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Plant Mucilages. XIV. Isolation and Characterization of a Mucous Polysaccharide, "Lilium-La-glucomannan" from the Bulbs of *Lilium lancifolium* *

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Water-soluble mucous glucomannans have been found in several lily bulbs. The polysaccharides possess β-1→4 glycosidic bonds to form main chains of component sugars, but different types of branching and different values of molecular weight are present in them. The presence and the location of O-acetyl groups in the native glucomannans are also important problems in connection with their properties. In this paper, the isolation and the structural feature of a new pure mucous polysaccharide from the fresh bulbs of *Lilium lancifolium* THUNB. are described. The bulbs have been used as a crude drug for the purpose of analeptic and cough medicine.

The material was crushed and extracted with hot methanol, then the residue was extracted with cold water. The crude mucilage was precipitated from the water 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 found to be homogeneous when analyzed by the ultracentrifugal analysis.

The polysaccharide showed a negative specific rotation. Its solution in water gave the intrinsic viscosity value of 5.1 at 31°. Mannose and glucose were identified as the component sugars by means of cellulose thin-layer chromatography of the hydrolysate and gas-liquid chromatography (GLC) of trimethylsilyl derivative of the hydrolysate in the other condition. Quantitative determination of them showed that the molar ratio of mannose: glucose is 5: 2. The measurement of osmotic pressure gave the value of 417000 as the molecular weight of the polysaccharide. The name "Lilium-La-glucomannan is proposed for it.

The infrared spectrum of it has the absorption bands suggesting the presence of ester linkages in addition to the absorption of 890 cm^{-1} being due to β-glycosidic linkages. When 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 glucomannan was determined to be 1.2% by GLC.

The location of O-acetyl groups in the glucomannan was established by the application of the method of de Belder and Norrman. The polysaccharide was first dige-

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sted with a hemicellulase preparation. The partially degraded polysaccharide having all ester linkages was isolated by the gel chromatography using Sephadex G-25. Then it was dissolved in dimethylsulfoxide and treated with methyl vinyl ether in the presence of *p*-toluenesulfonic acid. The derivative was deacetylated, then methylated with methyl iodide and silver oxide in dimethylformamide. The resulting product was subjected to acid hydrolysis, and the final products were analyzed by paper partition chromatography (PPC) and by gas-liquid chromatography-mass spectrometry (GLC-MS) after conversion to alditol acetates. Besides mannose and glucose, three hexose methyl ethers were detected and identified as 6-mono-O-methyl-D-mannopyranose, 2-mono-O-methyl-D-mannopyranose and 3-mono-O-methyl-D-mannopyranose. The result of GLC showed that the molar ratio of them is 1.0: 0.9: 1.5. Owing to this result, it is able to conclude that the residues of 6-mono-O-acetyl-D-mannopyranose, 2-mono-O-acetyl-D-mannopyranose and 3-mono-O-acetyl-D-mannopyranose are partially present in the molecule of the glucomannan.

The methylation of the glucomannan was performed with sodium methylsulfinyl carbanion and methyl iodide in dimethylsulfoxide. The fully methylated product was hydrolyzed, and the products were separated by PPC. Then they were analyzed by 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, 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: 53.3: 24.5: 0.6: 1.1. The tetramethyl 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 isolated by the gel chromatography using Sephadex G-15. Analysis of alditol acetates derived from its hydrolysate by GLC showed that the yields of erythritol and mannose were 61.4% and 3.6%.

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 positions 2 and 3 in part. From the value of formic acid liberation and the yield of mannose as the hydrolysis product after periodate oxidation, it is able to conclude that the glucomannan has about thirty aldohexose units per one non-reducing group on the average. The yield of tetramethyl ether of mannose was low in comparison with these values. The cause for such a discrepancy may be attributed to unavoidable losses of sugar methyl ethers.

Partial acetolysis of the 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 the manner of sequence of component sugars in the main chain is similar to those of Lilium-A-glucomannan and Lilium-S-

glucomannan. These two glucomannans and Lilium-La-glucomannan all possess D-mannopyranose residues as the branching points and as the terminals in the molecules. However, they have respectively different types of branching, and have different values of molecular weight and of the molar ratio of component sugars. Moreover, there are various values of O-acetyl content in them, and Lilium-La-glucomannan has different O-acetylated D-mannopyranose units from those of the other two lily glucomannans previously obtained by us. Further studies of the mucilages from other lily bulbs are now in progress.