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

IV. DIMETHYLHEXOSES

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During work on the GLC-mass spectrometry of acetates of partially methylated methyl hexosides, we have investigated the spectra of acetates of dimethyl ethers of Me α- and β-D-Glc, Me α- and β-D-Gal, and Me α-D-Man and their relative retention time (T values).*

Initial methyl ethers of methyl glycosides	*T*	Initial methyl ethers of methyl glycosides	*T*
Me 3,4-OMe_2-α-Glc	5.63	Me 2,6-OMe_2-α-Gal	6,03
Me 2,6-OMe_2-α-Glc	6.06	Me 2,3-OMe_2-β-Gal	5.51
Me 2,3-OMe_2-α-Glc	6,29	Me 2,6-OMe_2-β-Gal	5,62
Me 2,4-OMe_2-α-Glc	7.28	Me 3,6-OMe_2-β-Gal	6,31
Me 2,6-OMe_2-β-Glc	5.25	Me 2,4-OMe_2-β-Gal	6.49
Me 2,3-OMe_2-β-Glc	5.61	Me 3,6-OMe_2-α-Man	4,98
Me 4,6-OMe_2-β-Glc	5.61	Me 4,6-OMe_2-α-Man	5,26
Me 3,6-OMe_2-β-Glc	6.39	Me 2,6-OMe_2-α-Man	5,76
Me 2,4-OMe_2-β-Glc	6.43	Me 2,3-OMe_3-α-Man	6,23
Me 2,3-OMe_2-α-Gal	5,66		

A previous study of the mass spectra of acetylated partially methylated methyl pentosides and of methyl OMe_1- and OMe_3-hexosides has permitted an interpretation of the spectra of the dimethyl ethers of methyl hexosides: the same series of ions (A, B, C, D, E, J, H, G, and K) as in the permethylated hexosides has been found. The relative intensities and positions of the peaks of the ions of this series are unambigously determined by the positions of the OAc groups. However, in a number of cases coincidence of the mass numbers of ions of different series is not excluded. Consequently, the nature of such ions will be discussed in a study of D-labelled compounds. For the same reason, below we shall discuss only individual features of the mass spectra of the methyl di-O-methylhexosides (I-IV). On the basis of their mass spectra (Table 1), the compounds considered can be divided into two groups: those with two methoxyls in the ring – Me 2,3-OMe_2-α-D-Gal (I), Me 2,4-OMe_2-α-D-Glc (II), and Me 3,4-OMe_2-α-D-Glc (III); and those with one methoxyl in the ring – Me 2,6-OMe_2-β-D-Gal (IV), Me 3,6-OMe_2-β-D-Glc (V), and Me 4,6-OMe_2-α-D-Man (VI), since the latter are distinguished by a considerable peak of ion E_1 with m/e 261.

As in the spectrum of the permethylated ether, the main peaks in the spectrum of (I) (2,3-OMe_2) with m/e 88 and 75 ($H_1^{1,2}$ and J_1^1) are due to the methoxy groups at $C_{2,3}$. In addition, as in the molecules of the methyl hexosides (III) and (V), the C_3-OMe and C_6-OAc fragments are responsible for the considerable peaks of ions of the D series with m/e 177.

The strong peak with m/e 101 of the ion G_1^2 characterizes the spectrum of (II), thanks to the presence in it of a $C_{2,4}$-OMe_2 grouping. As in the spectrum of (III) C_4-OMe and C_6-OAc fragments are responsible

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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 D-galactononitrile; 3% of NPGS, 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 the Acetates of Dimethyl Ethers of Methyl Hexosides (relative intensities, %)

m/e	I	II	III	IV	V	VI	m/e	I	II	III	IV	V	VI
43	60	100	100	>100	100	>100	144	—	0,20	0,18	0,68	0,10	5,75
45	15	16	20	29,5	27	25	145	0,44	0,20	0,23	0,43	0,30	4,12
70	—	—	—	14	—	—	155	1,44	0,50	0,14	0,60	0,14	2,0
71	—	58	45	10,5	36	41	157	—	—	0,07	—	0,09	1,00
74	5	92	57	100	56	47	159	0.44	—	0,16	0,15	0,30	2,12
75	85	42	86	16	48,5	14	161	—	0,10	0,14	—	—	—
85	9	7	—	22	8,5	6	169	—	—	0,10	—	0,23	6,75
87	8	34	50	37	11,5	45	172	0,56	—	0,21	0,25	0,11	—
88	100	35	61	9,5	9	—	173	0,37	0,2	0,14	—	0,14	8,00
99	28	10	6	9,5	8	17	177	1,18	—	0,12	—	0,03	—
100	—	—	—	9	—	—	183	0,94	0,20	—	—	0,04	0,50
101	5	67	30	4	31,5	20	186	0,20	0,30	0,07	0,53	—	4,37
102	—	—	—	—	—	28	187	0,13	0,30	0,07	0,80	0,27	3,25
112	1,3	—	—	23	—	14	201	0,20	0,05	0,18	0,08	0,15	0,87
113	4,6	5	6	36	—	13	203	—	0,05	—	0,15	0,05	0,62
115	0,6	—	—	—	5	7	204	1,62	0,02	0,28	—	—	—
116	2,4	69	19	38	23	10,5	214	0,81	—	0,19	0,02	0,03	1,37
117	3,0	10	10	—	5	—	215	0,50	0,36	—	0,04	0,10	2,62
127	2,7	24	7	13,5	11	10.5	232	—	—	0,03	—	0,08	—
129	3,9	5	10	27,3	6	43	233	0,12	—	0,04	—	—	—
130	0,6	8	17	—	—	—	243	—	—	0,34	—	0,03	—
141	1,8	0,25	0,80	0.18	0,54	6,60	261		—	—	0,12	—	8,25
142	—	0,10	0,16	0,51	0,10	1,25	275	1,56	0,05	0,21	0,11	0,02	1,25
143	0,90	0,16	0,18	0,42	0,15	2,50	305	—	0,005	0,002	0,01	0.01	—

for an appreciable peak with m/e 130 of the ion K_1. In the spectrum of (VI) (4,6-OMe_2), the latter is shifted to m/e 102.

In the spectrum of (III) (3,4-OMe_2), the main peak with m/e 75 corresponds to the ion J_1^1. In the region of high mass numbers, the spectrum is characterized by peaks with m/e 243 (A_1-32) and 214 (C_p-32). The results of a comparison of the spectrum of (III) with that of (IV) (2,6-OMe_2) shows that the C_3 and C_4 positions for substituents are the most labile, regardless of their nature.

A high intensity of the peak with m/e 74 (H−42) is characteristic for the spectrum of (IV), as of (II), i.e., compounds including the fragment C_2-OMe, C_3-OAc.

The spectrum of (V) (3,6-OMe_2) is distinguished from the spectra of the other C_6-OMe-containing glycosides by an appreciable peak of the B_1 ion with m/e 232. The reason for this is the increased sensitivity of the OMe group as compared with OAc at C_3.

The spectrum of (VI) is characterized by the peaks of the ions K_1 with m/e 102 and G with m/e 129. In the region of high mass numbers, the spectrum is characterized by strong peaks with m/e 169 (E_3) and 173 (A_1-102).

Bearing in mind the larger number of dimethyl ethers of methyl hexosides than of tri- or monomethyl ethers, it is not always possible to distinguish their stereoisomers from their T values when using a single type of phase.

SUMMARY

GLC−MS results have been obtained for the acetates of dimethyl ethers of methyl hexosides which permits the positions of the OMe groups to be determined unambiguously and, from their T values, their assignment to a definite stereoisomer.

LITERATURE CITED

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