7. A. F. Bochkov, V. A. Afanas'ev, and G. E. Zaikov, The Formation and Cleavage of Glycosidic Bonds [in Russian], Moscow (1978), p. 83.
8. V. P. Panov and R. G. Zhbankov, The Conformations of Sugars [in Russian], Minsk (1975), p. 130.
9. Y. Kondo, Agr. Biol. Chem., 41, 2089 (1977).
10. G. J. Robertson and R. A. Lamb, J. Chem. Soc., 1321 (1934).
11. P. Kovac and R. Brezny, Chem. Zvesti, 29, 544 (1975).

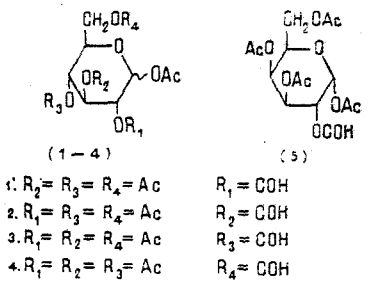
MASS SPECTROMETRY OF COMPLETELY ACETYLATED MONOSACCHARIDE FORMATES

A. F. Pavlenko, N. I. Belogortseva, and Yu. S. Ovodov

UDC 543.544.51 + 547.917

The mass-spectrometric fragmentation of model samples of fully acetylated monoformates of D-glucose and D-galactose has been studied. It has been shown that it is similar to the fragmentation of the full acetates of the hexoses, is characteristic, and permits the position of a formyl group in a monosaccharide to be determined.

We have previously developed a method for determining the positions of sulfate groups in sulfated carbohydrates through their replacement by formyl groups with the subsequent mass-spectrometric identification of the compounds formed. In this connection, it is a matter of interest to study the mass spectra of formyl derivatives of monosaccharides. In the present paper we consider the interpretation of the mass spectra of the peracetates of formyl derivatives of D-glucose (compounds 1-4) and of D-galactose (compound 5).



Fully acetylated monosaccharide formates

The mass-spectrometric characteristics for these compounds, which are given in Table 1, enable us to judge that the decomposition of the fully acetylated monosaccharide formates is similar to the decomposition of fully acetylated hexoses [2]. The mass spectra contain two main series of fragments, B and C (using Heyns and Muller's symbols [2]).

Series B (scheme 1, next page) begins by the elimination of the glycosidic acetoxy group (ion with m/z 317), and the subsequent ejection of formic or acetic acid and a molecule of ketene leads to fragments with m/z 211 (compounds 1, 3-5), 197 (1, 2, 4, 5), 169 (1-3, 5), and 155 (4). The ion with m/z 271 is absent from the spectra of 1, 3-5 and is characteristic for 2. The ion with m/z 211 is observed only in the mass spectra of compounds (1), (3), (4), and (5) and is strongest for (1) and (5).

Series C (scheme 2, next page) begins with fragment C_1, which is formed by the cleavage of the C_1—C_2 bond. The elimination of a Ac_2O molecule leads to the fragment C_2 with m/z 274 (1, 3-5). The following fragment, C_3, is formed by the ejection of formic acid. The peak with m/z 274 is present in the spectra of compounds (1, 3-5), and an ion with m/z 242 only in the spectrum of (2). Table 1 gives information on the relative intensities of the peaks observed in

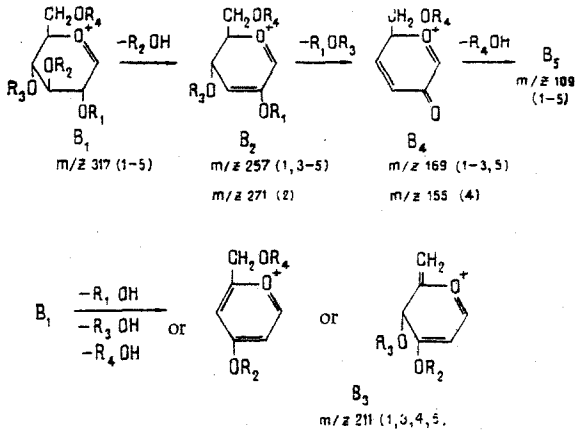
Pacific Ocean Institute of Bioorganic Chemistry, Far-Eastern Scientific Center, Academy of Sciences of the USSR, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 31-35, January-February, 1982. Original article submitted June 18, 1981.

