

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

VII. MONO- AND DIMETHYLHEPTOSES

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The partial methylation of methyl β -glucoheptopyranoside has given a complex mixture of methyl ethers, from which five monomethyl ethers have been isolated by preparative GLC. Methylation of the latter gave a mixture in which ten dimethyl ethers were detected. The retention indices on the phase NPGS of the mono- and dimethyl ethers of methyl β -glucoheptopyranoside have been measured, and their mass spectra have been recorded and discussed. The mass spectra of these position isomers unambiguously characterize the pattern of methylation.

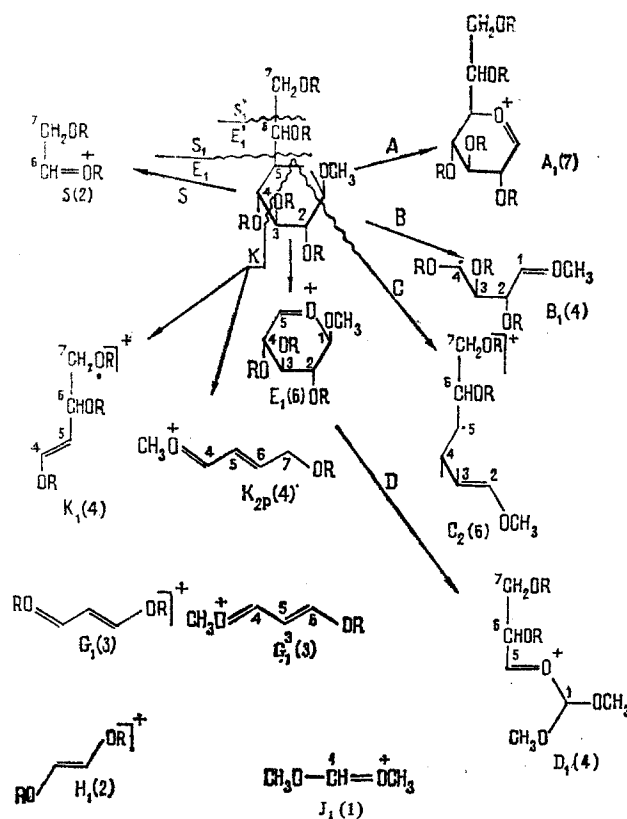
The determination of the positions of the glycosidic bonds from the position of the free OH groups in partially methylated monosaccharide residues formed as the result of the hydrolysis of a permethylated polysaccharide (methylation analysis) is the main method in the establishment of their structures. As a rule, GLC and/or the GLC-MS technique is used to identify the methyl esters of the monosaccharides. The monosaccharides are analyzed in the form of derivatives at the hemiacetal hydroxy group. To ensure volatility, the free OH groups are acetylated or silylated. By the use of the GLC-MS technique methylation analysis has been brought to a considerable degree of perfection for the acetates of polyols [1] and aldonitriles [2]. The preparation of these derivatives presupposes the acid hydrolysis of the polysaccharide. For glycoproteins and lipopolysaccharides, it is preferable to perform methanolysis, the products of which will be partially methylated methyl glycosides. Their identification has involved the acquisition of MS [3] and GLC [4] characteristics for pentoses, 6-deoxyhexoses, and hexoses. Such information for methyl esters of heptoses even in the form of polyol acetates is limited [5], while heptoses are widespread in lipopolysaccharides. This fact has induced us to study the mass spectra of acetates of partially methylated methyl heptosides.

The molecule of a methyl heptopyranoside contains five hydroxy groups, which permits 31 possible combinations of positions of the methoxyls. These combinations are distributed in the following way with respect to the number of methoxy groups (from one to five): 5, 10, 10, 5, 1, i.e., the mono- and tetramethyl ethers of a methyl heptoside each number five position isomers; the di- and trimethylethers, ten; and the pentamethyl ethers, one. The elucidation of the possibility of identifying the position isomers from their mass spectra was the aim of the present investigation.

