## BRIEF COMMUNICATIONS

# THE STRUCTURE OF THE GLUCOMANNAN FROM *Eremurus altaicus*

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Continuing an investigation of the glucomannan from the tuberous roots of E. altaicus Pall (Stev.) [1], we fractionated the initial polysaccharide (100 ml of a 1% solution) by precipitation with ethanol (50-ml portions). The precipitate deposited was separated by centrifuging, washed with ethanol, acetone, and ether, and dried in vacuum over $P_2O_5$. Another 50 ml of ethanol was added to the supernatant liquid and the precipitate was treated similarly. The operation was repeated until all the polysaccharides had been precipitated. The yields of the fractions were: I – 0.51 g; II – 0.25 g; III and IV – 0.13 g. Chromatography of hydrolyzates of the polysaccharide purified through the copper complex (CPP) and also of fractions I and II showed their identity.

The presence in the IR spectra of fractions I and II of absorption in the 1735 and 1250 $cm^{-1}$ regions (which are absent from the CPP) is explained by the presence of O–acetyl (O–Ac) groups as described for the glucomannan of Lilium auratum [2]. The glucomannan contains 4.4% of O–Ac groups and on deacetylation it becomes insoluble in water. To determine the O–Ac groups, a sample of the polysaccharide (50 mg) was hydrolyzed with 1 N HCl in a sealed tube (30 min). The hydrolyzate was treated with ether and the extract was made alkaline with diethylamine, concentrated, chromatographed on paper [3], and the substance was shown to be identical with acetic acid ($R_f$ 0.28).

A sample (0.5 g) of the CPP was oxidized with a 0.03 M solution of $NaIO_4$ and was then reduced with sodium tetrahydroborate and hydrolyzed with 0.5 N $H_2SO_4$ (8 h). Mannose, glucose, erythritol, and glycerol were found in the hydrolyzate.

The acetylated glucomannan (42.8% of O–Ac) was methylated twice by Haworth's method [4] and once by Hakomori's method [5]. The products contained 41.2% of $OCH_3$ groups, $[\alpha]_D^{23}$ –16.6° (c 0.9; $CHCl_3$). On a chromatogram [TLC, KSK silica gel (methyl ethyl ketone–1% ammonia (30:4)], di-, tri-, and tetra-O-methylhexoses were detected: The tetra compounds were identified as 2,3,4,6-tetra-O-methyl-D-mannose and 2,3,4,6-tetra-O-methyl-D-glucose.

TABLE 1. Oligosaccharides Formed in the Partial Hydrolysis of the Glucomannan

| Oligosaccharide | Chromatographic mobility | | Monomeric composition | Reducing end | DP |
|---|---|---|---|---|---|
| | $R_m^*$(PC) | $M_{Cel}^*$(PE) | | | |
| A. 4-O-β-*D*-Glcp*D*-Manp | 0,8 | 2,2 | Glc Man | Man | 2 |
| B 4-O-β-*D*-Manp-*D*-Manp | 0,61 | 2,8 | Man | Man | 2 |
| C 4-O-β-*D*-Manp-*D*- Glcp | 0,48 | 2,0 | Glc Man | Gl | 2 |
| D O-β-*D*-Manp-(1→4)-O-β-*D*-Manp-(1→4) -*D*-Manp | 0,32 | 3,9 | Man | Man | 3 |
| E† | — | 1,1 | | — | — |
| F† | — | — | Glc Man | — | — |

*$R_m$ with respect to mannose; $M_{Cel}$ with respect to cellobiose.
† The structure of E and F are being investigated.

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In the products of partial acid hydrolysis (45% formic acid, 2.5 h), in addition to glucose and mannose a series of oligosaccharides was detected. Six of them (A-F) were isolated in the chromatographically and electrophoretically pure form by fractionation on a column (carbon–Celite 535) and by comparative paper chromatography (PC) in the butan-1-ol–pyridine–water (6:4:3) system. Paper electrophoresis (PE) was performed in a 0.05 M solution of $Na_2B_4O_7 \cdot 10H_2O$, pH 9.2, 400 V, and 4 h. The degree of polymerization (DP) of the oligosaccharides was determined by the method of Peat et al., (Table 1).

Thus, the results of periodate oxidation, methylation, and partial acid hydrolysis show that the glucomannan, which contains O–acetyl groups, consists mainly of $\beta$-1 → 4-linked aldohexopyranose residues of mannose and glucose having a very small degree of branching, both mannose and glucose being found at the reducing ends. The chain of the glucomannan possibly has alternating hexose sections: -[-Manp-Glcp-Manp-Manp-Manp-]$_n$-.

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# THE POLYSACCHARIDES OF PLANTS OF THE GENUS *Eremurus*


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Continuing a study of the chemical composition of the polysaccharides (PSs) of *Eremurus* (desert candle) [1-3], we have investigated the amount of PSs in eight of its species.

The dried and comminuted tuberous roots (20-30 g) which had been treated with ethanol were extracted with water (1:40) for 3 h. The extract was poured into a double volume of ethanol, the precipitate that deposited was dissolved in water and dialyzed against distilled water, and the protein impurities were eliminated by Sevag's method [4]. The PSs were precipitated from the solution with ethanol, and the precipitate was dehydrated with acetone, washed with ether, and dried over $P_2O_5$. Information on the polysaccharide contents are given in Table 1.

Samples of the PSs consist of white fibrous powders with a creamy tinge containing no nitrogen. They are soluble in water, forming sticky highly opalescent solutions which give a cherry-red color coloration with a 0.1 N solution of iodine and are converted into gels on standing. To determine the qualitative carbohydrate composition, the PSs (0.05-0.1 g) were subjected to complete acid hydrolysis (2 N $H_2SO_4$ at 100°C for 8 h). The hydrolyzate was neutralized with $BaCO_3$. The precipitate was filtered off and washed with hot water until the washings gave a negative reaction for carbohydrates (phenol–sulfuric acid). The filtrate and the washing solutions were combined, treated with Amberlite IR-120 ($H^+$), and evaporated to 0.5-1 ml. This concentrate was studied by descending PC [butan-1-ol–pyridine–water (6:4:3)] and by paper electrophoresis (0.05 M $Na_2B_4O_7 \cdot 10\ H_2O$, 20-25 mA, 200 V). The chromogenic agent was aniline hydrogen phthalate. As a result, we identified glucose and mannose. Thus, the polysaccharides of the species that we studied are glucomannans, like those which we


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