 0009-3130/82/1801-0028$07.50

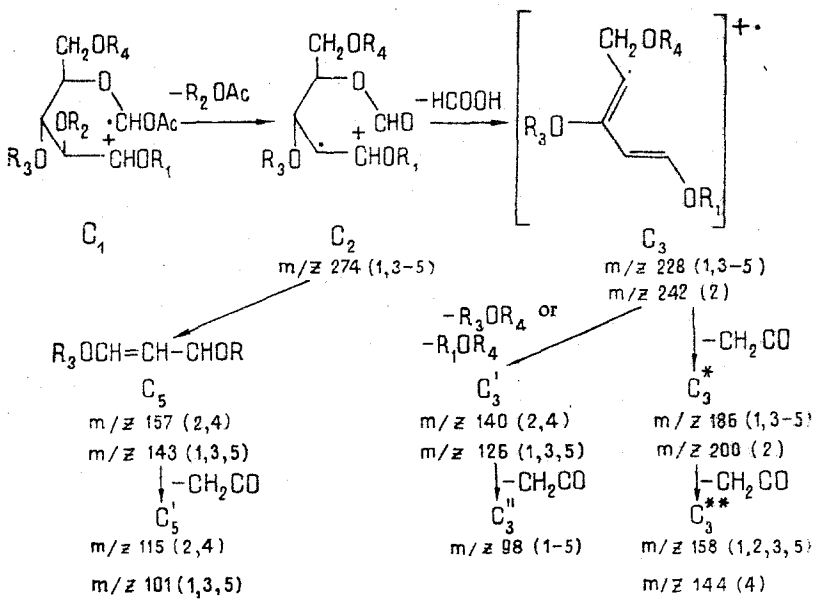
TABLE 1. Mass-Spectrometric Characteristics of the Peracetates of Formyl Derivatives of D-Glucopyranose and of D-Galactopyranose

m/z	Relative intensities of the peaks				
	D-glucopyranose				D-galactopyranose
	2-O-Formyl (1)	3-O-Formyl (2)	4-O-Formyl (3)	6-O-Formyl (4)	2-O-Formyl (5)
69	10,4	100	11,7	8,4	7,5
70	8	7,9	9,1	6,6	7,4
71	8,4	6,6	6,5	5,1	7
73	32,1	81,6	29	21,6	30,8
80	5	9,6	10,7	5,9	4 2
81	18,8	41	21,3	10,8	19,3
84	4	3,3		2,3	2,7
85	11,4	11	14	11,5	8,3
86	12,9	92	13,2	15,6	11,5
89					
98	100	74	100	89,2	100
99	32,8	20	14	83	13
101	39,5	5,5	36,4	6,9	37,4
102	6,4	6	10	6,9	5,2
103	45,5	29,6	62,8	35	33,8
104		1			2,1
109	28,6	30,6	14	10,3	18,1
110	3,2	3,3			2,4
112	7,9	5		5,5	4,8
113	6,4	5,6	7,3	7,1	3,9
114	10,9	13	19	2,7	9,7
115	67,5	93	36,4	100	61,8
116	10,1	11,5	5,6	7,1	8,4
117		1,6		1,7	
125		6		1,6	
126	19,7	12	29,7	8,7	14,2
127	18,8	12,4	9,8	5,6	16,4
128		2,3		1,5	2,1
131	8,8	4,6	9,5	3,2	7,3
139	6,8	3,7	8,1	4,9	4,8
140	15,8	24,4	9,1	21,1	15,4
141	4,9	11	5,2	2,3	4
143	59,3	6,3	52,9	5,5	52,2
144	9,9	3,7	8,2	13,1	7,3
145	28,7	21,5	30,1	13,8	15,7
154	5,4	4,7		13,8	3
155	15,8	3,5	10,7	12,4	12,7
156		1,9			
157	23,8	59,3	13,4	8	23,6
158	14,7	18,5	42,9	7,6	13,3
168	13,1	2	57,4	3,2	11,5
169	35,6	22,5	15,7	2,2	13,6
169	35,6	22,5	15,7	2,2	13,6
170	3,9	1,9			
172	4,9			3,2	2,7
185	8,8				8,7
186	16,8		11,8	30,6	16,3
187	4,9	7		3,7	4,2
197	6,4	4,1	2,8	3,7	5,7
199		6,9			2,4
200	7,4	24,5	5,3		8,2
201	6,1	12,1	9,9		2,9
211	9,8		1	0,7	6,5
214	10,9	1,5		4,7	7,3
215	3,9	1,4	5,2	7,8	2,7
228	11,6		9,5	30,2	15,1
229	3,7	1,7	1,7	3,1	3,6
231		1		3	3,3
242		7			
256	1,5				
257	0,5		0,4	0,9	0,5
271		0,5			
274	1,9		1,2	1,8	0,7
275	0,5			0,5	0,5
279			3,4		0,6
303	1	1,1	2		0,5
317	10,9	2,8	1,2	2	26,6

