

Title	Plant mucilages. XXXV. isolation and characterization of a mucous polysaccharide, "hippeastrum-H-glucomannan," from the bulbs of hippeastrum hybridum
Sub Title	
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Publisher	共立薬科大学
Publication year	1984
Jtitle	共立薬科大学研究年報 (The annual report of the Kyoritsu College of Pharmacy). No.29 (1984. ) ,p.26- 28
JaLC DOI	
Abstract	
Notes	抄録
Genre	Technical Report
URL	<a href="https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000029-0026">https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000029-0026</a>

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**Plant Mucilages. XXXV. Isolation and Characterization of a  
Mucous Polysaccharide, "Hippeastrum-H-glucomannan,"  
from the Bulbs of *Hippeastrum hybridum*\***

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Acetyl-rich mucous glucomannans have been isolated from the bulbs of several plants in the Amaryllidaceae family. These polysaccharides possess  $\beta$ -1 $\rightarrow$ 4 glycosidic main chains in common, but differ in types of branching and acetyl group location. In addition, different values of component sugar ratio and molecular weight were observed. We have now obtained a new acetyl-rich mucous polysaccharide from the bulbs of *Hippeastrum hybridum* HORT. This plant provides a famous ornamental flower. The properties and the structural features of the polysaccharide are described in the present paper.

The bulbs were sliced and extracted with cold water. The crude mucilage was precipitated from the extract by addition of ethanol, then dissolved in water and applied to a column of diethylaminoethyl (DEAE)-cellulose (acetate form). A mucous polysaccharide was obtained from the eluate with water. The polysaccharide gave a single spot on glass-fiber paper electrophoresis, and was homogeneous as determined by ultracentrifugal analysis.

The polysaccharides was readily soluble in water and it showed a negative specific rotation ( $[\alpha]_D^{25} -35.1^\circ$  in  $H_2O$ ,  $c=0.8$ ). Its aqueous solution gave an intrinsic viscosity value of 4.0 at 30°C. It gave a single peak on gel chromatography with Sephacryl S-400, and a value of 331000 was obtained for the molecular weight from a calibration curve based on the elution volumes of standard dextrans.

Mannose and glucose were identified as the component sugars, and quantitative determination showed that the molar ratio of mannose: glucose is about 5: 2. Total hexose content was estimated to be 86.3%. The polysaccharide contained no nitrogen. The name Hippeastrum-H-glucomannan is proposed for this compound.

The infrared (IR) spectrum of the glucomannan has absorption bands at 1245 and 1730  $cm^{-1}$ , suggesting the presence of ester linkages. The proton magnetic resonance ( $^1H$ -NMR) spectrum showed acetyl signals at  $\delta$  1.90 and  $\delta$  2.18 ppm. Analysis of the acid hydrolysate of the glucomannan by gas-liquid chromatography (GLC) showed the occurrence of acetic acid, and the content of *O*-acetyl groups was determined to be 13.2%.

The glucomannan was exhaustively treated with methyl vinyl ether, as a protective reagent for the free hydroxyl groups, in the presence of *p*-toluenesulfonic acid in dimethyl

\* 本報告は *Chem. Pharm. Bull.*, 33, 48—51 (1985) に発表.

sulfoxide. After conversion of the free hydroxyl groups to 1-methoxyethyl ethers, the derivative was deacetylated, then methylated with methyl iodide and silver oxide in *N,N*-dimethylformamide. The product was hydrolyzed, reduced, and acetylated. The final products were analyzed by gas-liquid chromatography-mass spectrometry (GLC—MS). A partially methylated alditol acetate was detected and identified as 1,3,4,5-tetra-*O*-acetyl-2,6-di-*O*-methyl-*D*-mannitol. This result indicates that 2,6-di-*O*-acetyl-*D*-mannose units are present in the glucomannan.

This glucomannan was methylated with methylsulfinyl carbanion and methyl iodide in dimethyl sulfoxide. The fully methylated product was hydrolyzed, reduced, and acetylated, and the products were analyzed by GLC—MS. As the hydrolysis products of the methylated polysaccharide, 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, 2,6-di-*O*-methyl-*D*-mannose, and 2,6-di-*O*-methyl-*D*-glucose were identified and obtained in a molar ratio of 5.0: 1.0: 49.8: 21.0: 4.8: 0.9. 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.

Further, partial hydrolysis of the glucomannan was carried out with dilute trifluoroacetic acid. The products were analyzed by thin-layer chromatography (TLC) and by GLC of the trimethylsilylated derivatives. Comparison with authentic samples showed the presence of *D*-mannose, *D*-glucose, *O*- $\beta$ -*D*-glucopyranosyl-(1 $\rightarrow$ 4)-*D*-mannose, *O*- $\beta$ -*D*-mannopyranosyl-(1 $\rightarrow$ 4)-*D*-mannose, *O*- $\beta$ -*D*-mannopyranosyl-(1 $\rightarrow$ 4)-*D*-glucose, *O*- $\beta$ -*D*-mannopyranosyl-(1 $\rightarrow$ 4)-*O*- $\beta$ -*D*-glucopyranosyl-(1 $\rightarrow$ 4)-*D*-mannose, *O*- $\beta$ -*D*-mannopyranosyl-(1 $\rightarrow$ 4)-*O*- $\beta$ -*D*-mannopyranosyl-(1 $\rightarrow$ 4)-*D*-mannose, and *O*- $\beta$ -*D*-mannopyranosyl-(1 $\rightarrow$ 4)-*O*- $\beta$ -*D*-mannopyranosyl-(1 $\rightarrow$ 4)-*D*-mannose. The relative yield ratio of these mono-, di-, and tri-saccharides was 100: 40.4: 27.7: 48.9: 14.9: 42.6: 42.6.

These results indicated that the glucomannan is mainly composed of  $\beta$ -1 $\rightarrow$ 4 linked *D*-aldohexopyranose units and has both mannopyranose and glucopyranose residues as terminals. It has branches at both position 3 of some mannopyranose units and position 3 of some glucopyranose units. The molar ratio of the terminal mannose and glucose units, the intermediate  $\beta$ -1 $\rightarrow$ 4 linked mannose and glucose units, and the branched mannose and glucose units must be approximately 5: 1: 49: 22: 5: 1. The presence of branched glucose units is a unique feature of *Hippeastrum*-H-glucomannan among the *Amaryllidaceae* glucomannans obtained by us. Upon partial hydrolysis, there is no great difference in the yields of three  $\beta$ -1 $\rightarrow$ 4 linked disaccharides and two  $\beta$ -1 $\rightarrow$ 4 linked trisaccharides, in contrast to *Narcissus*-T-glucomannan, *Lycoris*-R-glucomannan, and *Lycoris*-S-glucomannan. No cellobiose was detected as a product, and it can be concluded that the presence of *D*-glucose residues is discontinuous in the polysaccharide, as in the other three *Amaryllidaceae* glucomannans.

*Hippeastrum*-H-glucomannan is the fourth example of acetyl-rich polysaccharides

from the bulbs of plants in the Amaryllidaceae family. On the basis of the content and the location of *O*-acetyl groups, we concluded that the molar ratio of *D*-mannose and 2,6-di-*O*-acetyl-*D*-mannose residues was approximately 7: 5 in the glucomannan. It is interesting that 2,6-di-*O*-acetyl-*D*-mannose is a common unit in the four acetyl-rich glucomannans from the Amaryllidaceae plants.