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Isolation and Structural Features of Two Glucans from the Rhizomes of *Crinum latifolium**

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In our previous papers, the isolation and the structural features of three highly *O*-acetylated glucomannans from plants in the Amaryllidaceae family have been reported. These glucomannans are characteristic polysaccharides because of their particularly high acetyl contents. For chemotaxonomical reasons, we have studied on polysaccharides of other genus plants in the Amaryllidaceae family. The present paper is concerned with the isolation and the structures of two pure glucans from the fresh rhizomes of *Crinum latifolium* L.

The rhizomes were sliced and extracted with cold water. After precipitation by addition of ethanol, the crude extract obtained was applied to a column of DEAE-cellulose (acetate form). A neutral polysaccharide fraction was obtained from the eluate with water, then the fraction was applied to a column of Sephadex G-50. Elution with water yielded two carbohydrate-containing fractions designated as peaks I and II. Peak I was subjected to rechromatography on the same column and peak II was rechromatographed on a column of Sephadex G-15. Thus, glucans A and B were obtained from peaks II and I, respectively. Glucan B was the only substance in peak I, while the presence of six minor components other than glucan A was observed in the eluates obtained by rechromatography of peak II.

The glucans A and B each gave a single spot on glass-fiber paper electrophoresis in both pyridine-acetic acid buffer and alkaline borate buffer. In addition, glucan A gave a single spot on TLC. Furthermore, each glucan gave a single peak on Sephacryl S-200 gel chromatography. Gel chromatography gave molecular weight values of 2000 for A and 18000 for B. Both substances were readily soluble in water and they showed high positive specific rotations (A, $[\alpha]_D^{24}+160.6°$ in H_2O, $c=1.2$; B, $[\alpha]_D^{24}+181.9°$ in H_2O, $c=0.6$). Glucose was identified as the only component sugar. They contained no nitrogen.

The proton magnetic resonance (^{1}H-NMR) spectra of the glucans showed an acetyl signal at δ 1.92 in A, while no acetyl signal was observed in B. The ^{1}H-NMR spectra also showed anomeric proton signals at δ 5.42 (d, $J=3.5$ Hz) in A and δ 5.40 (d, $J=3.5$ Hz) in B. These data suggest that the glucose residues in A and B are α-linked

The ratio of integrals of acetyl and anomeric proton signals in the ^{1}H-NMR of glucan

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A was 6 : 12. The presence of acetyl groups in glucan A was also confirmed by GLC of the acid hydrolysate, and the acetyl content was determined to be 4.2%. Thus, close agreement of acetyl values as determined by the ^{1}H-NMR and GLC methods was obtained.

Each glucan was methylated with methylsulfinyl carbanion and methyl iodide in dimethyl sulfoxide. The product was hydrolyzed, reduced, and acetylated. The partially methylated glucitol acetates thus obtained were analyzed by GLC–MS. Three peaks were detected on the gas chromatogram in each case. These were identified as 2,3,4,6-tetra-*O*-methyl-, 2,3,6-*O*-methyl-, and 2,3-di-*O*-methyl-D-glucitol acetates in moler ratios of 2.0 : 9.6 : 1.0 from A and 1.0 : 8.9 : 1.0 from B.

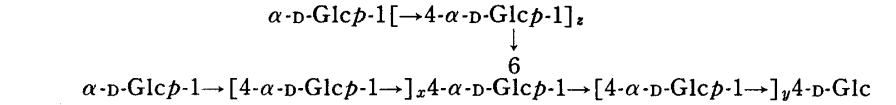
The glucans A and B were oxidized with periodate. It was found that 1.12 mol and 0.92 mol of periodate per mol of component anhydrohexose unit were consumed with liberation of 0.36 mol and 0.06 mol of formic acid by glucans A and B, respectively.

In order to elucidate the locations of the *O*-acetyl groups, glucan A was exhaustively treated with methyl vinyl ether, as a protective reagent for the free hydroxyl groups, in the presence of *p*-toluenesulfonic acid as a catalyst in dimethyl sulfoxide. After conversion of the free hydroxyl groups to 1-methoxyethyl ethers, the derivative was deacetylated, then methylated as described above. The product was hydrolyzed and analyzed by GLC–MS after conversion to alditol acetates. A glucose methyl ether was detected and identified as 2,3-di-*O*-methyl-D-glucose. This result indicates that glucan A is composed of a 2,3-di-*O*-acetyl-D-glucose and eleven D-glucose units.

Glucan B was treated with isoamylase (glycogen 6-glucanohydrolase [3.2.1.68] from *Pseudomonas amyloderamose*), and the reaction products were analyzed by TLC. Ten kinds of oligosaccharides in the range of disaccharide to undecasaccharide were detected. This result indicates that glucan B has various polymerized side chains.

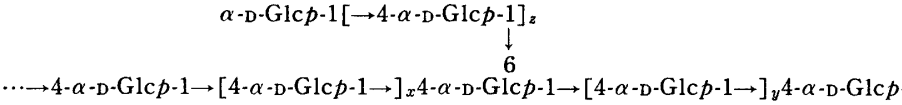
Based on the accumulated evidence described above, the structural features of glucan A are shown in Chart 1, and the average structural unit of glucan B is given in Chart 2.

Among the carbohydrates of higher plants, glucan A, the main water-soluble neutral polysaccharide from the rhizomes of *Crinum latifolium*, is a unique dodecasaccharide having acetyl groups.



($x+y+z=8$; 1/12 unit of D-glucose residues has 2,3-di-*O*-acetyl groups)

Chart 1. Structural Features of Glucan A



(The average value of "$x+y+z$" in the unit is 7; $z=2\sim11$)

Chart 2. Structural Unit of Glucan B