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Author	友田, 正司(Tomoda, Masashi) 金子, 幸子(Kaneko, Sachiko)
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Plant Mucilages. XIII. Isolation and Characterization of a Mucous Polysaccharide, "Lilium-S-glucomannan", from the Bulbs of *Lilium speciosum* *

MASASHI TOMODA and SACHIKO KANEKO

友田正司, 金子幸子

In a previous paper of this series, the isolation and the structural feature of a glucomannan from the bulbs of *Lilium auratum* have been reported by us and the necessity of reinvestigation of the presence of O-acetyl groups in the native Lilium glucomannans was pointed out. Now we obtained a new pure mucous polysaccharide from the fresh bulbs of *Lilium speciosum* THUNB., and its properties are described in the present paper.

After treatment with hot methanol, the crushed bulbs were 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 (carbonate form), 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 homogeneous when analyzed by the ultracentrifugal analysis.

The polysaccharide showed a negative specific rotation. Its solution in water gave the intrinsic viscosity value of 6.6 at 25°. Cellulose thin-layer chromatography of the hydrolysate and gas-liquid chromatography (GLC) of trimethylsilyl derivative of the methanolysate of the polysaccharide revealed that its component sugars are mannose and glucose. Quantitative determination of them showed that the molar ratio of mannose : glucose is 2 : 1. The measurement of osmotic pressure gave the value of 388000 as the molecular weight of the polysaccharide.

Its infrared spectrum has the absorption bands suggesting the presence of ester linkages. When the acid hydrolysate of the polysaccharide was analyzed by GLC, it gave one peak, whose retention time was the same as that of authentic sample of acetic acid. The acetyl content of the polysaccharide was determined to be 2.0% by GLC. The name "Lilium-S-glucomannan" is proposed for the polysaccharide.

The methylation of the polysaccharide was performed with sodium methylsulfinyl carbanion and methyl iodide in dimethylsulfoxide. The fully methylated product was formolyzed and hydrolyzed, then analyzed by gas-liquid chromatography-mass spectrometry (GLC-MS) after conversion to 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 and 2, 6-di-O-methyl-D-man-

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nose were identified and obtained in a molar ratio of 1.0: 2.2: 1.9: 0.3. The tetra-methyl ether of mannose was also confirmed as its methyl glycoside by GLC.

The periodate-oxidized polysaccharide was treated with sodium borohydride, and the reduction product was obtained after purification with gel chromatography on Sephadex G-15. Analysis of trimethylsilyl derivative of the methanolysate of it by GLC revealed the presences of erythritol and mannose as the main products and the yields of them were 31.6% and 14.9%.

These results indicated that the polysaccharide is mainly composed of 1→4 linked aldohexopyranose units and has some mannopyranose residues as terminals and branching points linking through position 3. From the result of methylation study and the value of quantitative analysis of mannose in Smith degradation product, it is able to conclude that the polysaccharide contains about six aldohexose units per one non-reducing end group.

Partial acetolysis of Lilium-S-glucomannan also gave the evidence that the straight chain parts in the polysaccharide are composed of β-1→4 linked aldohexopyranose residues. The results elucidated the fact that most of D-mannopyranose and D-glucopyranose residues are connected one another by β-1→4 glycosidic linkages and, on the whole, the manner of sequence of the main chain is similar to those of Bletilla-glucomannan and Lilium-A-glucomannan.

The method of de Belder and Norrman was applied to the determination of the location of O-acetyl groups. Because the polysaccharide is hardly soluble in dimethylsulfoxide, the sample was digested with a hemicellulase preparation. After gel chromatography using a column of Sephadex G-15, the partially degraded polysaccharide having all ester linkages was isolated. It was dissolved in dimethylsulfoxide and treated with methyl vinyl ether in the presence of *p*-toluenesulfonic acid for conversion of the free hydroxyl groups to 1-methoxyethyl ethers. The derivative was deacetylated by refluxing with methanolic sodium methoxide, then methylated with methyl iodide and silver oxide in dimethylformamide. The resulting product was subjected to acid hydrolysis, and the the final products were analyzed by GLC-MS of the alditol acetate after reduction and acetylation of the hydrolysate and by paper partition chromatography of it. Besides mannose and glucose, a hexose methyl ether was detected and identified as 3,6-di-O-methyl-D-mannopyranose. None of hexose monomethyl ether was detected as the product of these reactions. Owing to this result, it is able to conclude that the O-acetyl groups are attached to positions 3 and 6 of a part of D-mannopyranose units in the polysaccharide. The value of quantitative analysis indicated that one mannose residue in about twenty-six component hexose units has 3, 6-di-O-acetyl group.

The presence of O-acetyl groups in native glucomannans from lily bulbs and the fact that deacetylation of them causes the insolubility of the products in water have

been already pointed out by us and the other investigators, so the location of O-acetyl groups in native polysaccharides is an interesting problem in connection with their properties. Lilium-S-glucomannan has 3, 6-di-O-acetylated D-mannopyranosyl units and β-1→4 linked aldohexose main chains just as Lilium-A-glucomannan, although the two glucomannans possess respectively different types of branching and widely different values of molecular weight.