## BRIEF COMMUNICATIONS

# POLYSACCHARIDES OF *Polygonatum*.

# V. ISOLATION AND CHARACTERIZATION OF THE GLUCOMANNANS OF *P. polyanthemum*

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Some species of the genus *Polygonatum* are used as medicinal plants [1, 2]. We have investigated *P. polyanthemum* (Bieb) A. Dietr. [Caucasian Solomon's seal] collected on the eastern slopes of the mountain region of Kislovodsk for its content of water-soluble polysaccharides (PSs). The extraction and purification of the polysaccharides was carried out as described previously [3]. The polysaccharides were hydrolyzed (2 N $H_2SO_4$, 100°C, 8 h), and the hydrolysis products were studied by PC and GLC with markers [3], the compositions of the PSs being given below (% on the air-dry weight of the raw material):

| Plant organ | PSs | Ratio of the monosaccharides | | | | | |
|---|---|---|---|---|---|---|---|
| | | *Rham* | *Ara* | *Xyl* | *Man* | *Glc* | *Gal* |
| Leaves | 2.6 | 2.5 | 8.0 | 1.1 | 1.1 | 1.0 | 19.5 |
| Stem | 1.8 | 4.1 | 1.0 | 9.6 | 2.0 | 1.5 | 16.2 |
| Rhizomes | 10.1 | 1.0 | 4.1 | 1.0 | 71.4 | 9.8 | 9.6 |
| Roots | 0.4 | 1.0 | 1.7 | 5.5 | 39.0 | 2.3 | 10.5 |

In addition to the monosaccharides given above, a uronic acid was detected in all the polysaccharide hydrolysates. The polysaccharides of different organs differed in their monosaccharide ratios. The quantitatively predominant component in the polysaccharides of the epigeal part was galactose, and in the roots and rhizomes it was mannose. The largest amount of polysaccharide was found in the rhizomes, and this was subjected to further study. The polysaccharide from the rhizomes was purified by column chromatography on DEAE-cellulose. The polysaccharide eluted by water amounted to 45% of the initial polysaccharide (neutral polysaccharide). The neutral polysaccharide was treated with 70% ethanol. The solution gave a 20% yield of polysaccharide (fraction A), and the precipitate 76% (fraction B). A hydrolysate of fraction A contained glucose and mannose in a ratio of 1:12.8. This ratio remained unchanged when the polysaccharide was fractionated by Fehling's reagent. Consequently, fraction A was a glucomannan.

Fraction B was subjected to fractional precipitation with ethanol. Four fractions were obtained, $B_1$, $B_2$, $B_3$, and $B_4$, with yields of 25.0, 43.0, 6.5, and 5.0%, respectively.

A hydrolysate of fraction $B_1$ was found to contain arabinose, xylose, mannose, galactose, and traces of rhamnose and glucose. In the products of the hydrolysis of fractions $B_2$ and $B_3$, glucose and mannose were detected in ratios of 1:10.2 and 1:6.6, respectively. The IR spectra of the glucomannans (A, $B_2$, and $B_3$) contained absorption bands at 890 $cm^{-1}$ (β-glucosidic bonds), 815 $cm^{-1}$ (pyranose ring), and 1250 and 1740 $cm^{-1}$ (ester group).

When a peracetate of glucomannan $B_2$ was oxidized with chromium trioxide [4], it was found that all the sugar residues underwent oxidation. This shows the presence of β-glycosidic bonds.

To establish the types of bonds between the monosaccharides, glucomannan $B_2$ was methylated by Hakomori's method [5]. This gave a permethylate with $[\alpha]_D^{20}$ −15° (c 1.0; acetone), the IR spectrum of which contained no absorption of OH groups. The glucomannan permethylate was subjected to formolysis and to hydrolysis. The hydrolysis product (in the form of polyol acetates) was studied by TLC and GLC, and 2,3,6-tri-O-methyl-D-glucose and 2,3,6-tri-O-methyl-D-mannose were found in a ratio of 1:10.2 with traces of 2,3,4,6-tetra-O-methyl-D-mannose.

Consequently, the bulk of the water-soluble polysaccharide consists of a mixture of three glucomannans acetylated in the native state.

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The results of methylation, chromium trioxide oxidation, and IR spectroscopy show that glucomannan $B_2$ has a linear chain with β–(1 → 4) bonds and differs from the glucomannans studied previously [6] by the ratio of monosaccharides.

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# THE STRUCTURE OF THE INULIN FROM *Inula grandis*


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Polysaccharides of the inulin type include fructans consisting of β–(2 → 1)-linked fructose units with a nonreducing glucose residue. The molecular weights and amounts of glucose in inulins from different plant sources are different.

The structure of the inulin isolated previously from *Inula grandis* Schrenk has not been studied in detail [1]. Here we give some information on its structure.

The initial inulin had $[\alpha]_D^{20}$ −38° (c 0.2; $H_2O$). When it was subjected to gel chromatography on a column of Sephadex G-75, three peaks were obtained corresponding to fractions with molecular weights of 5670, 10,000, and 16,000 and having specific rotations of −26°, −37°, and −40°, respectively. The fraction present in largest amount was represented by the peak corresponding to a molecular weight of 5670, and we studied this fraction. By paper chromatography, in the products of the complete acid hydrolysis of the inulin we detected fructose, identified in the form of isopropylidene derivative [2], and glucose. The quantitative amount of fructose was 97.3% [3]. The IR spectrum of the inulin had absorption bands at 820, 860, and 940 $cm^{-1}$, which are characteristic for 2 → 1 bonds [4]. The $^{13}C$ NMR spectrum contained signals corresponding to the chemical shifts of β–(2 → 1)-bound fructofuranose units [5].

| $^{13}C$ NMR CSs of inulin | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ |
|---|---|---|---|---|---|---|
| β-(2→1)-bound fructofuranose residues | 61.7 | 103.7 | 77.9 | 75.3 | 81.5 | 62.7 |
| α-D-glucopyranose residues | 93.6 | 73.3 | 73.5 | 70.5 | 72.5 | — |

Periodate oxidation was carried out as described previously [6], the consumption of sodium periodate amounting to 1.01 mole and the amount of formic acid formed being 0.080 mole per anhydro unit.

After Smith degradation, fructose and glycerol were detected by PC and GLC in a ratio of 1:34, which shows the presence of branching at a fructose residue.

Acetylation of the inulin with acetic anhydride in pyridine gave a triacetate of the inulin with $[\alpha]_D^{24}$ −42.5° (c 0.25; chloroform). According to the literature [7], $[\alpha]_D^{20}$ −34° (c 1.5; chloroform).

When a peracetate of the inulin was subjected to chromium trioxide oxidation, no fructose was detected, which shows the β configuration of the glycosidic bonds between the fructofuranose residues [8].


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