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

II. MONOMETHYLHEXOSIDES

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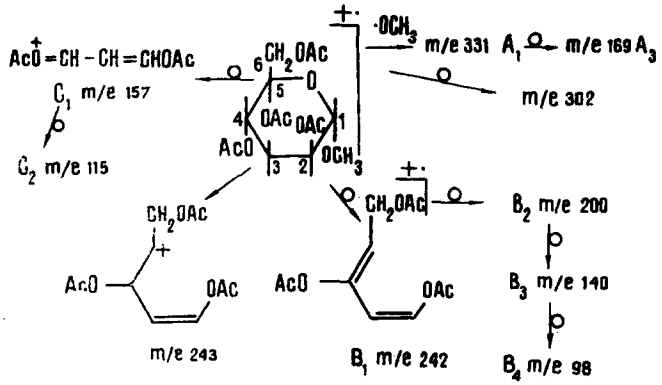
In this paper we give the GLC-MS characteristics of the acetates of monomethylhexosides. The relative retention times* of the acetates of monomethyl ethers of methyl D-hexopyranosides (T values) can be judged from the following information:

Acetates of monomethyl glycosides	T	Acetates of monomethyl glycosides	T
6-β-Glc	6.90	4-β-Gal	8.44
2-β-Glc	7.10	β-Gal	8.73
4-β-Glc	7.83	3-α-Gal	7.07
3-β-Glc	8.14	2-α-Gal	7.75
β-Glc	8.64	6-α-Man	6.38
3-α-Glc	7.62	3-α-Man	6.94
2-α-Glc	7.93	4-α-Man	7.47
α-Glc	8.41	2-α-Man	7.67
2-β-Gal	7.24	α-Man	8.19
3-β-Gal	8.02		

For the full acetate of methyl α-D-mannopyranoside, Biemann proposed the following pattern of decomposition [1].



The mass spectra of methyl β-2-O-methyl-D-mannopyranoside given in Biemann's paper and that of methyl α-2-O-methyl-D-mannopyranoside (Fig. 1a) correspond completely to this scheme.

The most characteristic feature for the acetate of 3-O-methyl-D-mannopyranoside (Fig. 1b) is the appearance of fragments formed by the migration of the methoxy group from position 3 to C_1 [2]:

*As 0 was taken the retention time of the full acetate of hydroxylamine, 3.80 min, and as 10 the retention time of the acetate of the aldononitrile of D-galactose, 27.5 min. Carrier gas N_2, 30 ml/min.

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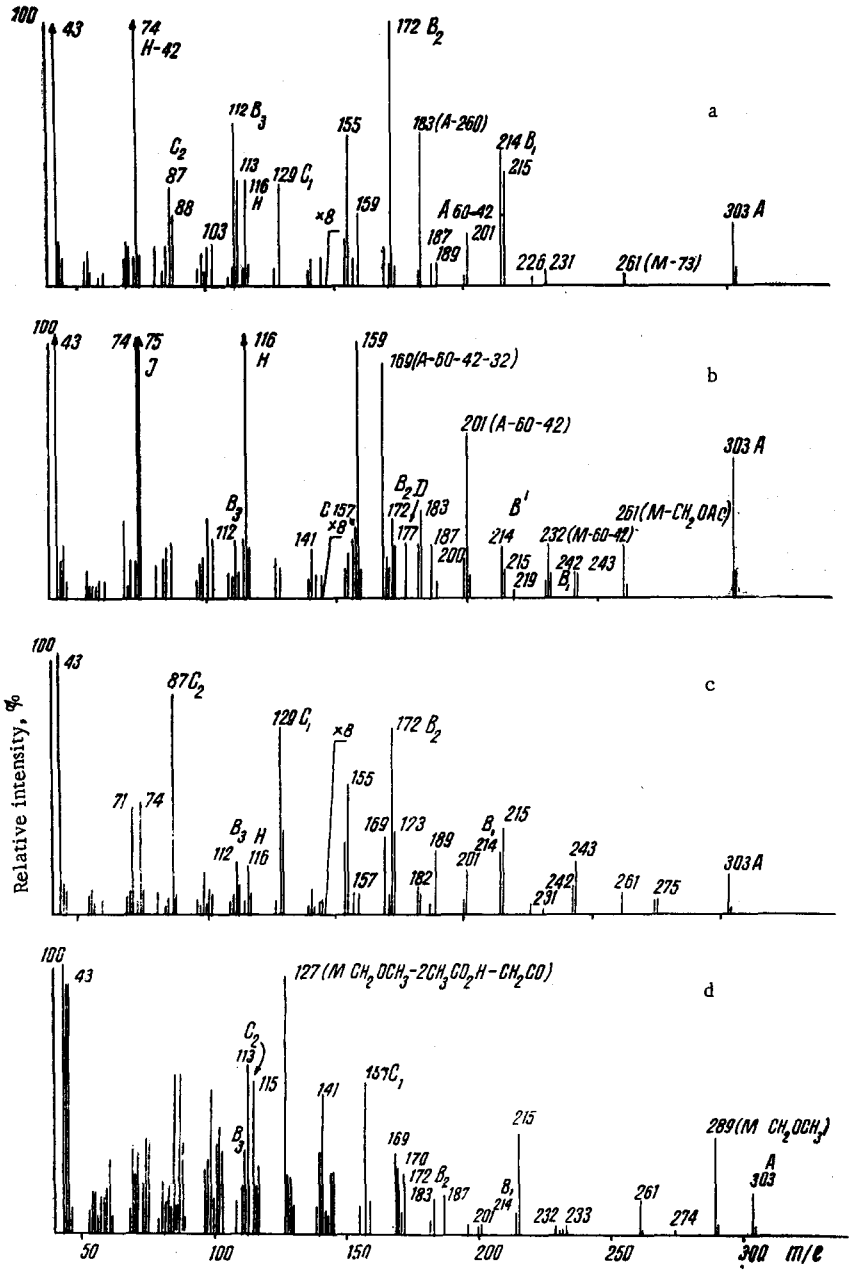
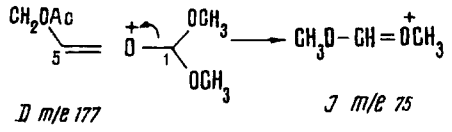


