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Plant Mucilages. XXVII. Isolation and Characterization of a Mucous Polysaccharide, "Narcissus-T-glucomannan", from the Bulbs of *Narcissus tazetta* var. *chinensis**

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Narcissus tazetta L. var. *chinensis* Roemer provides an ornamental flower. The bulb of this plant has been used as a crude drug to treat tumors of the breast. We have now obtained a native pure mucous polysaccharide from the fresh bulbs of this plant, and its properties and structural features are described in the present paper.

The bulbs were crushed and extracted with cold water after treatment with hot methanol. 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 was homogeneous as determined by ultracentrifugal analysis, and gave a single spot on glass-fiber paper electrophoresis in both a pyridine-acetic acid buffer and an alkaline borate buffer. Furthermore, it gave a single peak on gel chromatography with Sephacryl S-200.

The substance was readily soluble in water and it showed a negative specific rotation ($[\alpha]_D^{20}$ $-24.3°$ in H_2O, $c=1.0$). Its solution in water gave an intrinsic viscosity value of 2.6 at 30°. Gel chromatography gave a value of approximately 119000 for the molecular weight. Mannose and glucose were identified as the component sugars by cellulose thin-layer chromatography (TLC) of the hydrolysate and by gas-liquid chromatography (GLC) of the trimethylsilyl derivatives. Quantitative determination showed that the molar ratio of mannose: glucose was 5: 1. The name "Narcissus-T-glucomannan" is proposed for this compound.

The infrared spectrum of the glucomannan has absorption bands at 1250 cm^{-1} and 1740 cm^{-1}, suggesting the presence of ester linkages in addition to the absorption of 890 cm^{-1}, which is due to β-glycosidic linkages. The proton magnetic resonance (^{1}H-NMR) spectrum showed an acetyl signal at δ 1.92, and the acetyl content of the glucomannan was determined to be 22.7%.

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 deacetylated, then methylated with methyl iodide and silver oxide in *N*,*N*-dimethylformamide. The resulting product was hydrolyzed and analyzed by GLC and gas-liquid chromatography-mass spectrometry (GLC–MS) after conversion into

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alditol acetates. Two hexose methyl ethers were detected and identified as 6-*O*-methyl-D-mannose and 2,6-di-*O*-methyl-D-mannose in a molar ratio of 1.0: 2.0. In addition, free D-mannose and D-glucose were detected in the hydrolysate in a molar ratio of 1.0: 1.1. These results indicate that many residues of 6-*O*-acetyl-D-mannose and 2,6-di-*O*-acetyl-D-mannose are present in the glucomannan.

The glucomannan was methylated with methylsulfinylmethyl sodium and methyl iodide in dimethyl sulfoxide. The fully methylated product was hydrolyzed and analyzed by GLC–MS after conversion into alditol acetate; 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-mannose were identified in a molar ratio of 1.3: 30.7: 6.7: 1.0. The identity of the tetra-*O*-methyl mannose was also confirmed by GLC of its methyl glycoside.

In order to avoid the blocking effect of *O*-acetyl groups, the original glucomannan was treated with dilute alkali solution, and the water-insoluble deacetylated polysaccharide thus obtained was oxidized with periodate under stirring. In this periodate oxidation, 1.06 mol of periodate per mol of component anhydro sugar unit was consumed with liberation of 0.05 mol of formic acid. The periodate-oxidized product was reduced, hydrolyzed, and analyzed. The yields of mannose and erythritol were 2.4% and 68.7%.

On the other hand, the glucomannan was peracetylated with acetic anhydride and pyridine in formamide, then partially degraded with sulfuric acid in acetic anhydride. After deacetylation, the products were analyzed by TLC and by GLC of trimethylsilylated derivatives. Comparison with authentic samples showed the presence of D-mannose, D-glucose, *O*-β-D-mannopyranosyl-(1→4)-D-mannopyranose, *O*-β-D-mannopyranosyl-(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. The relative yield ratios of these mono-, di-, and trisaccharides were 16.6: 7.8: 45.8: 5.1: 20.3: 4.4.

In addition, the glucomannan was treated with a β-D-mannanase obtained from Driselase (Kyowa Hakko Kogyo Co.) prepared from culture solutions of *Irpex lacteus*. The products were analyzed as described above, and the results showed the presence of D-mannose, D-glucose, β-D-1→4-linked mannobiose, β-D-1→4-linked glucosyl mannose, β-D-1→4-linked mannotriose, and β-D-1→4-linked mannosyl glucosyl mannose in relative yield ratios of 4.9: 6.0: 59.1: 6.6: 22.4: 1.0. The appearance of free glucose is probably due to the coexistence of a β-D-glucanase activity in the enzyme preparation.

Based on these results, it can be concluded that the glucomannan is mainly composed of β-1→4 linked aldohexopyranose units and has some mannopyranose residues as terminals and branching points, linked in part through position 3. The average chain length of the polysaccharide was determined by methylation analysis and Smith degradation to be about 42.

In the results of both acetolysis and enzymatic degradation, β-D-1→4-linked mannobiose and mannotriose were major products, while no cellobiose was detected as a product in these treatments. Therefore it is possible that the presence of D-glucose residues is discontinuous in the polysaccharide.

An important characteristic of Narcissus-T-glucomannan is its fairly high acetyl content. On the basis of the content and the location of *O*-acetyl groups, we concluded that the molar ratio of D-mannose, 6-*O*-acetyl-D-mannose, and 2,6-di-*O*-acetyl-D-mannose residues was 2.0: 3.0: 6.0 in the glucomannan. This conclusion was also supported by the fact that free D-mannose and D-glucose were detected in a molar ratio of 1.0: 1.1 in the hydrolysate of the product obtained after treatment of the glucomannan by the method of DeBelder and Norrman.

The nature of the relationship between the presence of many *O*-acetyl groups and the high water-solubility is still unclear. Further studies are in progress.