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P A R T I A L M E T H Y L A T I O N O F C A R B O H Y D R A T E S

PARTIAL METHYLATION OF METHYL β-L-ARABINOPYRANOSIDE

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UDC 547.917+543.544.45

We have previously [1] studied the kinetics of the partial methylation of methyl β-L-arabinopyranoside by Purdie's method. We have now obtained information on the methylation of methyl β-L-arabinopyranoside by other methods.

As can be seen from Tables 1-3, in the initial stages of the partial methylation of methyl β-L-arabinopyranoside the 2-O-methyl ether predominates in the monomethyl ether fraction, and the amount of 3-O-methyl ether formed is greater than that of the 4-O-methyl ether.

It must be noted that in methylation by Kuhn's method in the presence of barium oxide the amount of 2,3-di-O-methyl ether rises sharply toward the end of the reaction (50.6% after 1.5 h), and this method is therefore suitable for the preparative production of the 2,3-di-O-methyl ether. The rate of methylation of methyl β-L-arabinoside by this method is considerably less than the rate of methylation of methyl β-D-xyloside [2]. The exhaustive methylation of the latter was complete in 1 h, while the conversion of methyl β-L-arabinoside into the fully methylated derivative was only 84% complete even after 2 h.

TABLE 1. Partial Methylation by Haworth's Method

Time, min	Initial arabinoside, %	Methyl ether, %					
		2	3	4	2,3	2,4+3,4	2,3,4
10	63,2	14,5	8,5	7,0	3,8	2,4	0,6
20	45,1	17,6	10,6	8,4	8,5	6,8	3,0
30	32,4	19,2	9,7	10,0	13,3	9,6	5,8
45	24,7	18,3	8,7	9,7	14,5	12,2	11,9
60	14,9	16,5	6,0	9,0	18,9	14,5	20,2
120	4,0	7,2	2,1	3,8	17,2	11,2	54,5

TABLE 2. Partial Methylation by Kuhn's Method (Ag_2O + CH_3I)

Time, min	Initial arabinoside, %	Methyl ether, %					
		2	3	4	2,3	2,4+3,4	2,3,4
10	78,3	9,8	7,8	4,1	—	—	—
20	67,3	10,9	12,9	6,5	1,2	1,2	—
30	43,7	21,2	17,9	9,6	2,5	5,7	—
45	25,5	21,6	25,7	13,2	4,6	9,1	0,3
60	13,7	18,9	35,1	11,4	10,4	9,8	0,7
90	1,6	12,7	35,5	8,2	20,1	18,6	3,3
120	—	11,7	19,8	7,9	15,5	17,0	13,1
180	—	—	7,6	3,0	36,7	15,6	37,1
240	—	—	6,1	2,2	33,5	14,8	43,4
480	—	—	2,1	1,1	25,8	10,6	60,4

Pacific Ocean Institute of Bioorganic Chemistry, Far Eastern Scientific Center of the Academy of Sciences of the USSR, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 753-755, November-December, 1977. Original article submitted July 1, 1977.

 0009-3130/77/1306-0634$07.50

TABLE 3. Partial Methylation by Kuhn's Method (BaO + CH_3I)

Time, min	Initial arabinoside, %	Methyl ether, %					
		2	3	4	2,3	2,4+3,4	2,3,4
5	79,0	10,0	6,5	4,2	0,3	—	—
10	61,8	17,6	13,2	6,7	1,1	0,6	—
20	36,6	25,4	23,1	10,7	2,9	1,2	0,1
30	24,6	29,1	25,8	12,9	4,8	2,7	0,1
45	12,6	27,5	32,0	12,3	10,8	4,4	0,4
60	5,3	26,9	31,7	11,9	16,6	6,6	1,0
75	0,4	17,6	35,7	3,6	29,4	9,5	3,8
90	0,2	6,4	11,4	2,5	50,6	4,1	24,6
120	—	—	—	—	13,3	2,6	84,1

TABLE 4. Partial Methylation by Hakomori's Method

CH_3I, $ml \times 10^2$	Initial arabinoside, %	Methyl ether, %					
		2	3	4	2,3	2,4+3,4	2,3,4
3	45,1	8,0	3,0	4,4	10,8	6,5	22,2
4	45,3	6,1	1,3	6,1	2,9	2,1	36,2
5	34,5	7,1	1,4	5,7	7,7	4,2	39,4
6	13,2	0,5	—	1,0	3,8	—	81,5
7	11,0	0,6	—	—	5,6	0,8	82,0
8	—	—	—	—	3,0	—	97,0

In contrast to methylation by Purdie's method, other methods give the 4-O-methyl ether in considerable amounts.

Methylation by Hakomori's method has a tendency from the very beginning to the predominant formation of the fully methylated compound. The other derivatives are obtained in considerably smaller amounts. It is desirable to use this method only for obtaining methyl 2,3,4-tri-O-methyl-β-L-arabinopyranoside. A similar tendency is observed in the case of methyl β-D-xylopyranoside [2].