As the source of the samples we selected the method of partial methylation of an individual methyl glycoside [6]. By the partial methylation of methyl β -glucoheptopyranoside we obtained a complex mixture of methyl ethers from which individual monomethyl ethers were isolated by preparative GLC. These compounds were subjected to further partial methylation. The resulting less complex mixtures were separated on the liquid phases QF-1 and NPGS, and the mass spectra of the acetates of the methyl esters of methyl heptopyranosides so obtained were recorded on a chromato-mass spectrometer.

In the present paper we discuss the mass spectra of the mono- and dimethyl ethers of methyl β -glucoheptopyranoside, the retention indices of which are given in Table 1, the mass spectra in Tables 2 and 3, while its main fragmentation pathways under electron impact are shown in the scheme.

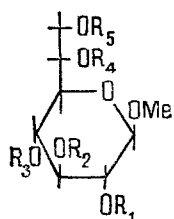
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The numbers of carbon atoms of the monosaccharide skeleton participating in the composition of the fragmentary ion are given in parentheses.

Since, apart from the spectra themselves, there is no other information on the behavior of these compounds under electron impact (D label, measurement of energies, etc.), their interpretation was made on the basis of a comparison with the spectra of analogously methylated methyl hexosides [7, 8] and a comparative analysis of the spectra of the completely methylated [9] and completely acetylated [10] methyl glycosides. For the completely methylated methyl glycosides, the overwhelming bulk of the ion current is due to the one-, two-, and three-carbon ions of the J, H, and G series (see scheme). In the case of the fully acetylated methyl glycosides, the ions of series C have the greatest yield and the ions of series J and B are not observed. A common feature of the decomposition of the M^+ ions of both methyl glycoside derivatives is the preferential cleavage of the pyranose ring at the C_1-C_2 , C_3-C_4 , C_4-C_5 , and C_5-O bonds with the formation of ions containing two, three, and five (for hexoses) carbon atoms. The ion with the highest mass number is due to the loss of the glycosidic substituent from M^+ . The partially methylated methyl glycosides studied occupy an intermediate position between the completely methylated and completely acetylated methyl glycosides. Their decomposition under electron impact will be determined by the laws of fragmentation for the extreme cases of substitution. To denote the ions we have used the nomenclature proposed previously [9].

The monomethyl ethers of a methyl heptoside number five position isomers:



- $R_1=OMe, R_2=R_3=R_4=R_5=OAc$ (I)
- $R_2=OMe, R_1=R_3=R_4=R_5=OAc$ (II)
- $R_3=OMe, R_1=R_2=R_4=R_5=OAc$ (III)
- $R_4=OMe, R_1=R_2=R_3=R_5=OAc$ (IV)
- $R_5=OMe, R_1=R_2=R_3=R_4=OAc$ (V)

TABLE 1. Retention Indices (R_T) of the Mono- and Dimethyl Ethers of Methyl β -Glucoheptopyranoside on the Phase NPGS

R_T	Position of the OMe group	R_T	Position of the OMe group
965	6—	655	4,7—
855	4—	645	3—
800	2—	640	2,4—
795	7—	600	3,6—
765	3,4—	560	2,7—
745	6,7—	550	3,7—
715	2,6—	450	2,3—
680	4,6—		

Note: Retention indices were determined according to a scale in which R_T of 2,3,4,6,7-penta-O-methyl- β -methylheptoside was taken as zero, while R_T of 2,3,4,6,6-penta-O-acetyl- β -methylheptoside was taken as 1000; glass column 2000 \times 3 mm; 150–225°C, 5°C/min, carrier gas flow rate 60 ml/min.

Analysis of the mass spectra of the acetates of the monomethyl ethers of methyl heptoside with methoxy groups in the pyranose rings (I–III) shows that their decomposition under electron impact is basically analogous to that established for their lower homologs [7, 8]. In both types of compounds the ions of series A, B, C, D, E, G, H, J, and K are observed (see scheme). The ions including the side chain (A, C, D, K) have masses 72 units greater in the case of the heptosides. Furthermore, the increase in the size of the side chain most considerably affects the decomposition of the ions of series C and consists in a rise in the yield of the ions as compared with the case of the hexosides.

