POLYSACCHARIDES OF *Eremurus*. XIV. STRUCTURE OF THE GLUCOMANNAN FROM *E. turkestanicus*

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The isolation of a water-soluble polysaccharide (PS) from the tuberous roots of *Eremurus turkestanicus* Regel. has been reported previously [1]. The PS was found to consist mainly of mannose (Man), glucose (Glc), and small amounts of arabinose (Ara), galactose (Gal), and uronic acids. Assuming that the PS is a mixture of neutral and a small amount of acid sugars, we separated it by chromatography on DEAE-cellulose (CO_3^{2-} form) into fractions A and B. The polysaccharide of fraction A, eluted with water, amounted to 66%. On its acid hydrolysis, Glc and Man were detected. Fraction B was eluted with 1 M CH_3COONa with a yield of 8%. It consisted of Ara, Man, Glc, Gal, and a uronic acid. Gel filtration of the PS of fraction A on a column of Sephadex G-200 showed its polydisperity. The further separation of the PS was carried out by fractional precipitation with ethanol from aqueous solution. This gave three fractions with yields of 58% (A_1), 20% (A_2), and 10% (A_3). All the fractions had negative rotations, contained O-C groups, and consisted of acetylated glucomannans with different ratios of Glc and Man. When the O-Ac groups were split off by the action of Fehling's reagent or sodium hydroxide, the glucomannans lost their gelling properties and their solubility in water. The glucomannans of the A_1 and A_2 fractions were homogeneous (according to the results of gel filtration on Sephadex G-200, and also of ultracentrifugation) and had mol. wts. of 115,000 and 97,000, respectively.

The structure of the glucomannan of fraction A_1 was studied by the methods of periodate oxidation, methylation, and partial hydrolysis. On the oxidation of the glucomannan, the consumption of $NaIO_4$ was 0.8 mole per anhydro unit. The products of the Smith cleavage of the glucomannan [2] were erythritol, and traces of Man and glycerol.

To determine the configurations of the glycosidic bonds, the glucomannan was first acetylated [3] and subjected to oxidation with chromium trioxide [4]. The oxidation products contained only traces of Man and Glc, which shows the predominance of β-glycosidic bonds.

The methylation of the glucomannan by the methods of Haworth [5] and of Purdie [6] gave a permethylate with $[\alpha]_D^{20}$ −21.5° (c 1.0; chloroform), with 44.3% of OCH_3 groups, from which after formolysis and hydrolysis, a mixture of methylated hexoses containing, according to results of TLC and GLC [7] of the corresponding polyol acetates, 2,3,6-tri-O-methylmannose and 2,3,6-tri-O-methylglucose in a ratio of 3.4:1, and traces of 2,3,4,6-tetra-O-methylmannose and 2,3,4,6-tetra-O-methylglucose.

In order to ascertain the distribution of the Man and Glc in the glucomannan molecule, we studied the structure of the oligosaccharide fragments formed as the result of the partial cleavage of the glycosidic bonds (0.5 N H_2SO_4, 90°C, 2 h):

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Oligosaccharide	R_f (PC relative to D-mannose)	Monosaccharide composition	Degree of polymerization	Reducing end	Structure of oligosaccharide
A	0.87	Glc-Man, 1 : 1	2	Man	β-D-Glcp-(1 → 4)-D-Manp
B	0.76	Man	2	Man	β-D-Manp-(1→4)-D-Manp
C	0.48	Man-Glc, 1:1	2	Glc	β-D-Manp-(1 →4)-D-Glcp
D	0.38	Glc-Man, 1 :2	3	Man	β-D-Manp-(1→ 4)-β-D-Glcp--(1 → 4)-D-Manp
E	0.32	Man	3	Man	β-D-Manp-(1 → 4)-β-D-Manp-(1 → 4)-D-Manp
F	0.24	Man-Glc, 2 :1	3	Glc	β-Manp-(1 →4)-β-D-Manp-(1 → 4)-Glcp
G	0.14	Man-Glc, 3 :1	4	Man	β-D-Manp-(1 → 4)-β-D-Manp-(1→ 4)-β-D-Glcp-(1→4)-D-Manp
H	0.07	Man	4	Man	β-D-Manp-[(1 → 4)-β-D-Manp]$_2$-(1 →4)-D-Manp

In a hydrolysate, in addition to Glc and Man were detected a number of oligosaccharides (A-3). The hydrolysate was fractionated with aqueous ethanol on a column (carbon-Celite). Individual oligosaccharides were obtained by preparative PC. The homogeneity of the oligosaccharides isolated was determined by PC [8], and their structures were established by studying the products of 1) complete and partial acid hydrolysis of the oligosaccharide before and after reduction with $NaBH_4$; 2) periodate oxidation; and 3) methylation. Oligosaccharides B and E were converted into the completely acetylated N-n-polyglycosylamines [9]. It was shown with the aid of mass spectrometry that substance B was a disaccharide and E a trisaccharide.

Such a set of oligosaccharides shows that the basis of the glucomannan molecule is a linear chain constructed of glucopyranose and mannopyranose residues with β-1 → 4 bonds. The glucomannan contains the following carbohydrate chain fragments: -[D-Manp-(1 → 4)-D-Manp-(1 → 4)-D-Glcp-(1 → 4)-D-Manp-(1 → 4)-D-Manp(1 → 4)-D-Manp-(1 → 4)-D-Manp-(1 → 4)-D-Glcp]$_n$-; -[Glcp-Manp-Manp-Glcp-Manp-Manp-Manp-Manp-]$_n$-

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