GAS – LIQUID CHROMATOGRAPHY – MASS SPECTROMETRY OF THE ACETATES OF ALDONONITRILES OF PARTIALLY METHYLATED SUGARS.

II. 6-DEOXYHEXOSES

Yu. N. El'kin, A. I. Kalinovskii,
A. F. Pavlenko, N. I. Shul'ga,
B. V. Rozynov, and A. K. Dzizenko

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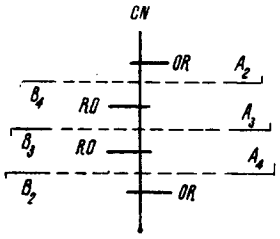
In a preceding paper [1] it was shown that the mass spectra of partially methylated pentoses in the form of acetates of the aldononitriles are characteristic and, from the mass numbers and relative intensities (RIs) of the peaks of four fragments, they permit the determination of the positions of the methoxy (OMe) groups. Continuing this work, we have investigated 6-deoxyhexoses using, as examples, L-fucose, D-quinovose, and L-rhamnose.

The relative retention times (T)* of the methylated 6-deoxyhexoses in the form of the aldononitriles are given below.

Initial sugar	T	Initial sugar	T
2,3,4-OMe_3-D-Qui	3.19	2-OMe-L-Rha	5.72
2,3,4-OMe_3-L-Fuc	3.43	4-OMe-D-Qui	5.89
2,3,4-$OMEe_3$-L-Rha	3.62	2-OMe-L-Fuc	5.98
2,4-OMe_2-D-Qui	4.38	3-OMe-L-Rha	6.08
2,3-OMe_2-L-Rha	4.73	3-OMe-L-Fuc	6.16
2,4-OMe_2-Rha	4.83	L-Rha	6.39
2,3-OMe_2-L-Fuc	4.93	4-OMe-L-Fuc	6.45
2,3-OMe_2-D-Qui	5.08	L-Fuc	6.60
2,4-OMe_2-L-Fuc	5.41	3-OMe-D-Qui	6.81
2-OMe-D-Qui	5.61	D-Qui	6.86

The mass spectra of the acetates of the aldononitriles of the partially methylated 6-deoxyhexoses are given in Figs. 1 and 2.

It has been reported previously that the fragmentation of the nitriles resembles the fragmentation of the corresponding alditols [2]. It must be added that not only the ions containing the C_1-C_2 atoms (A_2) are observed in the spectra.



The results of a comparison of the mass spectra of the compounds studied show that to determine the position of the OMe groups it is necessary to evaluate the mass numbers and RIs of the peaks of the

* T = 0 is the retention time of the full acetate of hydroxylamine (2.70 min) and T = 10 is the retention time of the full acetate of the aldononitrile of D-Gal (23.96 min).

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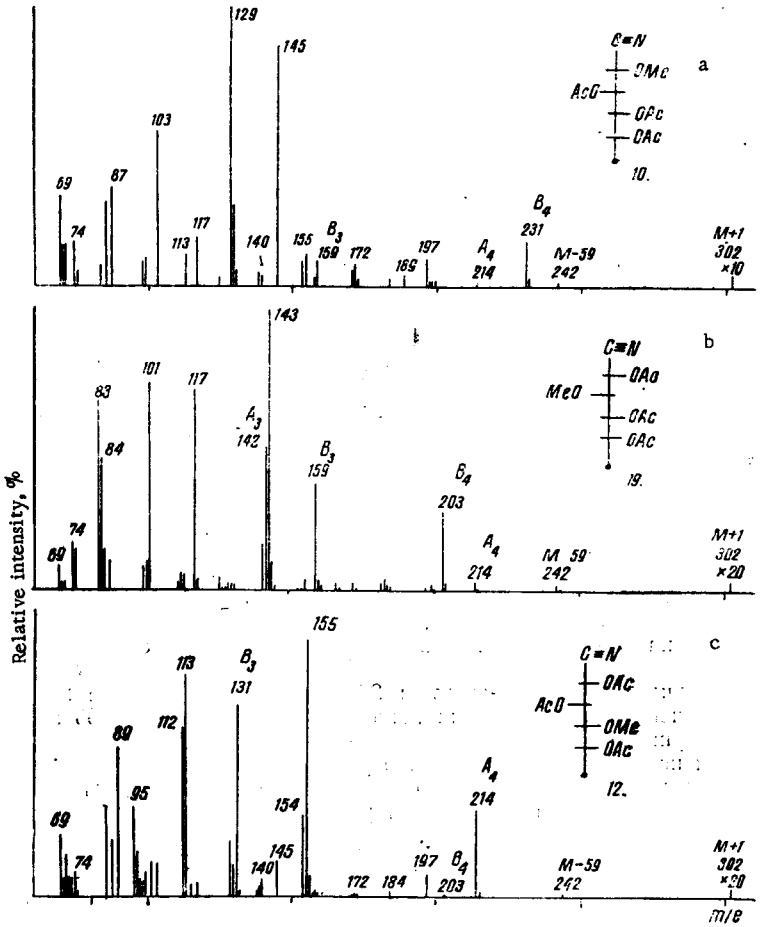

Fig. 1. Mass spectra of the acetates of the aldononitrile of 2-O-methyl-D-quinovose (a), of the aldononitrile of 3-O-methyl-D-quinovose (b), and of the aldononitrile of 4-O-methyl-D-quinovose (c).

