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Note

Identification of methyl *O*-methylpentopyranosides by mass spectrometry

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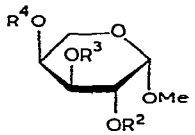
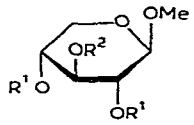
The comparison of electron-impact mass-spectral fragmentation of partially methylated methyl hexopyranosides[1,2], methyl 6-deoxyhexopyranosides[3], methyl (methyl hexopyranosid)uronates[4,5], methyl hexopyranosiduronamides[6], and methyl (methyl 4-deoxy-β-L-*threo*-hex-4-enopyranosid)uronates[7] with that of their fully methylated analogues[7–11] showed that the presence of free hydroxyl groups results not only in a shift of the ion masses but also in a change of their abundances. The molecular ions of methyl *O*-methylpyranosides containing free hydroxyl groups disintegrate by processes occurring with fully methylated derivatives and also by other pathways. The important factors determining the individual fission processes are the substituent at C-5 of the tetrahydropyran ring and the location of the free hydroxyl group(s). We now report on a comparison of the fragmentation of methyl *O*-methylpentopyranosides with that[12–14] of their fully methylated analogues. These data are useful for the determination, without derivatisation, of the number and the location of methyl groups in the title compounds.



1 – 7

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



8 R^1 = H, R^2 = Me
9 R^1 = Me, R^2 = H

The compounds studied include the series of methyl *O*-methyl-β-L-arabinopyranosides (**1**–**7**), methyl 3-*O*-methyl-β-D-xylopyranoside (**8**), and their *O*-deuterated analogues. Compounds **1**–**7** were prepared by known procedures[15–19], and **8** was synthesised by treatment of methyl 2,3-anhydro-β-D-ribopyranoside with sodium methoxide in methanol (*cf.* Ref. 20).

Since there is a stereochemical difference between **8** and the series of methyl *O*-methyl-β-L-arabinopyranosides, the effect of this factor on the mass spectra was

TABLE I

MASS-SPECTRAL DATA[a] FOR METHYL *O*-METHYLPENTOPYRANOSIDES **1–8**

m/e	% Σ_{45} × *100*							
	—	2[b]	3	4	2,3	2,4	3,4	2,3,4
176								168
175								64
162					20	32	12	
161					385	50	321	
148		8	8	10				
147		64	83	46				
146			20					
143						12		51
134	10							
133	65							
131								32
130		49		23	81		41	
129		39	8	23	235		73	
117			13					
116			46					
115	32	42	53			57	36	168
114	16	56	401	40	128		64	
105			18		8		10	12
103		24	27	28				
101		49	60	75	535	3066	321	3160
100	40	49	160	34	85		96	
99			36	40	85		59	109
97				28			27	
91	28							
88		593			1939	192	344	2257
87	77	2018	435	2018	685	514	1216	58
86	106		267	46				
85	90	568	174	75	449	115	73	64
83								96
75			1472	150	1740		1825	1616
74	1064	3213	2778	927	878	3312	2225	
73	1556	296	435	434	856	154	151	904
72					64		78	
71	573	138	328	75	154	141	458	122
69	73	98	401	156	257	90	458	51
68			93	46				38
61	1187	494	468	57	128	102	68	
60	3634	444	130	1942				
59	163	593	803	1159	154	514	413	84
58	65	84	164	1304		546	711	387
57	532	182	307	579	119	154	119	58
56	49		76					
55	98	74	120	92			68	109
53								58
45	532	815	602	579	1006	932	734	323