Unfortunately, the 2,4- and 3,4-di-O-methyl ethers are not separated by GLC on any of the phases used.

EXPERIMENTAL

The methyl ethers of methyl β-L-arabinopyranoside were analyzed quantitatively by the gas—liquid chromatography of their acetates at 160°C using for this purpose a "Tsvet-4-67" chromatograph. The other conditions for GLC analysis were the same as in our previous work [1]. The components of the mixture of methyl ethers were identified by comparison with authentic samples.

The partial methylation of methyl β-arabinoside was performed by the methods of Haworth and of Kuhn as described previously [2]. Hakomori's method was used in the following variant. Methyl β-arabinoside (0.05 g) was dissolved in DMSO (3 ml), and 0.42 ml of methylsulfinyl carbanion was added. The mixture was stirred, and methyl iodide was added in the amounts given in Table 4. After the usual working up [2], aliquots were analyzed by GLC.

SUMMARY

1. The kinetics of the partial methylation of methyl β-L-arabinopyranoside by the methods of Haworth, Kuhn, and Hakomori have been studied and the compositions of the products have been determined.

2. In the methylation of methyl β-L-arabinopyranoside by the methods of Haworth and Kuhn, the following sequence of relative reactivities is observed: 2-OH > 3-OH > 4-OH.

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COMPARATIVE CHARACTERISTICS OF LIPOPOLYSACCHARIDE–PROTEIN COMPLEXES FROM THE NUCLEI OF BACTERIA OF THE FAMILY PSEUDOMONACEAE

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UDC 547.917+576.809.8

Ethanol-assimilating bacteria of the family Pseudomonaceae are good sources of fodder protein. They give about 5 g of dry biomass per 1 liter of cheap synthetic medium. The study of the cell walls of some bacteria of the family Pseudomonaceae has shown considerable differencs in their chemical compositions, particularly in the composition of the lipopolysaccharides [1].

These facts have led to the necessity of searching for the most effective producing agents of lipopolysaccharide–protein complexes (LPPC's) among the bacteria of this family and for a comparative characterization of the complexes isolated. We have investigated *Pseudomonas fluorescens* 361, *Acinetobacter* sp. 34, 154, and 30, and their mutants. The LPPC's from the various strains of bacteria were isolated by Boivin's method [2]. The general characteristics of the extracts obtained are given below (%):

	P. fluorescens			*Acinetobacter sp.*		
	361	*55*	*154*	*30*	*34*	*18*
Yield of extracts	3,4	1,6	0,6	1,2	3,1	1,0
Yield of lipid A	16,1	2,3	11,7	10,7	9,1	8,1
Monosaccharides	36,9	15,0	18,9	1 ,3	15,5	15,7
Amino sugars	6,6	5,5	2,5	5,9	1,2	0,9
KDO	2,7	Tr.	Tr.	1,1	0,0	0,0
Pentoses	10,7	4,6	0,0	Tr.	0,0	0,0
Protein	16,8	11,5	32,9	30,9	18,9	22,9
Nucleic acids	0,7	0,7	8,1	0,8	1,7	4,5
Phosphorus	3,1	1,4	1,3	0,7	0,5	0,7
Nitrogen	4,6	2,6	4,1	5,1	3,3	4,2
Ash	9,0	4,6	7,3	5,6	17,0	5,9

The yield of extracts amounted to 1-3.5% of the weight of the dry microbial mass. All the extracts contained a relatively small amount of monosaccharides. These facts are in harmony with the results obtained by Fensom and Grey, who showed that the LPS's from bacteria of the family Pseudomonaceae contain a smaller amount of monosaccharides than the LPS's from the family Enterobacteriaceae [3].

The results of a determination of the qualitative monosaccharide composition of the extracts by the PC and GLC methods were as follows:

Bacterium	*X*	*Rha*	*Fuc*	*Xyl*	*Man*	*Gal*	Glc	*Hep*
P. fluorescens 361	+++	+	+++	+	++	+	+++	+++
" 55	+	+	–	+	+	Tr.	++	+
Acinetobacter sp. 154	+	–	+	Tr.	–	+++	++	–
" 34	+	–	–	Tr.	Tr.	+++	+++	–
" 18	–	–	+	+	–	+++	++	–
" 30	+	Tr.	–	+	+	++	+++	+

X) unidentified; Rha) rhamnose; Fuc) fucose; Xyl) xylose; Man) mannose; Gal) galactose; Glc) glucose; Hep) heptose.

Pacific Ocean Institute of Bioorganic Chemistry, Far Eastern Scientific Center of the Academy of Sciences of the USSR, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 755-760, November-December, 1977. Original article submitted July 7, 1977.

 0009-3130/77/1306-0636$07.50