Carbohydrate Research, 58 (1977) 203–208

Note

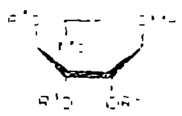
Identification of methyl 6-deoxy-*O*-methylhexopyranosides by mass spectrometry

Vladimír Kováčik, Vincent Mihálov, Štefan Karácsonyi, and Rudolf Toman
Institute of Chemistry, Slovak Academy of Sciences, 809 33 Bratislava (Czechoslovakia)

(Received August 31st, 1976; accepted for publication, November 18th, 1976)

A comparison of the fragmentation in electron-impact mass spectrometry of partially methylated methyl hexopyranosides[1,2], methyl hexofuranosides[3], and methyl (methyl *O*-methylhexopyranosid)uronates[4,5] with that of their fully methylated analogues[6–10] shows that the presence of a free hydroxyl group causes a shift of ion masses and a change of ion intensities. Compounds containing free hydroxyl groups disintegrate on electron impact *via* fragmentation processes not observed for the methylated derivatives. An objective of the present work was to elucidate the fragmentation pattern of methyl *O*-methyl-α-L-rhamnopyranosides **1–8** and compare it with the known fragmentation of per-*O*-methylated methyl 6-deoxyhexopyranosides[7,11].

Elucidation of the fragmentation of compounds **1–8** could provide information useful for the determination of the number and the location of methyl groups in this class of substances.



	R	R^1	R^2
1	H	H	H
2	Me	H	H
3	H	Me	H
4	H	H	Me
5	Me	Me	H
6	Me	H	Me
7	H	Me	Me
8	Me	Me	Me

The 12-eV spectra of **1–8** are summarized in Table I. The values are given as percentages of the total ion content (% Σ_{45}). Because of the complexity of 70-eV spectra, 12-eV spectra were preferred for purposes of interpretation.

The fragmentation of methyl 2,3,4-tri-*O*-methyl-α-L-rhamnopyranoside (**8**, Table II) was essentially similar to that of methylated hexopyranosides[7,11], except that ions of the E series were not formed.

TABLE I

MASS-SPECTRAL DATA[a] FOR METHYL *O*-METHYL-α-L-RHAMNOPYRANOSIDES

m/e	% Σ_{45}							
	--	*2*[b]	*3*	*4*	*2,3*	*2,4*	*2,4*	*2,3,4*
189								2.02
176								6.08
175					1.89	1.45	1.73	
174					0.84			
162					0.29	1.22	0.40	
161		1.44	2.46	2.14	1.19	0.49	0.86	
160			0.23					
157								0.32
148		0.05		0.85				
147	3.70			1.82				
145							0.40	0.46
143					0.49	0.52	0.66	
142					0.54			
134	0.20					0.39		
133	0.26							
131				0.85		0.52		0.41
130		5.17			12.56	0.36	1.73	
129	2.27			1.50		0.26		0.82
128			3.53					
127							0.40	
120	1.56			2.14				
119				1.28	1.19	0.19	2.46	3.77
118	2.60		0.77	1.71				
117						0.19		
116	2.87		6.08					
115						0.39	0.86	
114				3.00	1.34	0.56	1.79	
105	2.13	1.44		3.96		0.72		
102						13.28		
101	0.30		1.54	1.28	2.49	9.23	4.52	7.83
100	2.50		3.15					
99	0.40	1.44			0.79	1.31		0.73
88	1.13	13.70	3.69	19.29	45.04	10.63	25.26	44.70
87	1.60	7.50	1.85	86	2.29	2.77	4.52	
85	3.83		3.77		3.19	1.05		
83					1.99			
75					11.99		17.19	26.72
74	17.78	60.60	65.38	19.29	5.59	33.06	21.18	0.69
73	2.60				1.09	6.92	0.22	0.46
72				22.50	0.74	11.54	13.30	3.45
71	4.67				0.59	0.52		0.36
70					0.84			
61	4.47	2.52		2.03	0.49	0.56		
60	30.05	1.87		6.43				
59	1.66		3.38		1.19	1.45	2.53	0.27
58	11.68	3.10			0.64			
45					0.49	0.29		0.27

---

[a] 12 eV. [b] The numbers refer to the positions of the methyl groups.