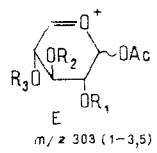
Scheme 1



Scheme 2



the mass spectra of the compounds studied. Here it must be borne in mind that the peak with m/z 43 is distinguished by the greatest intensity in all the spectra and in comparison with this the intensities of the other peaks are very small. In view of this, Table 1 gives the intensities of the peaks in relation to the peak with the second-highest intensity (for compounds (1), (3), and (5) the peak with m/z 98, for compound (2) the peak with m/z 69, and for compound (4) that with m/z 115). It must be mentioned that in addition to series B and C, an ion with m/z 303 is characteristic for the mass spectra of (1-3) and (5), while it is absent from the spectrum of (4).



Thus, the mass spectra of the peracetylated formates of monosaccharides are characteristic and can be used to determine the positions of the formyl groups.

EXPERIMENTAL

The mass spectra were obtained on a LKB 9000S instrument (Sweden). TLC was performed on plates coated with silica gel in the chloroform–acetone (98:2) system. The spots were revealed by spraying with sulfuric acid. Specific rotations were determined on a Perkin-Elmer 141 polarimeter. PMR spectra were recorded on a ZKR-60 instrument (GDR). Melting points were determined on a Boetius stage.

Preparation of Peracetylated Formates of Monosaccharides. 1,3,4,6-Tetra-O-acetyl-2-O-formyl-α-D-glucopyranose (1). A solution of 1 g of 1,3,4,6-tetra-O-acetyl-α-D-glucopyranose [3] in absolute pyridine (10 ml) was treated with acetic-formic anhydride (1.5 ml). The solution was stirred with a magnetic stirrer until the evolution of gas ceased and it was then poured into ice-containing water (70 ml). The crystals that deposited were separated off by filtration and were dried in vacuum over P_2O_5. This gave compound (1) with a yield of 0.995 g (95%), homogeneous on TLC, mp 127-128°C; $[\alpha]_D$ +97° (c 1.0; $CHCl_3$). Found, %: C 47.45, H 5.27. Found, %: C 47.37; H 5.32. PMR (δ, ppm): 6.3 (H-1, J = 2 Hz; 4.8-5.7 (H-2, H-3, H-4); 3.8-4.5 (H-5, 2H-6); 1.9-2.4 ($4COCH_3$); 7.9 (–C–H).

