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Plant Mucilages. XXI. Isolation and Characterization of a Mucous Polysaccharide, "Lilium-Ma-glucomannan," from the Bulbs of *Lilium maculatum* *

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In the previous papers of this series, the structural features of *O*-acetylated glucomannans from the bulbs of *Lilium auratum, Lilium speciosum, Lilium lancifolium,* and *Lilum longiflorum* have been reported from this laboratory. Now we obtained a new mucous polysaccharide from the fresh bulbs of *Lilium maculatum* THUNB. This paper is concerned with its properties and structure.

After treatment with hot methanol, the material was extracted with cold water. The crude mucilage obtained was applied to a column of DEAE-cellulose, and a mucous polysaccharide was isolated from the eluate with water. It gave a single spot on glass-fiber paper electrophoresis in alkaline borate buffer, and was found to be homogeneous when analyzed by the ultracentrifugal analysis.

The substance showed a negative specific rotation ($[\alpha]_D^{24}$ −32.4°in H_2O). Its solution in water gave the intrinsic viscosity value of 5.6 at 28°. Mannose and glucose were identified as the component sugars by means of TLC of the hydrolyzate and GLC of its trimethylsilyl derivative. Quantitative determination of them showed that the molar ratio of mannose: glucose is 7 : 4. The measurement of osmotic pressure gave the value of 184000 as the molecular weight of the polysaccharide. The name "Lilium-Ma-glucomannan" is proposed for it.

The glucomannan was methylated with methylsulfinylmethyl sodium in dimethyl sulfoxide and methyl iodide. The fully methylated product was hydrolyzed and analyzed by GLC-MS after conversion into 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 : 19.0 : 11.5 : 0.4 : 0.3. The tetramethyl ether of mannose was also confirmed as its methyl glycoside by GLC.

As the result of periodate oxidation, 0.97 mol of periodate per one mol of component anhydro sugar unit of the glucomannan was consumed with 0.15 mol of formic acid liberation. The periodate-oxidized polysaccharide was reduced and hydrolyzed.

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Analysis of the products showed that the yields of erythritol and mannose were 61.5 % and 15.1 %.

On the other hand, partial acetolysis of the glucomannan was carried out. The sample was acetylated, then partially degraded with sulfuric acid in acetic anhydride. After deacetylation, the products were applied to HPLC, and the fractions obtained were analyzed by TLC and by GLC of trimethylsilyl derivatives. The comparison with authentic samples showed the presences of *O*-β-D-mannopyranosyl-(1→4)-D-mannopyranose, *O*-β-D-glucopyranosyl-(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-mannopyranosyl-(1→4)-D-mannopyranose, *O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→4)-D-mannopyranose, and *O*-β-D-mannopyranosyl-(1→4)-*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 glucomannan is mainly composed of β-1→4 linked aldohexose units and has some mannopyranose residues as 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 seven aldohexose units per one non-reducing group on the average.

The infrared spectrum of the 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 it by GLC showed the occurrence of acetic acid. The acetyl content of the glucomannan was determined to be 4.7% by GLC.

After conversion of the free hydroxyl groups in the glucomannan into 1-methoxyethyl ethers by the exhaustive treatment with methyl vinyl ether in the presence of *p*-toluenesulfonic acid in dimethyl sulfoxide, the derivative was deacetylated, then methylated by Kuhn method. The resulting product was hydrolyzed and analyzed by GLC-MS after conversion into alditol acetates. Seven hexose methyl ethers were detected and identified.

Based on this result, it is able to conclude that the residues of 2-mono-*O*-acetyl-D-mannose, 3-mono-*O*-acetyl-D-mannose, 6-mono-*O*-acetyl-D-mannoso, 6-mono-*O*-acetyl-D-glucose, 3,6-di-*O*-acetyl-D-mannose, 2,3,6-tri-*O*-acetyl-D-mannose, and 2,3,6-tri-*O*-acetyl-D-glucose are partially present in Lilium-Ma-glucomannan. We have already reported the presence of partially 2,3,6-tri-*O*-acetylated D-manno- and D-gluco-pyranosyl units in addition to several di- and mono-*O*-acetylated hexose residues in the glucomannan isolated from the bulbs of *Lilium longiflorum*. Thus this is the second example showing the presence of partially tri-*O*-acetylated hexose units in lily glucomannans.