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

TABLE II

CHARACTERISTIC FEATURES OF THE FRAGMENTATION OF METHYL *O*-METHYLPENTOPYRANOSIDES **1–8**

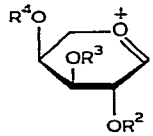
Symbol of ions	m/e	% Σ_{45}[a]							
		—	2[b]	3	4	2,3	2,4	3,4	2,3,4
A_1	175								..
	161					...	.	...	
	147		..	..	.				
	133	.							
A_1 — ROH	143						.		..
	129		.	.	.	...		..	
	115	.	.	.					
B_1	176								...
	162					.	.		
	148			.	.				
	134	.							
B_1 — ROH	130		.		.	..		.	
	116			.					
B_1 — · CH_2OMe	131								
	117								
	103			.	.				
B_1 — ROH — · CH_2OMe	85	..	x	...	.	...	...	..	..
	71	x	...	...	..	...	...	...	...
M — MeOH	146			.					
M — 2MeOH	114		.	.	.				
C_1 — ROH	114					...		..	
	100	.	.	...	.	..		.	
	86	...	...						
C_1 — · OR	115						..	.	..
	101		.	..	..				
D_1	105			.		.		.	.
F_1	101					x	xxx	...	xxx
	87	..	xxx	. .	xxx	xx	x	xx	
	73	xx		...	...				
H_1	88		x			xx	...	...	xxx
	74	xx	xxx	xxx	x	x	xxx	xxx	
	60	xxx	..		xx				
H_2	73		. .			x		. .	x
	59	...	x	x	xx	...	x	...	
J_1	75			xx	. .	xx	...	xx	xx
	61	xx	...	...	..	..		..	
K_1	58	..	..	...	xx		x	x	...

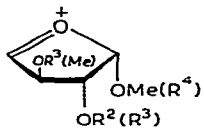
[a]Peak intensities: ., < 0 5%; ., 0 5–1.0%; .. , 1–5%; x, 5–10%; xx, 10–20%; xxx, > 20%. [b]The numbers refer to the positions of the methyl groups.

first investigated. The 70- and 12-eV spectra of **5** and methyl 2,4-di-*O*-methyl-β-D-xylopyranoside (**9**) were qualitatively identical, with minor differences in the intensity of a few peaks. The 12-eV spectra of **1–8** are given in Table I, and the characteristic features of the fragmentation of **1–8** are shown in Table II.

The fragmentation of the partially methylated derivatives **1–6** and **8** occurs

only in part according to the A–K Series established for the fully methylated pentopyranosides[12–14] (*cf.* the data for **7** in Tables I and II). Only ~10–20% of the $[M - 31]^+$ ions, formed from **1–4**, **6**, and **8** having a free hydroxyl group at C-2 or C-4, belong to the common A_1 species of structure **10**. A larger proportion of the $[M - 31]^+$ fragments are furanoid, $[M - \cdot CH_2OH]^+$ E_1-ions having structure **11**. Their formation involves a process in which the leaving fragment contains C-5, the hemiacetal oxygen, and the hydrogen atom of the hydroxyl group. The formulation of the furanoid ions **11** (*cf.* Heyns *et al.*[1]) reflects their formation after a transfer of hydrogen from HO-4. The substituents in parentheses in **11** represent ions formed after a transfer of hydrogen from HO-2. The *m/e* values in parentheses for Formulae **10** and **11** were extracted from the spectra of *O*-deuterated compounds.

