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Plant Mucilages. XXXIII. An Acetyl-Rich Mucilage, "Lycoris-S-glucomannan," from the Bulbs of *Lycoris squamigera**

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The bulbs of *Lycoris squamigera* Maxim. were used as a source of galanthamine. In addition, the isolation of various alkaloids has been reported. The bulbs of this plant also contain many mucous polysaccharides, but no structural study on the mucilages has been reported so far. The present paper is concerned with the isolation and the structural analysis of a pure mucilage from the fresh bulbs of this plant.

The bulbs were sliced 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 crude mucilage obtained was applied to a column of DEAE-cellulose (acetate form), and a mucous polysaccharide was obtained from the eluate with water. The polysaccharide gave a single spot on glass-fiber paper electrophoresis in both a pyridine-acetic acid buffer and an alkaline borate buffer, and was homogeneous as determined by ultracentrifugal analysis. Furthermore, it gave a single peak on gel chromatography with Sephacryl S-400.

The substance was readily soluble in water and it showed a negative specific rotation ($[\alpha]_D^{22}-23.1°$ in H_2O, $c=1.0$). Its aqueous solution gave an intrinsic viscosity value of 3.9 at 30°C. Gel chromatography gave a value of approximately 1800000 for the molecular weight. Mannose and glucose were identified as the component sugars by cellulose TLC of the hydrolysate and by GLC of the trimethylsilyl derivatives. Quantitative determination showed that the molar ratio of mannose : glucose was 7 : 2. The name "Lycoris-S-glucomannan" is proposed for this compound.

The glucomannan was methylated with methylsulfinyl carbanion and methyl iodide in dimethyl sulfoxide. The fully methylated product was hydrolyzed and analyzed by GLC-MS after conversion into alditol acetates, 2,3,4,6-tetra-*O*-methyl-D-mannose, 2,3,4,6-tetra-*O*-methyl-D-glucose, 2,3,6-tri-*O*-methyl-D-mannose, 2,3,6-tri-*O*-methyl-D-glucose, and 2,6-di-*O*-methyl-D-mannose were identified in a molar ratio of 2.0 : 1.0 : 10.5 : 3.5 : 2.9. The identity and the ratio of the two tetra-*O*-methyl hexoses were confirmed by GLC of the methyl glycosides obtained by methanolysis of the methylated product.

Furthermore, the glucomannan was partially hydrolyzed with dilute sulfuric acid. The products were analyzed by TLC and by GLC of the trimethylsilylated derivatives. Comparison with authentic samples showed the presence of D-mannose, D-glucose, *O*-β-D-

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mannopyranosyl-(1→4)-D-mannose, *O*-β-D-mannopyranosyl-(1→4)-D-glucose, *O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→4)-D-mannose, *O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-mannopyranosyl-(1→4)-D-mannose, and *O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-mannopyranosyl-(1→4)-D-mannose.

The infrared spectrum of the glucomannan has absorption bands at 1240 cm^{-1} and 1735 cm^{-1}, suggesting the presence of ester linkages, while the absorption at 870 cm^{-1} is due to β-glycosidic linkages. The ^1H-NMR spectrum showed acetyl signals at δ 1.89 and δ 2.17, and the acetyl content of the glucomannan was determined to be 16.7%. In addition, the glucomannan contains a small quantity of protein. The determination of protein content was carried out by the method of Lowry *et al.*, and a value of 2.5% was obtained.

In order to elucidate the location of *O*-acetyl groups, the glucomannan was exhaustively 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 de-*O*-acetylated, then methylated as described above, and the methylation was completed with methyl iodide and silver oxide in *N,N*-dimethylformamide. The resulting product was hydrolyzed and analyzed by GLC-MS after conversion into alditol acetates. A hexose methyl ether was detected and identified as 2,6-di-*O*-methyl-D-mannose. This result indicates that 2,6-di-*O*-acetyl-D-mannose units are present in the glucomannan.

The glucomannan was treated with dilute alkali solution, and after neutralization, the resulting de-*O*-acetylated product was oxidized with periodate. As a result of the reaction, 0.94 mol of periodate per mol of component anhydrohexose unit was consumed with liberation of 0.12 mol of formic acid. The periodate-oxidized product was reduced, hydrolyzed, and analyzed. The yields of mannose and erythritol were 12.4% and 36.4%, respectively.

Based on these results, it can be concluded that the glucomannan is mainly composed of β-1→4 linked aldohexopyranose units and has both mannopyranose and glucopyranose residues as terminals, and that it has branches at position 3 of some mannopyranose units. The terminal mannopyranose and glucopyranose units, the intermediate β-1→4 linked mannopyranose and glucopyranose units, and mannopyranose units at the branching points must be present in a molar ratio of approximately 4 : 2 : 21 : 7 : 6. Upon partial hydrolysis, β-1→4 linked mannobiose and mannotriose were major oligosaccharides in the products, while no cellobiose was detected as a product. Therefore it is highly probable that the presence of D-glucose residues is discontinuous in the polysaccharide moiety. From the value of acetyl content, it can be presume that about half of the mannose residues carry 2,6-di-*O*-acetyl groups.

Recently, Tomoda *et al.* reported two highly *O*-acetylated glucomannans from plants in the Amaryllidaceae family, namely, the bulbs of *Narcissus tazetta* L. var. *chinensis*

ROEMER and *Lycoris radiata* HERDERT. Lycoris-S-glucomannan is the third example of acetyl-rich glucomannans from the bulbs of plants in the Amaryllidaceae family. This substance has both mannopyranose units and glucopyranose units as terminals, and contains a small amount of protein. In addition, the glucose content in it was relatively high, while the molar ratios of mannose and glucose were 5 : 1 in Narcissus-T-glucomannan and 12 : 1 in Lycoris-R-glucomannan. However, the latter two glucomannans contain no protein, and they have no glucose residue terminals. It is interesting that these three acetyl-rich glucomannans possess 2,6-di-*O*-acetyl-D-mannose residues in common, although Narcissus-T-glucomannan has about half 6-*O*-acetyl-D-mannose units in addition. Further studies on the mucilages from other plants in the Amaryllidaceae family are in progress.