1,3,4,6-Tetra-O-acetyl-3O-formyl-α-D-glucopyranose (2) [1]. A solution of 0.1 g of the sodium salt of 1,2,4,6-tetra-O-acetyl-D-glucopyranose 3-sulfate in absolute dimethylformamide (0.3 ml) was cooled in ice, and, with stirring, oxalyl chloride was added in drops. The mixture was heated at 60°C for 2 h and was then poured into ice water, the aqueous solution was extracted with chloroform, and the chloroform extract was dried over calcined sodium sulfate and evaporated in vacuum. This gave compound (2) with a yield of 0.07 g (87.5%), homogeneous on TLC. Found, %: C 47.54; H 5.28. Calculated, %: C 47.87; H 5.32. According to the results of PMR spectroscopy, the main product was the α anomer: δ 6.25 ppm, J = 2 Hz (H-1).

1,2,3,6-Tetra-O-acetyl-4-O-formyl-β-D-glucopyranose (3). A solution of 0.5 g of 1,2,3,6-tetra-O-acetyl-β-D-glucopyranose [4] in absolute pyridine (5 ml) was treated with acetic-formic anhydride (1 ml). The reaction mixture was worked up as described above for compound (1). This gave compound (3), with yield of 0.48 g (89%), homogeneous on TLC, mp 148-150°C, $[\alpha]_D$ +6.4° (c 0.598, $CHCl_3$). Found, %: C 48.18; H 5.64. Calculated, %: C 47.87; H 5.32. PMR (δ, ppm): 5.74. J = 4 Hz (H-1); 5.15-5.3 (H-2, H-3, H-4); 3.82-4.3 (H-5, 2H-6); 1.94-2.2 ($4COCH_3$); 8.01 (–C–H).

1,2,3,4-Tetra-O-acetyl-6-O-formyl-β-D-glucopyranose (4). A solution of 1 g of 1,2,3,4-tetra-O-acetyl-β-D-glucopyranose [4] (1 g) in absolute pyridine (10 ml) was treated with acetic-formic anhydride (1.5 ml). The reaction mixture was worked up as described for (1). This gave compound (4) with a yield of 0.987 g (93%) homogeneous an TLC, mp 139-140°C, $[\alpha]_D$ +7.5° (c 1.2; $CHCl_3$). Found, %: C 47.87; H 5.40. Calculated, %: C 47.87; H 5.32. PMR spectra (δ, ppm): 5.72 (H-1, J = 4 Hz); 4.9-5.5 (H-2, H-3, H-4); 3.7-4.4 (H-5, 2H-6); 1.9-2.4 ($4COCH_3$); 7.8 (–C–H).

1,3,4,6-Tetra-O-acetyl-2-O-formyl-α-D-galactopyranose (5). A solution of 0.5 g of 1,3,4,6-tetra-O-acetyl-α-D-galactopyranose [4] in absolute pyridine (5 ml) was treated with acetic-formic anhydride (1 ml). The reaction mixture was worked up as described above for (1). This gave compound (5) with a yield of 0.46 g (85%), homogeneous on TLC, mp 111-112°C, $[\alpha]_D$ +115° (c 0.29; $CHCl_3$). Found, %: C 47.63; H 5.37. Calculated, %: C 47.87; H 5.32.

CONCLUSION

The mass-spectrometric fragmentation of a number of acetylated D-glucopyranose and D-glactopyranose formates has been studied. It has been shown that it is similar to the fragmentation of monosaccharide peracetates and permits the position of the formyl group in the monosaccharides to be determined.

LITERATURE CITED

1. A. F. Pavlenko, N. I. Belogortseva, S. V. Moroz, and Yu. S. Ovodov, Khim. Prir. Soedin., 607 (1980).
2. H. Heyns and D. Muller, Tetrahedron Lett., 6061 (1966).
3. B. Helferich and J. Linner, Chem. Ber., 95, 2604 (1962).
4. B. Helferich, Ann. Chem., 455, 173 (1972).
5. J. O. Mastronardi, S. M. Flematti, J. O. Defferarri, and G. Gros, Carbohydr. Res., 3, 177 (1966).