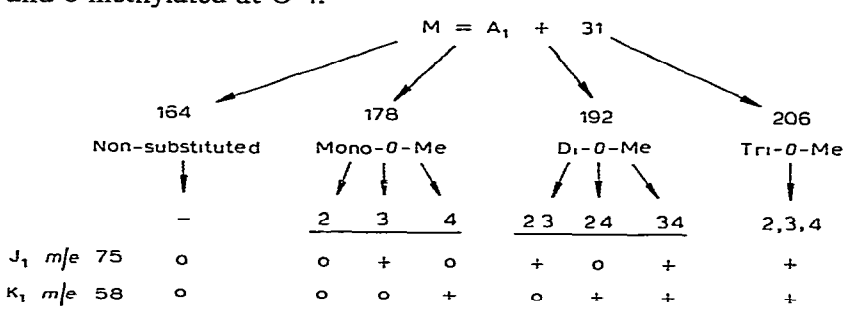




10 A_1 *m/e* 175, 161 (162), 147 (149), 133 (136) 11 E_1, fur *m/e* 161 (161), 147 (148), 133 (135)

The foregoing ions disintegrate next *via* eliminations of methanol and water. In the B and C Series, the eliminations are preferred to the fission of radicals; the hydroxyl groups take part in the former processes, as shown by *O*-deuteration. Characteristic of the 3-*O*-methyl derivative **8** is the elimination of methanol from the molecular ions, to give rise to ion radicals $[M - MeOH]^{+\cdot}$ and $[M - 2MeOH]^{+\cdot}$ having signals at *m/e* 146 and 114. In these eliminations, observed[3] also in the fragmentation of methyl 3-*O*-methyl-α-L-rhamnopyranoside, the hydrogen atoms of the hydroxyl groups also take part. The elimination and radical fissions of the B_1 ions give rise to ions $[B_1 - ROH - \cdot CH_2OMe]^{+\cdot}$ at *m/e* 85 and 71 having the elemental compositions $C_4H_5O_2$ and $C_3H_3O_2$, respectively. A portion of the peak at *m/e* 71 represents particles having the composition C_4H_7O. The foregoing cleavage reactions were confirmed by metastable-transition measurements.

The formation of D_1 ions of low intensity was observed only with the 3-*O*-methylated derivatives **4**, **6**, and **8**. The intense fragments produced from these substances are J_1 ions, whereas intense K_1 ions are formed from compounds **3**, **5**, and **6** methylated at O-4.



Scheme 1

The 70- and 12-eV mass spectra of the methyl *O*-methylpentopyranosides **1–8** (Table I) show pronounced characteristics that can be used to determine the number and location of the methoxyl groups. The simplest interpretation of the spectra for analytical purposes, based on the peaks for A_1, J_1, and K_1 ions, is given in Scheme 1. When an unknown substance is being identified, the low-intensity (~5%) peaks at *m/e* 75 and/or 58 should be neglected.

In conclusion, it can be stated that, except for the stereochemistry, methyl *O*-methylpentosides can be unambiguously identified by mass spectrometry alone and without derivatisation.

EXPERIMENTAL

Methyl β-L-arabinopyranoside (**1**) and its per-*O*-methyl derivative **7** were prepared according to published procedures[15,16]. The syntheses of **2–6** and **9** have been described[17–19,22].

Mass spectra (70- and 12-eV; emission, 100 μA) were obtained with a JMS D-100 instrument. The temperature at the site of evaporation was 25–160° and that in the ionising chamber was 180°. Exact mass measurement was performed at a resolution of 10,000. Metastable-transition measurements were performed by using a metastable-ion detector MS-MT-01.

^{13}C-N.m.r. spectra and p.m.r. spectra were measured with JEOL FX 60 and FX 100 Spectrometers (internal Me_4Si).

Methyl 3-O-methyl-β-D-xylopyranoside (**8**). — Sodium (1 g) was dissolved in dry methanol (25 ml) and, after addition of methyl 2,3-anhydro-β-D-ribopyranoside[23] (1 g), the solution was boiled under reflux, with the exclusion of atmospheric moisture and carbon dioxide, for 24 h. T.l.c. (chloroform–acetone 10:1) then revealed only traces of the starting material (R_F 0.5). After deionization with Dowex-50 W(H^+) resin, decoloration with charcoal, and concentration, the residue was crystallised from ethyl acetate–ether to give a chromatographically pure product (880 mg, 72%), R_F 0.3 (chloroform–acetone 3:1). Recrystallization from the same solvent (twice) gave **8**, m.p. 102.5–103°, $[\alpha]_D^{22}$ −85.7° (*c* 1.02, chloroform) (Found: C, 47.23; H, 8.01. $C_7H_{14}O_5$ calc.: C, 47.18, H, 7.91%). ^{13}C-N.m.r. data: δ −104.3 (C-1), −73.10 (C-2), −84.90 (C-3), −69.03 (C-4), −64.97 (C-5), −57.09 (MeO-1), and −60.50 (MeO-3). P.m.r. data: δ 4.19 (d, 1 H, $J_{1,2}$ 6.7 Hz, H-1), 3.44 (q, 1 H, $J_{2,3}$ 7.9 Hz, H-2), 3.15 (t, 1 H, $J_{3,4}$ 8 Hz, H-3), 3.70 (o, 1 H, $J_{4,5}$ 9, $J_{4,5'}$ 4.7 Hz, H-4), 3.28 (q, 1 H, H-5), 4.01 (q, 1 H, ^2J 11 Hz, H-5'), 3.65 and 3.53 (2 s, 6 H, 2 OMe), and 3.02 (bs, 2 H, disappears on deuteration, OH).