Fig. 1. Mass spectra of the acetate of methyl α-2-O-methyl-D-mannopyranoside (a), the acetate of methyl α-3-O-methyl-D-mannopyranoside (b), the acetate of methyl α-4-O-methyl-D-mannopyranoside (c), and the acetate of methyl α-6-O-methyl-D-mannopyranoside (d).



In the spectrum there are two types of ions B including the C_2-C_6 chain: with m/e 242, which is characteristic for the full acetate of methyl mannoside [1], and with m/e 214, which is characteristic for the acetate of 2-O-methyl-D-mannopyranoside (Fig. 1a). The same is found for the acetate of 4-O-methyl-D-mannopyranoside (Fig. 1c). In the formation of these fragments the loss of the substituents both from C_3 and from C_4 apparently takes place (we shall consider this question in more detail in later papers).

The results of a comparison of the spectra (Fig. 1, a, b, and c) show that fragment H contains mainly C_2 and C_3. The shifts of the m/e value of ion C with C_2, C_3, and C_4 corresponds in all cases (Fig. 1, a, b, c, d) to the position of the methoxy group: m/e 129, 87; 157, 115; 129, 87; 157, 115.

The peak A^I with m/e 261 ($M - CH_2OAc$) in the acetate of 6-O-methyl-D-mannopyranoside (Fig. 1d) is shifted to m/e 289 ($M - CH_2OCH_3$). In addition, the spectrum of this compound does not include fragments of type H.

The mass spectra of the acetates of the monomethyl ethers of other hexosides that we have studied differ insignificantly from the mass spectra of the acetates of the mannopyranosides. The mass spectra of the anomers available also show insignificant and irregular differences. Thus, the spectra of the acetates of the monomethyl ethers of methyl hexosides are characteristic and permit the positions of the OMe groups in the molecules of these ethers to be determined unambiguously.

EXPERIMENTAL

The methyl α-O-methyl-D-mannopyranosides were obtained by the partial methylation of methyl α-D-mannopyranoside by a known method [3], and mixtures of the ethers of the other hexosides by partial methylation according to Purdie.

The mass spectra were taken on an LKB-9000 mass spectrometer (column 1.5 m × 3.4 mm, 3% of NPGS on Aeropak 30, 60-80 mesh), and the T values were measured on a Pye-Unicam series 104 chromatograph (glass columns 1.5 m × 6 mm, NPGS 3% on Aeropak 30, 60-80 mesh at 125-223°C, 5°C/min).

SUMMARY

GLC-MS characteristics have been obtained for the acetates of monomethyl ethers of methyl hexosides which permit the type of initial monosaccharide and the position of the OMe group to be established.

LITERATURE CITED

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