GAS – LIQUID CHROMATOGRAPHY – MASS SPECTROMETRY OF THE ACETATES OF PARTIALLY METHYLATED METHYL GLYCOSIDES

III. TRIMETHYLHEXOSES

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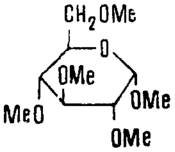
In preceding communications of this series, the mass spectra of the acetates of partially methylated methylpentopyranosides and monomethyl ethers of methyl hexosides, and their GLC behavior, have been considered. Considerations have been put forward on the nature of the main fragments that have enabled the number and position of the methoxy groups to be unambiguously determined from mass spectra. The particular anomer present can be found from the spectra of a dimethyl ether of a pentopyranoside.

The present paper gives the results of a study of acetates of trimethyl ethers of Me α-D-Glc, Me α-D-Gal, Me α-D-Man, Me β-D-Glc, and Me β-D-Gal, given below, and their relative retention times.*

Initial sugar	T	Initial sugar	T
Me 3,4,6 OMe$_3$-α-Glc	3.49	Me 2,3,4-OMe$_3$-α-Man	4.10
Me 2,3,4-OMe$_3$-α-Glc	4.40	Me 2,3,6-OMe$_3$ α- Man	4.44
Me 2,3,6-OMe$_3$ α-Glc	4.39	Me 2,3,6-OMe$_3$-β-Gal	3.82
Me 2,4,6-OMe$_3$-α-Glc	5.27	Me 2,4,6-OMe$_3$-β-Gal	4.44
Me 2,3,6-OMe$_3$-β-Glc	3.66	Me 2,3,6-OMe$_3$-α-Gal	3.93
Me 2,4,6-OMe$_3$-β-Glc	4.32	Me 2,4,6-OMe$_3$-α-Gal	4.79
Me 3,4,6-OMe$_3$-α-Man	2.78	Me 2,3,4-OMe$_3$-α-6Gal	4.78
Me 2,4,6-OMe$_3$-α-Man	4.10		

As examples, the mass spectra of Me 2,3,4-OMe$_3$-6-OAc-α,D-Gal (I), Me 2,3,6-OMe$_3$-4-OAc-α,D-Gal (II), Me 2,4,6-OMe$_3$-3-OAc-α,D-Man (III), and Me 3,4,6-OMe$_3$-2-OAc-α,D-Glc (IV) are given in Table 1.



In the spectra of (I–IV), as in the spectrum of Me 2,3,4,6-OMe-α-D-Glc (V) [1], it is possible to see precisely the same fragments, since an OAc group affects only the yields and mass numbers of the ions. The main fragments are considered below on this basis.

Fragments G. The fragments of this series are composed of three neighboring atoms with two substituents from them. The main contribution to the peak with m/e 101 in the spectrum of (V) is made by G_1^2 with the substituents from $C_{2,4}$. Hence, the peak with m/e 101 is the main peak in the spectrum of Me 2,4,6-OMe$_3$-α-D-Man (III) and is the second peak in the spectrum of Me 2,3,4-OMe$_3$-α-D-Gal (I). If the ion G bears an OAc group, it is represented in the spectrum by two peaks with m/e 129 and 87 (129 – 42).

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* T = 0 is the retention time of the full acetate of hydroxylamine, T = 10 is the retention time of the full acetate of galactononitrile. 3% of NPGS on Aeropak 30, 60-80 mesh, 6 mm × 1.5 m, 125-225°C 5°C/min, FI detector, Pye Unicam chromatograph.