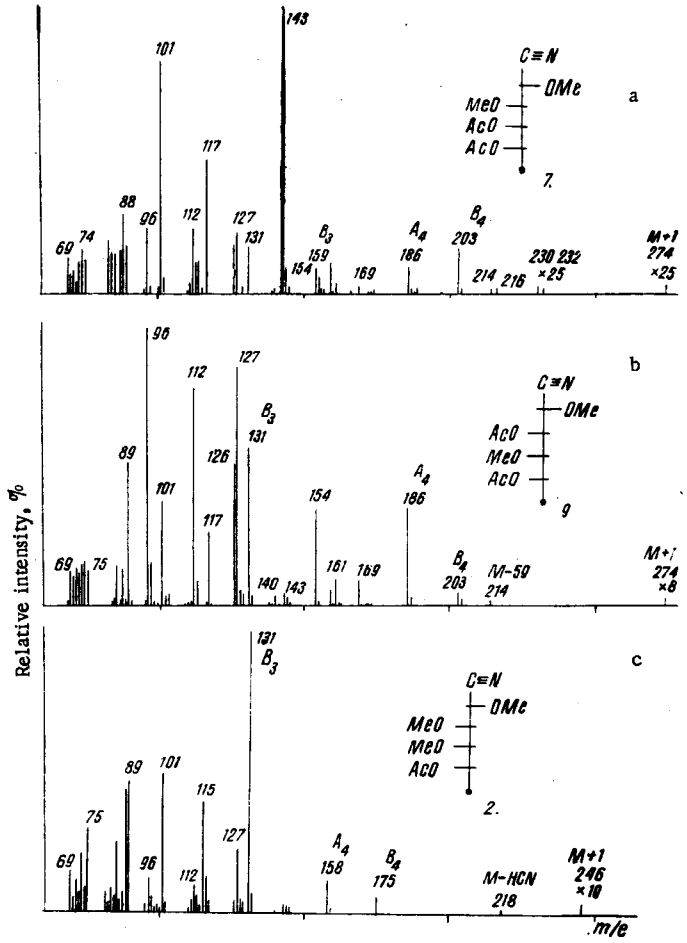

Fig. 2. Mass spectra of the acetates of the aldononitrile of 2,3-di-O-methyl-L-fucose (a), of the aldononitrile of 2,4-di-O-methyl-L-fucose (b), and of the aldononitrile of 2,3,4-tri-O-methyl-L-fucose (c).

TABLE 1. Mass Spectra of Methylated 6-Deoxyhexoses in the Form of Acetates of the Aldononitriles (partial)

Type of ion	m/e	Position of the OMe group					
		2-	3-	4-	2,3-	2,4- 3,4-	2, 3, 4-
B_4	231	1,00*					
	203		1,00	1,00	1,00	1,00	
	175						1,00
A_4	214	0,08	0,07	27,0			
	186				0,60	5,40	
	158						2,30
B_3	159	1,00	1,10		0,71		
	131			56,0		11,0	16,0

* $RI_3 = 20\%$.

primary ions B_4, A_4, and B_3 (Table 1). Thus, on passing from the 2-OMe to the 3-OMe isomer, the peak of the B_4 ion with m/e 231 shifts to m/e 203. At the same time the 4-OMe isomer differs from the 2-OMe isomer by an increase of an order of magnitude in the RIs of the peaks of the ions A_4 and B_3 and a shift of the latter to m/e 131.

The mass spectra of the 2,3-di-OMe and the 2,4-di-OMe isomers also differ, apart from the fact that the peak of the ion A_4 is shifted to m/e 186 because of the 2-OMe group.

In an investigation of the partially methylated pentoses, no satisfactory separation in a polyester gas chromatograph was achieved [1]. In the performance of this work, to improve the separation of the substances we increased the length of the columns.

EXPERIMENTAL

By selecting the times of methylation of L-Rha, D-Qui, and β-Me-L-Fuc by a known method [3] with subsequent hydrolysis of the methyl glycosides (after appropriate working up), we isolated methyl ethers from which the nitriles were prepared as described previously [2]. The mass spectra were taken on an LKB-9000 instrument (column 1.5 m × 3.4 mm, 3% of NPGS on Aeropak 30, 60-80 mesh), and the T values were obtained by using a Pye-Unicam series 104 chromatograph (glass columns 1.5 m × 6 mm, 3% of NPGS on Aeropak 30, 60-80 mesh, $125° \xrightarrow{5°/\text{min}} 223°$, helium, 3 ml/min.

SUMMARY

GLC-MS characteristics have been obtained for methylated 6-deoxyhexoses in the form of the acetates of the aldononitriles which permit the determination of the positions of the OMe groups in them and their assignment to a definite stereoisomerism from their T values.

LITERATURE CITED

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