[a]

m/e	*Pentoses*		*Hexoses*	
	Pyranoside	*Furanoside*	*Pyranoside*	*Furanoside*
219	—	—	0.1	0.1
205	—	—	0.1	0.5–1.5
187	—	—	0.5–2.0	0.1–0.4
176	5	—	1–2	—
175	2	1–1.5	—	—
173	—	—	0.3	2–4
161	—	5–6	—	10–20
159	—	—	0.3–1.0	0.3–1.0
155	—	—	0.7	2–4
149	—	—	6–11	—
145	—	—	1–1.5	5–6
143	2–3	1–1.5	—	—
129	—	1.0–1.5	—	1.5–3.0
127	—	—	2–4	1–2
115	5–6	4–4.5	—	—
111	0.3	—	2–4	—
105	0.4	—	—	—
101	90–100	100	50	100
89	—	—	—	10
88	50	4–5	100	10

[a]All values are intensities relative to that of the ion *m/e* 101.

m/e 205 might be another precursor of the ion *m/e* 117. Loss of a 1,2-dimethoxyethylene moiety (C-1/C-2 or C-2/C-3) from II results in the formation of an ion at *m/e* 117 as shown in Fig. 4.

As expected, the methylated methyl hexofuranosides show a fragmentation pattern containing features of hexopyranosides and pentofuranosides. However, a detailed examination of the data revealed certain differences. A number of characteristic differences between the mass spectra of methylated methyl aldopyranosides and aldofuranosides were published by Heyns *et al.*[3]. In order to increase the applicability of mass-spectral data for discrimination between pyranose or furanose rings in monosaccharides, we have extended these data, and the compilation is presented in Table III.

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