BRIEF COMMUNICATIONS

MASS SPECTROMETRY OF SULFATED MONOSACCHARIDES

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To investigate sulfated polysaccharides, which are widely distributed in nature [1], it is necessary to develop reliable methods of identifying sulfated monosaccharides, the residues of which are present in the biopolymers mentioned. We have used mass spectrometry for this purpose and have studied the mass spectra of the pyridinium salts of the 2-, 3-, and 6-sulfates of D-glucose and methyl D-glucopyranoside acetylated at the free hydroxyls and have established the characteristic nature of the spectrum for each derivative (Table 1). The interpretation of the features of the mass spectra is difficult because of the decomposition of the salts, and in view of this we prepared the methyl ester of the 2-sulfate of 1,3,4,6-tetra-O-acetyl-D-glucose and studied its mass spectrum (Fig. 1). To obtain this compound, the barium salt of the 2-sulfate of 1,3,4,6-tetra-O-acetyl-D-glucose [2] was passed through Dowex-50W cation-exchange resin (H^+), treated with an excess of ethereal diazomethane at +4°C, and chromatographed on a column of silica gel in the chloroform–acetone (98 : 2 by volume) system.

TABLE 1. Mass Spectra of the Pyridinium Salts of Sulfates of D-Glucose (intensities, % of the total ion current)

m/e	6-	4-	2-	m/e	6-	4-	2-
331	0,5	—	—	149		3,4	0,4
288	0,2	—	—	144	3,2		
273	0,5	—	—	140	4,7		0,8
242	6,5	—	—	139			1,5
229	2,6	—	—	127			0,7
228	2,1	—	—	126	4,7	52,0	0,5
200	3,9	—	—	115	14,2		0,6
186	5,6	—	—	114	3,0		0,5
184	3,7	—	—	110			0,6
169	3,2	—	1,3	109		21,1	11,0
168	—	3,4	—	99			3,2
157	12,6	—	—	98	31,6	9,4	67,1
156	—		2,0	97		10,5	9,6

On comparing the mass spectra of the compound obtained (see Fig. 1) and that of D-glucose pentaacetate [3], we found that the natures of the decompositions of the two compounds are similar and that the mass spectra contain three main series of fragments: A, beginning with the splitting off of the substituent from C_1 followed by the elimination of CH_3CO_2H, CH_2O, and $CH_4O_4S_2$ (m/e 383, 323, 263, 229, 221, 211, and 219); B, the origin of which gives a C_2-C_6 fragment formed with the elimination of the substituent at C_3 (m/e 294, 252); and C from C_2-C_4 fragments without a substituent at C_3 (m/e 209, 167).

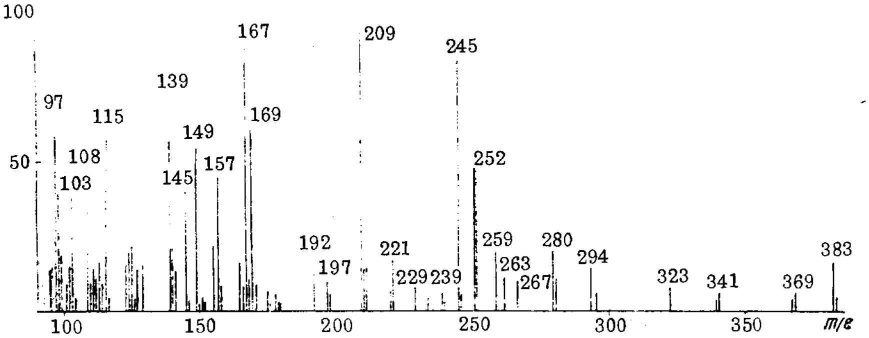

Fig. 1. Mass spectrum of the methyl ester of the 2-sulfate of 1,3,4,6-tetra-O-acetyl-D-glucose (LKB-9000 mass spectrometer).

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The ions with m/e 157 and 115, which are characteristic for full acetates of hexoses, may have a C_4-C_6 composition and be formed from the fragments with m/e 245, containing the C_1, C_4-C_6, and the ethereal oxygen atom. The corresponding two-carbon fragment must be located at m/e 197.

Thus, if the hypotheses on series B and C are correct, the formation of these series depends strongly on the position of the sulfo group which apparently opens up the possibility of determining the position of the sulfo groups in monosaccharides by mass spectrometry.

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