Thanks to the location of methoxy groups in positions 1 and 2, under electron impact compound (I) undergoes preferential cleavage at the C_1 – C_2 bond. As a result of this, the strongest peaks in its spectrum are due to the ions of series C, and also to the two- and three-carbon ions of series H and G with m/z 74 and 116 and m/z 87 and 129. At the same time, the peaks of the ions of series H predominate. The spectrum of (I), just like the spectrum of its lower homolog, is characterized by a higher intensity of the peak of ion A_1 as compared with the 3- and 4-OMe derivatives.

Compound (II) undergoes the rearrangement reaction that is well known for permethylated methyl glycosides with the formation of the ions D_1 , m/z 249, and I_1 , m/z 75 [9]. The peak of the latter is the main one in the mass spectrum of (II). Other products of the pyranose ring with high yields are the ions of series H with m/z 74 and 116. The formation of the ion B_1 , m/z 232, and the fall in the yield of the ions of series C as compared with the 2- and 4-OMe-substituted methyl glycosides is assigned to a number of characteristic features of the fragmentation of methyl glycosides with a OMe group at C_3 .

In the mass spectrum of (III), the ions of series C are responsible for considerable peaks. However, the strongest and most characteristic peaks are given by the ions of series G, m/z 129 and 87, and K, m/z 202, 142, and 100. The formation of the ions of series K (the C_4 – C_5 – C_6 – C_7 chain with its substituents) is a characteristic feature of the methoxy group at C_4 .

Compounds (IV) and (V) have completely acetylated pyranose rings. In the molecule of a methyl heptoside, a methoxy group in the two-carbon side chain is responsible for two possibilities of its fragmentation. Consequently, in the spectrum of these compounds, in addition to the ions E_1 and S_1 (cleavage of the C_5 – C_6 bond) there are the ions E_1^+ and S_1^+ (the cleavage of the C_6 – C_7 bond).

It follows from the spectrum of (IV) that a methoxy group at C_6 exerts a considerable influence on the decomposition of the pyranose ring, which is expressed in a low yield of the ions of series C as compared with the completely acetylated methyl heptoside. The

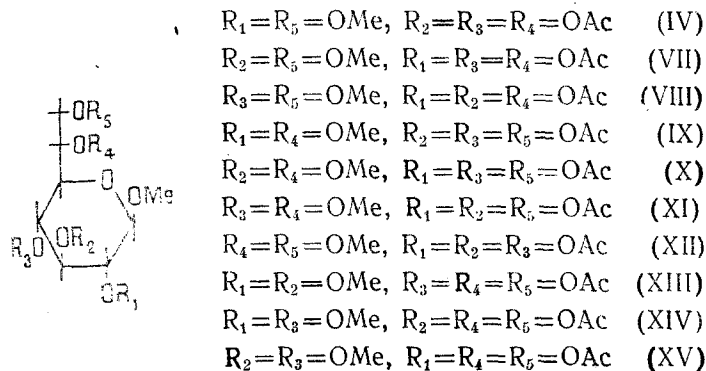
TABLE 2. Mass Spectra of the Acetates of the Monomethyl Ethers of Methyl β -Glucoheptopyranoside (relative intensities, %)