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TABLE 1. Mass Spectra of Acetates of Trimethyl Ethers of Methyl Hexosides (relative intensities, %)

m/e	I	II	III	IV	V	*m/e*	I	II	III	IV	V
247 (A_1)	0,6	1,0	12,7	0,6	—	117	3,2	0,8	9,1	17	—
219	-	—	—	—	0,22	116	0,7	1,7	66,4	28	—
233 (E_1)	—	0,05	2,	2,8	—	115	1,1	3,2	3,4	10	—
201	—	—	—	—	0,18	114	1,0	1,3	4,1	3	—
219 (C)	—	—	1,8	—	—	113	1,5	6,3	3,2	12	—
218 (C_p)	—	—	4,1	—	—	112	—	0,4	—	6	—
215 (A_2)	2,0	0,3	0,9	2,3	—	111	1,5	1,9	6,8	8	2
204 (B_1)	—	2,4	1,8	3,7	—	103	—	2,0	—	4	—
176	1,3	—	—	—	1,4	102	2,7	0,5	18,2	24	1,8
187 (A_2)	0,6	0,3	5,9	0,6	2,4	101	57,2	7,1	100	54	38
186 (C_{2p})	0,45	0,9	1,4	0,4	—	99	2,3	2,8	—	14	2
177 (D_1)	5,2	—	—	—	—	97	—	1	—	8	1,8
149	—	1,6	—	1,3	4,8	95	1,8	0,7	—	7	1,2
175		—	5,5	—	—	89	9,1	5	11,4	6	5
173	0,34	0,63	25.5	3,2	0,21	88	100	100	68,2	80	100
159 (C_2)	1,7	0,52	22,3	2,5	0,37	87	30	11,3	18,2	19	—
158 (C_{2p})	—	0,2	12,7	—	—	85	4,6	9,4	6,8	15	3,5
155	3,6	2,6	7,7	1,0	0,8	84	—	4,7	8,2	7	—
145	—	0,63	14,6	1,8	2,5	75	50	62,5	72,7	100	34
144	—	0,42	6,8	0,8	—	74	3,6	5,6	90,9	60	1,3
143	0,7	1,0	10,9	1	—	73	16,4	11,8	13,6	—	10
141	6	0,6	10,5	2,9	—	71	9,1	5,8	77,3	70	12
131	2,4	1,0	2,3	4	2,9	59	5	3,7	9,1	14	2,2
130	1,5	0,1	—	2	—	57	—	1,4	1,4	12	3,5
129	1,3	2,9	3,4	7	0,7	45	12,7	19,8	43,6	30	18
127	5,1	3,0	12,5	8	2,1	43	22,7	25,0	56,8	43	6

TABLE 2. Mass Spectra (partial) of Acetates of Me 2,4,6-OMe$_3$-α- and -β-Glc

Type of ion	*m/e*	α	β
A_1	247	33,9	4,7
A^2	215	8,7	1
B_1	204	100	100
A_2	187	44,2	18
A_3	155	132	33,3

An acetoxy group at C_4 or C_2 lowers the yield of the ions G_1^2, G_1^3, and G_1^6: for Me 2,3,6-OMe$_3$-α-D-Gal (II), $RI_{129+87}/RI_{101} = 1.1$. If the yields of the ions of series G remained as for (V), this ratio should be 5. Such a ratio has been found in the spectrum of the 2,3-OMe$_2$-pentopyranosides. This fact, like the absence of an appreciable peak of the K_1 ion with m/e 130 in the spectrum of (II), is explained by the fact that the cleavage of the bond at a C atom bearing an OAc group and the retention of the charge on the fragment with the OAc are unfavorable processes [3].

Fragments D and J. The formation of the fragments of this series predicates the migration of the C_3 OMe to C_1, but not OAc: in the spectrum of (III) no appreciable peaks of the ions J_1^1 with m/e 103 and D_1 with m/e 177 are observed.

Fragments H. These fragments include two neighboring atoms and their substituents, and in the spectrum of (V) they are responsible for the main peak with m/e 88. Regardless of the position of OAc, the total yield of the ions of this series (m/e 74, 88, 116) remains the highest in the decomposition of the trimethyl ethers (I-IV).

Fragment J. This fragment is composed of $C_{4,5,6}$ with their substituents. In contrast to (V), in the spectra of the trimethyl ethers (I, III, and IV) the ion K_1 is responsible for the considerable peaks at m/e 102 and 130.

