Fraction	$[\alpha]_D^{20}$, deg (*c* 0.5; H_2O)	Uronic anhydride, % [2]	Monosaccharides composition, moles			
			Rham	*Ara*	*Xyl*	*Gal*
A	+150	73	20	3.6	2.3	3.7
B	+190	65.8	14.8	1	1	1.5
C	+165	69.9	19.49	4.1	4.1	4.2

Periodate oxidation was carried out in a neutral medium. The consumption of sodium perchlorate was 0.2 mole per mole of anhydrohexose unit for fraction A, 0.205 for fraction B, and 0.33 for fraction C. On Smith degradation followed by PC (1-butanol—pyridine—water (6:4:3) system; revealing agent: periodate—$KMnO_4$—benzidine), rhamnose, arabinose, galactose, xylose, glycerol, and erythritol, and also galacturonic acid were detected.

The comparatively low consumption of periodate and the presence of unoxidized monosaccharides indicates a branched structure for the pectin.

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3-DEOXYNON-2-ULOSONIC ACID IN THE CAPSULAR POLYSACCHARIDE FROM *Klebsiella ozaenae*

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UDC 547.458+576.8+542.66

The enterobacterium *Klebsiella ozaenae* is the causative agent of a disease of the upper respiratory tracts, ozaena. A polysaccharide has been isolated from the capsule of the microorganism by mechanical degradation and has been purified by ion-exchange chromatography.

The acetylated products of the optimized methanolysis [1] of the polysaccharide were separated by GLC on the liquid phases OV-225, QF-1, and NPGS. A study of the composition of the mixture of methyl glycoside acetates so obtained by the GLC-MS method (QF-1) showed the presence of two minor components: mannose (R_a = 4) and glucosamine (R_a = 5); and of two major components: glucose (R_a^* = 57) and methyl 3-deoxynon-2-ulosonate (I) (R_a^* = 34). The latter, (I) was identified on the basis of the results of a study of mass spectra in comparison with the spectrum of the deuterium analog (II) and results on the breakdown under electron impact from the octoanalogs [2].

The mass spectrum of (I) in the characteristic region (above m/z 150) was due to the decomposition of molecular ions (M^+) of three types (1, 2, and 3) into five large fragments: P, A, E, B, and D. This fragmentation was accompanied by the loss of ketene and acetic acid molecules and of acetyl and acetoxy radicals, which gave a complex mass-spectral pattern.

The splitting out of the substituents of the pyranose ring S_1 and S_2 from the branched C_2 and C_6 atoms of the M^+ ions of types 2 and 1 explains the high content of oxonium ions of the P, A, and E series. In the spectrum of the deuterium analog (II) the ions of series D, P, and A are responsible for peaks 3 m.u., and the ions of series B and E 6 m.u., higher than in the spectrum of (I). Among the fragments mentioned, only ions B and D arise as the result of the breakdown of the pyranose ring of (I) and form an inconsiderable fraction of the ion

*Sum of the R_a values of the anomers and forms.

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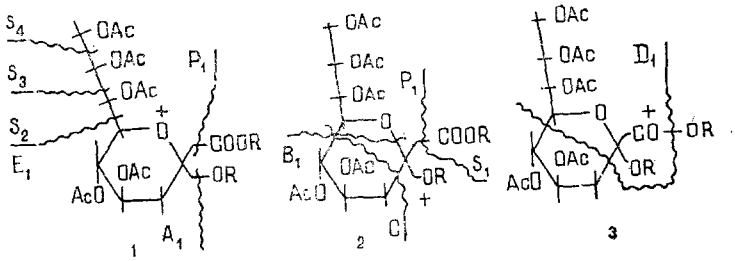
current, while in the case of the neutral aldoses the M^+ ions of type 4, in which the charge is distributed over the carbonyl oxygen atoms of the acetoxy groups, predominate. Consequently, two-carbon (H) and three-carbon (G) fragments, including different units of the monosaccharide ring, predominate among the ionic products of their breakdown, and the ions of series C, the C-2—C-5 unit, in the case of the hexoses. The pyranose ring of (I) and that of 2-deoxyglucose tetraacetate (III) [3] are identical. The mass spectrum of neither of these compounds contains the peaks of series C. In the spectrum of (I) the proportion of ions H (m/z 144, 102) and G (m/z 157, 115, 98, 97) is considerably smaller than in the spectra of the neutral aldoses. This is in spite of the fact that part of the ion current of the peaks mentioned may be due to the side-chain ions S_2 and S_3. The smaller amounts of the M^+ ion of type 4 also appear in a decreased proportion of the acetoxonium ions **a**, **b**, and **c** on passing from (I) to (III). The height of the m/z 43 peak in the spectrum of (I) is four times greater than the height of the second peak in the spectrum, m/z 447 (P_1), while in the neutral aldoses this ratio is greater than 10.



I. R = CH_3

II. R = CD_3

H, $C_2H_2(OAc)_2^+$

G, $C_3H_3(OAc)_2^+$

a, Ac^+

b, Ac_2O^+

c, Ac_3O^+

The breakdown of M^+ of compound (I) also takes place by other pathways but the charge remains on the C_1—C_2 unit of the molecule, since in the spectrum of (I) there are appreciable peaks with m/z 167, 141, 139, 111, and 99 that are shifted by 3 m.u. in the spectrum of (II).

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