m/z	Type of ion	Position of the OMe group				
		2	3	4	6	7
43		100,0	161,0	274,0	100,0	638,0
45	S ₁	23,0	14,0	12,0	12,3	100,0
69		2,0	15,0	38,0	28,6	38,2
73		10,5	5,5	3,0	6,4	—
74	H ₁ -42	100,0	74,0	35,0	13,0	34,0
75	I ₁	11,5	100,0	20,5	11,9	36,2
81	E ₄	13,0	8,0	12,0	10,0	19,2
85		24,0	9,0	10,0	9,0	19,2
87	G ₁ -42	35,0	13,0	100,0	50,0	40,0
97	G ₂	15,0	7,5	8,0	13,0	32,0
99	E ₃ -42	9,0	4,0	13,0	11,2	17,0
100	K ₂ -42	7,0	3,0	52,0	6,2	14,9
101	G ₁	6,0	6,0	8,0	2,9	12,8
102	H ₁ -42	7,0	1,5	12,0	23,8	38,3
103		19,0	8,0	11,0	11,9	32,0
111		24,0	9,5	22,0	16,7	27,7
113		12,0	17,5	7,5	15,5	38,3
115	G ₁ -42	22,0	13,0	9,0	23,0	74,5
116	H ₁	59,0	36,0	14,5	—	17,0
117	S ₁	8,0	10,0	7,6	100,0	17,0
124		11,5	3,0	16,0	6,9	10,6
125	C ₄ -42	72,0	4,5	34,5	14,2	72,4
127	E ₃ -42	7,0	4,0	6,0	11,9	14,9
129	G ₁	52,0	18,0	69,0	47,6	21,3
139		9,0	5,0	4,5	14,3	27,6
141	E ₃	7,0	13,0	7,0	5,7	12,7
142	K ₂	48,0	5,0	80,0	9,8	27,6
143		13,0	1,6	23,5	7,1	14,9
144	H ₁	8,0	—	5,0	14,0	25,2
153	A ₄ -42	17,5	7,2	19,0	9,5	25,5
157	G ₁	14,0	3,9	1,7	16,6	55,3
167	C ₄	14,0	1,6	4,0	—	6,4
169	E ₃	6,7	2,8	6,4	35,7	14,9
170		4,9	5,6	1,6	4,7	17,0
171		6,5	4,7	4,0	28,5	4,3
183		3,8	1,3	2,3	—	4,3
184		43,0	3,1	6,8	—	17,0
185	C ₃ -42	21,0	1,2	8,8	8,8	21,3
187		1,3	0,8	1,3	—	2,4
189		2,9	1,6	5,2	8,5	12,7
195	A ₄	2,5	1,9	1,6	—	5,3
199	E ₃ -42	3,2	1,6	—	4,7	14,9
201	E ₂	1,5	2,1	6,0	4,0	3,4
202	K ₁	—	—	1,7	—	—
212		1,3	0,5	1,3	—	2,1
213	A ₃ -42,E ₃	2,5	3,6	3,6	17,8	3,4
217		9,5	0,3	2,6	0,9	0,8
226		2,1	0,5	1,8	—	2,1
227	C ₃	2,2	0,5	3,6	1,4	4,2
232	B ₁	—	0,5	—	—	—
241	E ₃	1,9	0,4	—	0,4	8,7
244		4,8	0,4	1,0	1,9	13,3
249	D ₁	—	1,9	—	—	—
255	A ₃	1,0	0,7	—	0,5	1,3
259		0,4	0,6	—	0,5	0,4
261	E ₁	0,6	0,6	2,3	—	0,4
273	A ₂ -42,E ₂	0,4	0,4	0,3	1,4	0,4
286		2,4	0,1	—	—	2,3
287	C ₂	13,3	0,5	10,0	2,1	31,9
289	E ₁	0,9	0,2	0,7	2,8	—
315	A ₂	0,5	0,8	0,4	0,3	—
333	E ₁ , A ₁ -42	0,2	1,6	0,3	5,7	—
346		0,5	0,4	0,5	0,1	1,1
347	M-59	0,4	—	0,5	0,2	0,4
361	E ₁	—	—	—	—	0,2
375	A ₁	3,0	0,5	1,0	0,2	2,5

preferential cleavage of the C₅-C₆ bond leads to the formation of the strongest peak of the ion S₁ with m/z 117, and the cleavage of the C₆-C₇ bond takes place with the formation of the ion E₁, m/z 333.

