Title	Plant mucilages. XIX. isolation and characterization of a mucous polysaccharide, "lilium-lo-glucomannan," from the bulbs of lilium longiflorum
Sub Title	
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Publisher	共立薬科大学
Publication year	1978
Jtitle	共立薬科大学研究年報 (The annual report of the Kyoritsu College of Pharmacy). No.23 (1978.) ,p.107- 109
JaLC DOI	
Abstract	
Notes	抄録
Genre	Technical Report
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000023-0107

Plant Mucilages. XIX. Isolation and Characterization of a Mucous Polysaccharide, "Lilium-Lo-glucomannan," from the Bulbs of *Lilium longiflorum* *

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The isolations and the structural features of several *O*-acetylated glucomannans from lily bulbs have been reported by us. The present paper is concerned with the isolation and the structure of a pure mucous polysaccharide from the fresh bulbs of *Lilium longiflorum* THUNB. This plant provides a famous ornamental flower.

The material bulbs were crushed and treated with hot methanol, then the residue was extracted with cold water. The crude mucilage was precipitated from the extract by addition of ethanol. The solution of the precipitate was applied to a column of DEAE-cellulose, and a mucous polysaccharide was obtained from the eluate with water. The polysaccharide gave a single spot on glass-fiber paper electrophoresis in alkaline borate buffer, and was found to be homogeneous in the ultracentrifugal analysis. Further, it gave a single peak on gel chromatography with Sephacryl S-200.

The polysaccharide showed an egative specific rotation ($[\alpha]_D^{23}$ -33.2° in H_2O). Its solution in water gave the intrinsic viscosity value of 4.1 at 28°. TLC of the hydrolyzate and GLC of trimethylsilyl derivative of the hydrolyzate revealed that the component sugars are mannose and glucose. Quantitative determination of them showed that the molar ratio of mannose : glucose is about 5 : 2. The measurement of osmotic pressure gave the value of 263000 as the molecular weight of this polysaccharide. The name "Lilium-Lo-glucomannan" is proposed for it.

The methylation of the polysaccharide was performed with methylsulfinylmethyl sodium and methyl iodide in dimethyl sulfoxide. The fully methylated product was successively hydrolyzed, then the products were analyzed by GLC-MS after conversion into the corresponding alditol acetates. As the hydrolysis products of the methylated polysaccharide, 2, 3, 4, 6-tetra-*O*-methyl-D-mannose, 2, 3, 6-tri-*O*-methyl-D-mannose, 2, 3, 6-tri-*O*-methyl-D-glucose, 2, 6-di-*O*-methyl-D-mannose, and 3, 6-di-*O*-methyl-D-mannose were identified and obtained in a molar ratio of 1.0 : 30.4 : 14.0 : 0.3 : 0.6. The identification of the tetra-*O*-methyl mannose was also carried out by GLC as its methyl glycoside.

The polysaccharide consumed 0.99 mol of periodate per anhydrohexose unit with

*本報告は *Chem. Pharm. Bull.* (Tokyo), 26, 2768 - 2773 (1978) に発表。

0.12 mol of formic acid liberation. The periodate-oxidized polysaccharide was treated with sodium borohydride, and the reduction product was isolated by the gel chromatography using a column of Sephadex G-15. The product was hydrolyzed and then converted into alditol acetates. Analyses of them by GLC showed that the yields of erythritol and mannose were 64.0% and 9.6%.

Further, partial acetolysis of the glucomannan was carried out. The sample was suspended in formamide and acetylated with acetic anhydride and pyridine. The product was partially degraded with sulfuric acid in acetic anhydride. After deacetylation, the products were trimethylsilylated and analyzed by GLC. The result showed the presences of *O*-β-D-mannopyranosyl-(1→4)-D-mannopyranose, *O*-β-D-glucopyranosy-(1→4)-D-mannopyranose, *O*-β-D-mannopyranosyl-(1→4)-D-glucopyranose, *O*-β-D-glucopyranosyl-(1→4)-D-glucopyranose, *O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→4)-D-mannopyranose, *O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-mannopyranosyl-(1→4)-D-mannopyranose in addition to the component monosaccharides.

These results indicated that the polysaccharide is mainly composed of β-1→4 linked aldohexose units and has some mannopyranosyl residues as non-reducing terminals and branching points linking through positions 2 or 3 in part. From the value of formic acid liberation after periodate oxidation and the yield of mannose as the Smith degradation product, it is able to conclude that the glucomannan has about ten aldohexose units per one non-reducing group on the average.

The infrared spectrum of this glucomannan has the absorption bands of 1250 cm^{-1} and 1740 cm^{-1} suggesting the presence of ester linkages in addition to the absorption of 890 cm^{-1} being due to β-glycosidic linkages. Analysis of the acid hydrolyzate of the glucomannan by GLC showed the occurrence of acetic acid, and the content of *O*-acetyl groups in the glucomannan was determined to be 3.2 %.

For the elucidation of the location of *O*-acetyl groups, the polysaccharide was repeatedly treated with methyl vinyl ether in the presence of *p*-toluenesulfonic acid in dimethyl sulfoxide. After conversion of the free hydroxyl groups into 1-methoxyethyl ethers, the derivative was deacetylated with methanolic sodium methoxide, then methylated with methyl iodide and silver oxide in *N,N*-dimethylformamide, The resultant product was subjected to acid hydrolysis, and the final products were analyzed by GLC-MS after conversion into alditol acetates. Six hexose methyl ethers were detected and identified.

These results indicate that the residues of 6-mono-*O*-acetyl-D-mannopyranose, 6-mono-*O*-acetyl-D-glucopyranose, 2,6-di-*O*-acetyl-D-mannopyranose, 3,6-di-*O*-acetyl-D-mannopyranose, 2,3,6-tri-*O*-acetyl-D-mannopyranose, and 2,3,6-tri-*O*-acetyl-D-glucopyranose are partially present in the glucomannan. All the results indicated that the manner of sequence of component sugars in the main chain and the type of branching were similar to those of Lilium-La-glucomannan. However, Lilium-Lo-glucoman-

nan has different *O*-acetylated hexopyranose units from Lilium-A-glucomannan, Lilium-S-glucomannan, and Lilium-La-glucomannan. The present report is the second example describing the presences of partially 2, 3, 6-tri-*O*-acetylated D-mannopyranosyl and D-glucopyranosyl units in natural glucomannnans.