TABLE II

CHARACTERISTIC FEATURES OF THE FRAGMENTATION OF METHYL *O*-METHYL-α-L-RHAMNOPYRANOSIDES

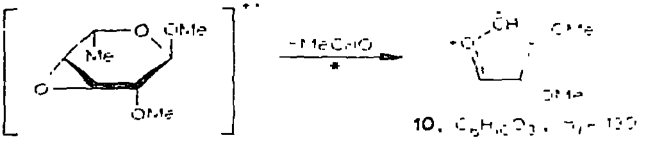
Symbol of ions	m/e	% Σ_{45}[a]							
		—	*2*[b]	*3*	*4*	*2,3*	*2,4*	*3,4*	*2,3,4*
A_1	189								..
	175					. .	...	.	
	161		...	...	...				
	147	...							
B_1	176								×
	162					.	..		
	148		.		.				
	134								
$B_1 - H\cdot$	161								
	147				...				
	133	.							
$B_1 - OR\cdot$	145								
	131				..		.		
A_2	157								
	143								
	129	.							
$M - 2\,MeOH$	142								
	128			...					
$M - MeOH$	174					..			
	160			.					
$B_1 - ROH$	130		×			× ×			
	116	...		×					
$B_1 - \cdot CH_2OMe$	131								.
	117						.		
C_2	129								.
	115						.	..	
	101	.							
$C_1 - ROH$	114				. .	.	.	.	
	100	...		..					
D_1	119					.		..	.
$C_5H_{10}O_4$	134				...		.		
$C_4H_8O_4$	120	...							
$C_4H_9O_3$	105	..	..		...				
$B_1 - HCOOMe$	102						× ×		
$F_1(G_1)$	101	.			...	.	×		×
	87	..	×	..	×	.			
	73	.							
H_1	88		× ×	. .	× ×	× × ×	× ×	× × ×	× × ×
	74	× ×	× × ×	× × ×	× ×	×	× × ×	× × ×	
	60	× × ×	...		×				
K_1	72				× × ×		× ×	× ×	..
	58	×				..			
J_1	75					× ×		× ×	× × ×
	61	. .	.	. .	...		..		

---

[a]Peak intensities: , <0.5%; .., 0.5–1.0%; ..., 1–5%; ×, 5–10%; × ×, 10–20%; × × ×, >20%.
[b]The numbers refer to the positions of the methyl groups.

The fragmentation of the partially methylated derivatives **1**–**7** followed known pathways to only a limited extent. For the fragmentation series common to both fully and partially methylated compounds, capital letters are used in Table II.

The B_1 ions (*m/e* 162) formed from the di-*O*-methyl derivatives **5**–**7** are cleaved further in a number of ways. In addition to the common splitting of ·OMe and ·CH_2OMe radicals, the hydrogen atom of the hydroxyl group is cleaved, giving rise to ions for which the *m/e* value of 161 is not affected by OH/OD exchange. The elimination of methanol from the B_1 ions gives rise to ions (**10**) at *m/e* 130 (no shift after deuterium exchange), with molecular composition $C_6H_{10}O_3$, which are stabilized by cyclization. Metastable transition measurements showed that the ions at *m/e* 130 are also formed in the reverse manner, *i.e.*, by the elimination of acetaldehyde from the ion-radicals $[M-MeOH]^{+\cdot}$ (**9**).

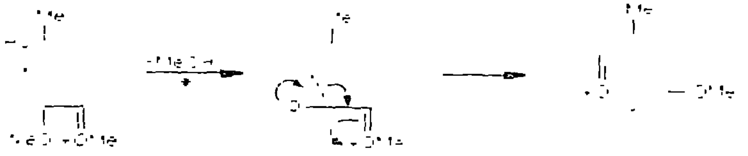


9, $M-MeOH$, *m/e* 174

10, $C_6H_{10}O_3$, *m/e* 130

The fission of the B_1 ions formed from the 2,4-di-*O*-methyl derivative **6** also occurs by elimination of methyl formate to give ions $C_5H_{10}O_2$ (*m/e* 102, no shift after deuterium exchange: m* for 162→102). The formation of these ions must involve complicated rearrangements.

The C_1 ions (**11**) disintegrate by loss of methyl radicals and by elimination of methanol to give ions (**12**) at *m/e* 114 ($C_6H_{10}O_2$).

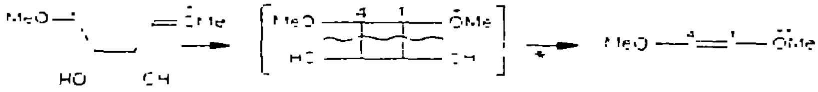


11, C_1, *m/e* 146

12, $C_6H_{10}O_2$, *m/e* 114

For the monomethyl ethers **2**–**4**, peaks corresponding to B_1 ions were found only for the 2-*O*- and 4-*O*-methyl compounds (*m/e* 148→149 after deuterium exchange). The loss of a hydrogen atom from a hydroxyl group to give the ions at *m/e* 148 was pronounced for the 4-*O*-methyl derivative.

A molecule of water is lost from the B_1 ions formed from the 2-*O*-methyl compound **2** to give an ion radical $[B_1-H_2O]^{+\cdot}$ at *m/e* 130 ($C_6H_{10}O_3$). The pronounced formation of H_1 ions (*m/e* 88) from the 4-*O*-methyl derivative was unexpected, as vicinal methoxyl groups, thought to be necessary for this process, are absent. The H_1 ions having the elemental composition $C_4H_8O_2$ are not affected by deuterium exchange. Metastable transition measurements showed that, for **4**, H_1 ions (**14**) are formed from B_1 ions (**13**).