A methoxy group at C₇ is sufficiently remote from the pyranose ring not to affect its fragmentation. Consequently, it may be expected that the spectrum of (V) will be close to that of the completely acetylated methyl heptoside, with the exception that the ions including the side chain will be 28 m.u. lighter. In actual fact, in the spectrum of (V) strong peaks are represented by the ions of series C, G and H. But the most characteristic feature of a methoxy at C₇ is an intense peak with m/z 45 from the S₁⁺ ion.

The dimethyl ethers number ten combinations of the positions of the methoxy groups:



Bearing in mind the spectrum of (V), it may be assumed that the dimethyl ethers with a single methoxyl in the pyranose ring and the other at C₇ (VI-VIII) will have similar fragmentation patterns to the 2-, 3-, and 4-monomethyl ethers. In actual fact, in the spectrum of (VI) the ratio of the strongest peaks of the ions H₁, m/z 116, and G₁, m/z 129, is the same as in the spectrum of (I). The ions of series C are shifted by 28 m.u. in the direction of lighter masses and at the same time, they are separated into those that have lost CH₃OH and those that have lost CH₃COOH on their formation. The spectrum of (VII) is characterized by the dominating peaks of the ions I₁, m/z 75, and D₁, m/z 221. The mass number of the latter indicates the presence of a methoxyl in the side chain. The formation of the ion B₁ and the low yield of the ions of series C are also characteristic features of a OMe group at C₃. The spectrum of (VIII), just like the spectrum of (III), is characterized by intense peaks of the ions of series G, and the peaks of the ions of series K are displaced to m/z 174 and 114. The cleavage of the C₆-C₇ bond leads to the formation of the ions S₁⁺ with m/z 45; the intensity of which in the spectra of (VI-VIII) is increased to 35% of the maximum as compared with the spectra of (I-III).

The fragmentation of the dimethyl ethers with a methoxy group at C₆ does not retain to such an extent as the 7-OMe derivatives the laws of the fragmentation of the 2-, 3-, and 4-monomethyl ethers. In the case of compound (IX), the yield of ions of series C is small, and the strongest peaks in the spectrum are those of the ions of the series H, G, and S₁. The peak of the latter with m/z 117 is characteristic for all 6-OMe-containing methyl heptosides having an acetoxy group at C₇.

The cleavage of the C₆-C₇ bond leads to the ion E₁⁺, m/z 305 with, however, no pronounced intensity. The spectrum of (X) is characterized by strong peaks of the ions I₁ and S₁⁺, and also by the peaks of the ions D₁, m/z 221, and B₁, m/z 232. The yield of ions of series C is very small as for all 3-OMe-containing methyl glycosides. The methoxy groups of compound (XI) are responsible for the preferential cleavage of the C₃-C₄ and C₆-C₇ bonds, leading to the formation of the three-carbon ion G₁⁺. In the spectrum of (XI), the peak of the ion G₁⁺ at m/z 101 is the main peak (chain of the C₄-C₆ atoms with their substituents).

The spectrum of compound (XII), a methyl heptoside with the completely methylated side chain, is characterized by strong peaks of the ion S₁ and S₁⁺, m/z 89 and 45, and E₁ and E₁⁺, m/z 289 and 333. On fragmentation, the acetylated pyranose ring gives the ions of series H, m/z 144 and 102, and series G, m/z 157 and 115. The yield of the ions of series C is insignificant because of the methylated side chain.

TABLE 3. Mass Spectra of Acetates of the Dimethyl Ethers of Methyl β -Glucoheptopyranoside (relative intensities, %)