REFERENCES

1 K. Heyns, K. R. Sperling, and H. F. Grützmacher, *Carbohydr. Res.*, 9 (1969) 79–97.
2 V. Kováčik and P. Kováč, *Chem. Zvesti*, 27 (1973) 662–667.
3 V. Kováčik, V. Mihálov, Š. Karácsonyi, and R. Toman, *Carbohydr. Res.*, 58 (1977) 203–208
4 V. Kováčik and P. Kováč, *Org. Mass Spectrom.*, 10 (1975) 376–383.
5 V. Kováčik, V. Mihálov, and P. Kováč, *Chem. Zvesti*, 32 (1978) 258–266.

6 V. MIHÁLOV, V. KOVÁČIK, AND P. KOVÁČ, *Carbohydr. Res.*, 70 (1979) 239–246.
7 V. KOVÁČIK AND P. KOVÁČ, *Anal. Biochem.*, 64 (1975) 45–52.
8 N. K. KOCHETKOV, N. S. WULFSON, O. S. CHIZHOV, AND B. M. ZOLOTAREV, *Tetrahedron*, 19 (1963) 2209–2224.
9 N. K. KOCHETKOV AND O. S. CHIZHOV, *Tetrahedron*, 21 (1965) 2029–2047.
10 N. K. KOCHETKOV, O. S. CHIZHOV, B. M ZOLOTAREV, AND V. S. SHEJNKER, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 3 (1967) 543–548.
11 V. KOVÁČIK AND P. KOVÁČ, *Org. Mass Spectrom.*, 9 (1974) 172–180.
12 V. KOVÁČIK AND P. KOVÁČ, *Carbohydr. Res*, 38 (1974) 25–34.
13 K. HEYNS AND D. MÜLLER, *Tetrahedron*, 21 (1965) 55–68.
14 K. HEYNS AND H. SCHARMANN, *Tetrahedron*, 21 (1965) 507–513.
15 M. A. OLDHAM AND J. HONEYMAN, *J. Chem. Soc*, (1946) 986–989.
16 S. C. WILLIAMS AND J. K. N. JONES, *Can. J. Chem.*, 45 (1967) 275–290.
17 P. KOVÁČ AND R. PALOVČÍK, *Carbohydr. Res*, 36 (1974) 379–384.
18 H. E. DEKANOSIDZE, J. HIRSCH, AND P. KOVÁČ, *Bull. Acad. Sci. Georgian SSR*, 74 (1974) 361–364.
19 P. KOVÁČ, *Carbohydr. Res.*, 20 (1971) 418–420.
20 R. D. GUTHRIE, in W. PIGMAN AND D. HORTON (Eds.), *The Carbohydrates*, Vol. IA., Academic Press, 1972, pp. 423–497.
21 V. KOVÁČIK AND P. KOVÁČ, *Carbohydr. Res.*, 24 (1972) 23–28.
22 P. KOVÁČ AND J. HIRSCH, *Chem. Zvesti*, 27 (1973) 668–675.
23 L. HOUGH AND J. K. N. JONES, *J. Chem Soc*, (1952) 4349–4351