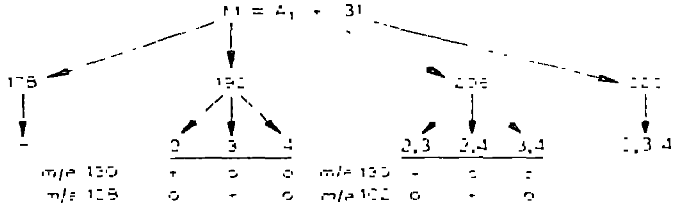
13, B_1, m/e 145 **14** H_1, m/e 88

The fragmentation of the 3-*O*-methyl compound **3** is unique, in that successive elimination of methanol molecules occurs to give ions $[M-MeOH]^{+\cdot}$ at m/e 160 and intense ions $[M-2MeOH]^{+\cdot}$ at m/e 128 ($C_6H_8O_3$). The formation of the former ions was confirmed by metastable transition measurements. The ions at m/e 116 ($C_5H_8O_3$) are also characteristic of the fragmentation of **3** and are formed from $[M-MeOH]^{+\cdot}$ ion-radicals by elimination of acetaldehyde (m* for 160→116). Elimination of methanol from the C_1 ions gives ions m/e 100 ($C_5H_8O_2$).

The formation of $[B_1-H_2O]^{+\cdot}$ and $[C_1-H_2O]^{+\cdot}$ ion-radicals from methyl α-L-rhamnopyranoside is also characteristic.

Comparison of the intensities of the ions of the H and K series (formed by conjugated transfer of the electrons in the pyranoid ring) with those of the series F_1, J_1, and D_1 (formed by transfer of a methoxyl radical from C-3 to C-1) indicates that fissions not involving a methoxyl transfer are preferred.

The mass spectra of **1**–**8** (Table II) show characteristic differences that permit determination of the number and the location of methyl groups in methyl 6-deoxy-*O*-methylhexopyranosides by use of the following scheme:



The molecular weight, which indicates the extent of methylation, is determined from the m/e value of the A_1 ions. The location of the methyl groups in the mono- and di-*O*-methyl derivatives follows from the presence or absence of peaks at m/e 130 and 128, and those at 130 and 102, respectively. Further, the 2,3- and 3,4-di-*O*-methyl derivatives can be distinguished by the presence or absence of the peak at m/e 72, which is characteristic of C-4 substitution.

EXPERIMENTAL

The syntheses of **1–8** have been described elsewhere[1,2]. For deuterium exchange, the compound (**3–6**, 1 mg) was dissolved in methanol-*d*-D_2O (10:1, 0.05 ml). The following extents of deuteration were achieved: **3**, 79%; **4**, 69%; **5**, 78%; **6**, 85%.

Mass spectra were measured at 70 and 12 eV with a JMS-D100 (JEOL) instrument. The temperature at the site of evaporation, measured with a direct-probe temperature-control unit MS-DPT-01, was 30–40°. The temperature of the ionizing chamber was 180°. Exact mass measurements were performed at a resolution of 10,000. Metastable transition measurements were performed with an MS-MT-01 metastable-ion detector.

REFERENCES

1 K. Heyns, K. R. Sperling, and H. F. Grützmacher, *Carbohydr. Res.*, 9 (1969) 79–97.
2 V. Kovacik and P. Kovac, *Chem. Zvesti*, 27 (1973) 662–667.
3 V. Kováčik and P. Kováč, *Carbohydr. Res.*, 24 (1972) 23–28.
4 V. Kováčik and P. Kováč, *Org. Mass Spectrom.*, 10 (1975) 376–383.
5 V. Kováčik, V. Mihálov, and P. Kováč, *Chem. Zvesti*, 31 (1977), in press.
6 N. K. Kochetkov, N. S. Wulfson, O. S. Chizhov, and B. M. Zolotarev, *Tetrahedron*, 19 (1963) 2209–2224.
7 N. K. Kochetkov and O. S. Chizhov, *Tetrahedron*, 21 (1965) 2029–2047.
8 K. Heyns and D. Müller, *Tetrahedron*, 21 (1965) 55–68.
9 K. Heyns and H. Scharmann, *Tetrahedron*, 21 (1965) 507–513.
10 V. Kováčik and P. Kováč, *Org. Mass Spectrom.*, 9 (1974) 172–180.
11 N. K. Kochetkov, O. S. Chizhov, B. M. Zolotarev, and V. S. Shejnker, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 3 (1967) 543–548.
12 R. Toman, S. Karácsonyi, and R. Palovčík, *Carbohydr. Res.*, 56 (1977) 191–194.