m/z	Type of ion	Positions of the OMe groups									
		2,7	3,7	4,7	2,6	3,6	4,6	6,7	2,3	2,4	3,4
43		101.0	118.0	100.0	190.0	115.0	151.0	3.72	61.7	97.6	126.0
45	S ₁	32.5	36.0	30.0	19.5	12.5	17.8	83.0	8.8	11.6	10.3
69		1.2	12.2	—	0.9	15.0	17.2	33.9	1.9	25.6	18.4
71		9.1	9.6	3.4	—	10.0	8.9	16.9	2.15	—	3.9
74	H ₁ —42	100.0	71.4	28.0	100.0	67.5	31.2	33.9	11.8	100.0	54.9
75	I ₁	19.5	100.0	15.5	34.2	100.0	33.4	38.9	100.0	72.1	100.0
81		9.1	7.5	4.7	7.5	2.5	4.9	33.9	1.9	3.2	5.5
82		15.6	—	4.3	12.2	2.7	3.1	—	1.0	1.4	3.5
83		3.0	11.2	3.9	5.1	5.7	4.6	28.8	0.8	2.5	5.2
85		22.1	14.7	10.8	24.4	10.2	8.7	25.4	6.8	6.5	10.0
87	G ₁ —42	33.8	20.4	100.0	48.8	22.7	10.1	100.0	10.8	37.2	54.9
88	H ₁	14.3	30.6	5.2	14.5	—	6.6	20.3	83.3	16.3	51.7
89	S ₁	—	—	2.2	2.9	—	—	54.2	4.9	2.3	5.5
97	G ₁ —32 C ₄ —42	15.6	10.2	10.3	7.8	7.6	4.5	37.3	2.5	6.9	9.0
99		13.0	8.6	10.8	—	5.7	12.9	18.6	1.6	5.3	3.2
100	K ₂ —42	6.5	6.1	6.5	9.0	3.0	6.0	—	1.3	18.6	22.6
101	G ₁ , G ₁ ³	8.5	14.3	1.3	7.3	13.7	100.0	—	4.6	62.8	22.6
111	E ₅	16.9	8.1	7.7	11.5	6.5	9.8	32.2	3.0	4.9	6.5
113	E ₁	18.2	11.6	6.0	5.4	7.0	9.8	22.0	6.8	5.8	9.4
114	K ₂	23.4	3.0	6.5	3.4	—	10.9	—	—	2.3	4.8
115	K _{2p}	14.3	14.3	30.1	7.1	5.5	8.9	35.6	4.9	4.6	6.8
116	H ₁	69.0	42.8	9.5	53.7	32.5	12.3	11.8	3.9	62.9	19.4
117	S ₁	9.1	10.2	3.4	68.3	92.5	75.8	8.5	1.5	7.2	11.9
125	A ₃ —42	39.0	7.5	22.4	18.3	—	7.6	23.7	4.1	23.2	10.3
127		4.3	5.7	4.3	8.0	12.5	4.9	16.9	1.2	1.8	5.2
129	G ₁ , G ₁ ³	50.7	16.3	100.0	36.6	20.7	4.7	62.7	10.8	18.6	25.8
139	C ₄	13.0	4.5	4.7	5.4	1.7	4.2	40.7	0.8	18.6	6.5
141	E ₃	4.3	12.2	4.7	4.9	13.0	7.8	15.2	1.5	—	6.8
142	K ₂ ; K ₁ —32	4.2	6.7	21.9	12.7	3.6	6.7	11.8	1.5	13.9	29.0
143	K _{2p}	5.5	6.3	—	21.2	4.7	11.1	15.2	1.4	23.2	16.1
153		—	2.3	1.7	3.6	2.5	4.2	6.8	1.0	1.8	4.8
156		24.7	4.3	4.3	5.4	—	—	—	3.1	7.7	3.2
157	C ₁	31.2	12.2	6.0	15.9	2.5	2.9	20.3	1.3	3.0	4.2
159		2.3	—	—	4.4	2.5	2.9	6.8	0.4	1.6	6.8
167	A ₄	2.3	1.8	2.2	2.9	1.2	2.0	—	0.3	1.6	—
169		1.3	2.2	2.6	3.9	2.2	15.6	15.2	—	0.9	3.2
171	E ₄	13.0	3.5	3.0	3.4	3.7	3.3	35.6	0.8	0.9	1.6
173	E ₂	—	—	5.6	—	—	9.8	6.8	—	1.6	1.9
174	K ₁	—	—	3.9	—	—	—	—	—	—	—
184		4.6	—	2.2	4.4	—	2.5	—	1.3	—	—
185	E ₃	2.2	4.9	2.2	26.8	2.5	7.6	8.5	0.8	1.4	2.3
189		13.0	—	5.2	7.1	1.2	4.5	—	0.2	0.7	—
198		1.7	—	—	1.5	—	—	—	—	0.7	—
199	C ₃	2.7	2.0	3.4	2.4	1.0	1.3	20.3	0.9	4.6	3.2
201	E ₂	—	3.0	—	1.9	3.5	1.6	—	0.2	0.6	1.6
202	K ₁	—	—	—	—	—	—	—	—	0.5	—
204	B ₁	—	—	—	—	—	—	—	1.5	—	2.3
213	E ₂ —42	14.3	—	3.9	1.4	3.2	4.2	20.3	0.2	0.2	2.3
217	C ₂ —42	—	0.81	—	—	—	—	—	0.1	0.4	—
221	D ₁	—	2.0	—	—	3.6	—	—	—	—	—
227	A ₃	0.9	0.6	0.4	0.8	—	2.5	—	0.1	0.3	0.9
232	B ₁	—	0.8	—	—	1.0	—	—	—	—	—
233	E ₁	—	0.8	—	0.4	0.7	—	—	0.1	0.3	1.5
245	E ₂ ; A ₂ —42	0.5	0.8	—	2.6	—	0.5	—	0.07	0.2	1.2
249	D ₁	—	—	—	—	—	—	—	3.3	—	1.3
258		5.3	1.4	0.5	0.6	—	—	—	0.1	1.0	1.1
259	C ₃	10.4	0.6	5.6	0.5	—	4.5	5.1	0.1	4.2	0.5
261	E ₁	0.8	—	1.3	0.8	1.7	3.8	—	0.03	0.2	0.4
273	E ₂	—	0.6	—	0.2	0.7	1.1	2.0	0.03	—	—
275		1.3	0.8	0.3	0.7	1.00	—	0.8	0.03	0.3	—
287	A ₂	5.3	2.0	0.9	0.8	—	0.7	3.7	0.2	0.3	1.6
289	E ₁	—	—	—	—	—	—	4.1	—	—	—
305	A ₁ —42; E ₁	—	0.4	—	0.1	0.7	—	—	0.1	0.05	—
318		0.2	0.6	0.3	—	—	0.6	—	0.03	0.2	0.2
319	M—59	0.4	0.4	0.2	0.2	0.1	0.3	0.5	0.03	0.3	0.3
333	E ₁	0.1	—	—	—	—	—	33.9	—	—	—
347	A ₁	0.5	0.2	0.3	0.2	0.1	0.5	0.5	0.1	0.4	0.3