Fragments A_1, B_1, E_1. As in the spectrum of (V), the peaks of these fragments have a very low intensity and, depending on the presence of OAc, are shifted 28 amu upwards.

Fragment S. This fragment includes C_6 and its substituent. Fragment S is responsible for a considerable contribution to the peak with m/e 45 in the spectra of (II, III, and IV), since in the spectrum of (I) the ratio RI_{45}/RI_{43} is smaller than in the spectra of the other compounds.

Fragments C. These fragments include C_2 and C_6. The spectrum of (V) shows a peak with m/e 159 of the C_2 ions the formation of which assumes the migration of an H atom to the large fragment and the loss of a molecule of methanol. In the spectra of (I-IV), the C_2 ions make a contribution to the peak with m/e 187. In addition, in the spectra of these compounds, peaks of ions of the C_p type appear, the formation of which takes place without the migration of an H atom. Consequently, they have mass numbers one unit lower than those of the C analogs. In the spectra of the compounds with OMe at C_3 (I, II, IV, V), the peaks of the primary ions C and C_p are absent, but in the spectrum of the 2,4,6-trimethyl ether (III) they have been detected at m/e 219 and 218. The loss of methanol or acetic acid molecules from C and C_p is responsible for peaks with m/e 187, 186, and 159, 158 in the spectrum of (III).

Because of the presence of an OAc group in the ion of any series in the mass spectrum of the compounds studied, the peaks of the ions of this series are shifted 28 mass units upwards and 14 and 42 mass units downwards in relation to the peaks in the spectrum of (V). Consequently, overlapping of the peaks of ions of series A, B, C, and E with the peaks appearing in the spectrum of (V) at m/e 127, 131, 145, and 155 is not excluded. In subsequent papers, the question of contributions will be discussed in connection with the study of compounds labelled with deuterium.

Use of Mass Spectra to Determine the Positions of OMe Groups. The spectrum of (I) (2,3,4-OMe_3) is characterized by strong peaks of the ions J, H, and G with m/e 75, 88, and 101, since they include mainly C_1-C_4 with their substituents. In the region of high mass numbers the strongest peak is that of the ion D_1 with m/e 177. This fragment bears substituents from $C_{3,6}$, and therefore in the spectra of (II) and (IV) it remains at m/e 149.

The spectrum of (II) (2,3,6-OMe_3) is characterized by two strong peaks of the ions J and H with m/e 75 and 88 because of the OMe groups at C_2 and C_3.

The spectrum of (III) (2,4,6-OMe_3) is characterized by a strongest peak with m/e 101 because of the contribution of the ion G_1^2 with methoxyls at $C_{2,4}$. The peaks of ions of series H are responsible for strong peaks at m/e 116 and 74. In the region of high mass numbers, the spectrum is characterized by the peaks of the ions of C series with m/e 158, 159, 218, and 219.

The spectrum of (IV) is characterized by a ratio of the intensities of the peaks with m/e 75, 88, 101, and 116 of 10 : 8 : 5 : 3.

The spectra of anomers differ in the ratio of the intensities of the peaks of ions A and B, as has been noted for the full methyl ethers [2]. In fact, it can be seen from Table 2 that the intensities of the peaks of ions A in relation to B increase on passing from the α-anomers to the β-anomers.

Differences have been observed between the spectra of epimers of one and the same anomer with the same distribution of methoxy groups. It is not proposed to use these differences, since sufficient statistical material has not yet been accumulated. Assignments to a definite epimer, i.e., to Glc, Gal, or Man can be done from the T values (see list on page 458).

The experimental conditions have been described in the first paper of the present series.

SUMMARY

GLC–MS results have been obtained for acetates of trimethyl ethers of methyl hexopyranosides which permit the determination of the position of OMe groups and the nature of the anomer from the mass spectra and the particular stereoisomer from T values.

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