Title	Plant mucilages. XXXI. an acetyl-rich mucous polysaccharide, "lycoris-R-glucomannan," from the bulbs of lycoris radiata
Sub Title	
Author	友田, 正司(Tomoda, Masashi) 清水, 訓子(Shimizu, Noriko)
Publisher	共立薬科大学
Publication year	1982
Jtitle	共立薬科大学研究年報 (The annual report of the Kyoritsu College of Pharmacy). No.27 (1982.) ,p.43- 45
JaLC DOI	
Abstract	
Notes	抄録
Genre	Technical Report
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000027-0043

Plant Mucilages. XXXI. An Acetyl-rich Mucous Polysaccharide, "Lycoris-R-glucomannan," from the Bulbs of *Lycoris radiata**

Masashi Tomoda and Noriko Shimizu

友田正司，清水訓子

The bulbs of *Lycoris radiata* Herbert (Amaryllidaceae) have been used as a crude drug with expectorant and emetic properties. In addition to various alkaloids, starch, and fructans, the isolation of a glucomannan was reported by Hayashi *et al.* in 1953. They reported that the glucomannan was purified by an alkaline copper complex method and it became insoluble in water, and in addition, the homogeneity of the polysaccharide was not established. The deacetylation of native water-soluble glucomannans having *O*-acetyl groups is known to result in insolubility of the products in water. Thus it is necessary to reexamine the glucomannans obtained by treatment with an alkaline solution. We have now obtained a native, pure, highly acetylated polysaccharide from the fresh bulbs of this plant, and its properties and structural features are described in the present paper.

The bulbs were sliced and extracted with cold water. 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 Sepharose CL-4B.

The substance showed a negative specific rotation ($[\alpha]_D^{24}-28.5°$ in H_2O, $c=0.4$), and its solution in water gave an intrinsic viscosity value of 4.7 at 30°. The measurement of osmotic pressure gave a value of 468000 for the molecular weight of the polysaccharide. Mannose and glucose were identified as the component sugars by means of cellulose thin-layer chromatography of the sulfuric acid hydrolysate and by gas-liquid chromatography of the trimethylsilyl derivatives. Quantitative determination showed that the molar ratio of mannose : glucose was 12 : 1. The name "Lycoris-R-glucomannan" is proposed for this compound.

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 890 cm^{-1} is due to β-glycosidic linkages. The proton magnetic resonance spectrum showed acetyl signals at δ 1.88 and δ 2.16, and the acetyl content of the glucomannan was determined to be 15.5%.

In order to elucidate the location of *O*-acetyl groups, the glucomannan was exhaustively

* 本報告は *Chem. Pharm. Bull.*, **30**, 3965–3969 (1982) に発表.

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 gas-liquid chromatography-mass spectrometry (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 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, 2,3,6-tri-*O*-methyl-D-mannose, 2,3,6-tri-*O*-methyl-D-glucose, and 2-*O*-methyl-D-mannose were identified in a molar ratio of 6.0 : 14.8 : 2.2 : 3.2. The identity of the tetra-*O*-methyl mannose was also confirmed by GLC of the methyl glycoside.

In order to remove the *O*-acetyl groups, the glucomannan was treated with dilute alkali solution, and after neutralization, the product was oxidized with periodate. In this periodate oxidation, 0.9 mol of periodate per mol of component anhydro sugar unit was consumed. The periodate-oxidized product was reduced, hydrolyzed, and analyzed. The yields of mannose and erythritol were 13.0% and 35.3%, respectively.

On the other hand, 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-mannopyranosyl-(1→4)-D-mannopyranose, *O*-β-D-mannopyranosyl-(1→4)-D-glucopyranose, *O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-glucopyranosyl(1→4)-D-mannopyranose, *O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-mannopyranosyl-(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 100 : 7.2 : 13.7 : 0.7 : 0.9 : 7.9.

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 positions 3 and 6. The terminal mannopyranose 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 6 : 15 : 2 : 3. From the value of acetyl content, it can be presumed that about nine out of every twenty-one terminal and intermediate mannose residues carry 2,6-di-*O*-acetyl groups.

Thus, Lycoris-R-glucomannan has a unique mode of branching, and also possesses an extraordinarily high ratio of mannose to glucose. Recently, we reported a highly acetylated glucomannan from the bulbs of *Narcissus tazette* L. var. *chinensis* ROEMER. This substance, named Narcissus-T-glucomannan, was composed of mannose and glucose in the molar ratio of 5 : 1, and the *O*-acetyl groups in it were located at positions 2 and

2,6 of most of the mannose units. Lycoris-R-glucomannan is the second example of acetyl-rich glucomannans from the bulbs of plants in the Amaryllidaceae family.