Dimethyl ethers with two methoxyls in the pyranose ring (XIII–XV) decompose under electron impact in a similar manner to the corresponding hexosides [8]. The spectrum of (XIII) is characterized by two dominating peaks of the ions I_1 and H_1 with m/z 75 and 88, and also weaker peaks of the ions D_1 , 249, and B_1 , 204. The spectrum of (XIV) is distinguished by a group of peaks of the ions of series H, m/z 116 and 74, G_1 , m/z 101, and I_1 , m/z 75, the latter having a different nature from the case of the 3-OMe-containing derivatives, where the bulk of the I_1 ions is due to C_1 with its substituent and the methoxyl at C_3 (see scheme). The spectrum of (XV), like the spectrum of (XIII) is characterized by strong peaks of the ions I_1 , m/z 75, and H_1 , m/z 88, but in a different ratio. A methoxyl at C_1 is responsible for the formation of the ions D_1 and B_1 , m/z 249 and 204. The most characteristic feature of a methoxy group at C_4 is the formation of the ions of series K. It is true that the peak of the ion K_1 itself can be seen only in the spectra of (III), (VIII), and (XIV), while in the spectra of (XI) and (XV), the products of its further fragmentation are observed. Particular attention is deserved by the ion K_{2p} which apparently has the stable structure of a conjugated oxonium ion. In the heptosides with a methoxyl at C_7 , it gives a peak at m/z 115, and in other cases the peak is shifted to m/z 143.

In the regions of high mass numbers in the spectra of the compounds described above, there are numerous peaks of low intensity which are characteristic for a given isomer. These peaks are mainly due to the ions of series A, C, and E. However, their assignment to a definite series is difficult in each concrete case because of the coincidence of mass numbers, and it requires a special investigation.

EXPERIMENTAL

GLC analysis was performed Pye-Unicam-104 and Shimadzu-5A chromatographs in glass columns 2000×3 mm and 2500×3 mm filled with 3% of QF-1 and 3% of NPGS.

PGLC was performed on a Tsvet-5 chromatograph re-equipped for preparative separation. The flow splitter set up on the chromatograph ensured a ratio of the flow of carrier gas (Ar) reaching the detector and the outflow of the chromatograph of 5:24, respectively; the temperature of the evaporator was 250°C , the temperature of the column 200°C , and the outlet of the chromatograph was kept at a temperature of 250°C . A 3000×12 mm column containing 3% of QF-1 on Chromosorb 60-80 mesh, with a 26-mg charge and a 2000×10 mm column with 3% of NPGS on Chromaton 60-80 mesh with charge of 3.4 mg were used.

The mass spectra were recorded on a LKB 9000S instrument with 3000×3 mm and 2000×3 mm columns filled with 3% of QF-1 and 3% of NPGS, respectively. The temperature of the ion source, of the separator and of the evaporator was maintained at 250°C and that of the column was raised from 150 to 230°C at $5^\circ\text{C}/\text{min}$, the rate of flow of carrier gas (helium) was 30 ml/min, and the ionizing voltage was 70 V.

Preparation of the Mono- and Dimethyl Ethers of the Methyl β -Heptoside. Boiling α -D-glucoheptose (10 g) in a 10% solution of hydrogen chloride in absolute methanol (240 ml) for 20 h gave a mixture of methyl α - and β -glucoheptopyranosides. This was separated into the individual anomers by ion-exchange chromatography using Neuberger's method [11]. The partial methylation of the methyl β -glucoheptopyranoside [12] gave a complex mixture of methyl ethers containing more than 50% of monomethyl ethers, which were separated by PGLC successively in columns with the phases QF-1 and NPGS. Methylation of the individual monomethyl ethers gave mixtures of methyl ethers from which the dimethyl ethers of methyl β -glucoheptopyranoside were studied.

SUMMARY

1. Five mono- and ten dimethyl ethers have been detected in the products of the partial methylation of methyl β -glucoheptopyranoside.

2. The mass spectra of the acetates of the mono- and dimethyl ethers of methyl β -heptoside have been recorded and discussed. Their retention indices on the phase NPGS have been measured.

3. The mass spectra of these position isomers unambiguously characterize the pattern of methylation.

4. The main peaks in the mass spectra of the acetates of the methyl ethers of the methyl heptoside have been assigned to the ions of series known previously — A, B, C, D, E,

G, H, I, and K for the corresponding methylated hexoses. Particularly close are the fragmentation patterns for the 2- and 3-methylated homologs. A methoxy group at C₇ likewise does not distort the pattern of fragmentation of the pyranose ring.

5. A methoxy group at C₄ or C₆ of the methyl heptoside molecule exerts an influence on the fragmentation of its molecular ion different from that which is found in the case of a methyl hexoside. The main result of this influence is the formation of three-carbon fragments including the C₄-C₅-C₆ chain and four-carbon fragments with the C₄-C₅-C₆-C₇ chain with their substituents and denoted by G₁³ and K_{2p}, respectively, in the spectra of compounds with a combination of methoxy groups at C₄, C₆, and C₇.

6. The increase in the size of the side chain leads to the formation of the ions S₁⁺ and E₁⁺ due to the cleavage of the C₆-C₇ bond and specific for heptosides.

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