

Title	Plant mucilages. XII. fourteen oligosaccharides obtained from bletilla-glucomannan by partial acetolysis
Sub Title	
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Publisher	共立薬科大学
Publication year	1976
Jtitle	共立薬科大学研究年報 (The annual report of the Kyoritsu College of Pharmacy). No.21 (1976.) ,p.110- 111
JaLC DOI	
Abstract	
Notes	抄録
Genre	Technical Report
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000021-0110

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**Plant Mucilages. XII. Fourteen Oligosaccharides obtained from
Bletilla-glucomannan by Partial Acetolysis***

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The properties of Bletilla-glucomannan, the mucous polysaccharide isolated from the tubers of *Bletilla striata* REICHENBACH fil., were investigated in this laboratory. Periodate oxidation and methylation studies revealed that the substance is mainly composed of 1→4 linked aldohexopyranose residues having a branched structure with 1→2 branch point at a part of mannose unit. The present work was undertaken to isolate and identify the oligosaccharides as the products of partial acetolysis of Bletilla-glucomannan. Data on the aldohexose chains in the polysaccharide are discussed in this paper.

Bletilla-glucomannan was dissolved in formamide and acetylated with acetic anhydride and pyridine. The acetate obtained was partially degraded with sulfuric acid in acetic anhydride. After deacetylation, the products were fractionated by active charcoal column chromatography. Then the fractions were further purified by paper partition chromatography. Five disaccharides (I, II, III, IV, and V), six trisaccharides (VI, VII, VIII, IX, X, and XI) and three tetrasaccharides (XII, XIII, and XIV) were obtained.

The homogeneity of each oligosaccharide was checked by the cellulose thin-layer chromatography (TLC). For the disaccharides and the trisaccharides, the gas-liquid chromatography (GLC) of their trimethylsilyl derivatives was also carried out. Most of the trimethylsilyl derivatives of the oligosaccharides gave two anomeric peaks on GLC, but those of the reduced oligosaccharides showed their own single peak.

The TLC of the hydrolysates and the GLC of the trimethylsilyl derivatives of the methanolysates of the oligosaccharides showed their component sugars. After reduction of the oligosaccharides with sodium borohydride, the products were methanolized, then analyzed by GLC after trimethylsilylation. The results revealed their constitutions and reducing terminals.

The methylation of each oligosaccharide was performed with sodium methylsulfinyl carbanion and methyl iodide in dimethyl sulfoxide. The fully methylated products were hydrolyzed with formic acid and dilute sulfuric acid. The hydrolysates were derived to corresponding alditol acetates, then analyzed by GLC.

* 本報告は *Chem. Pharm. Bull.* (Tokyo), 24, 1807—1812 (1976) に発表

The comparison by TLC and by GLC of trimethylsilyl derivatives with authentic samples and their values of the specific rotation showed that I, III, IV, V, VI, X and XII are O- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-D-mannopyranose, O- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-D-glucopyranose, O- β -D-glucopyranosyl-(1 $\rightarrow$ 4)-D-mannopyranose, O- β -D-glucopyranosyl-(1 $\rightarrow$ 4)-D-glucopyranose, O- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-O- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-D-mannopyranose, O- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-O- β -D-glucopyranosyl-(1 $\rightarrow$ 4)-D-mannopyranose and O- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-O- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-O- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-D-mannopyranose, respectively.

Finally, the structures of the trisaccharides and the tetrasaccharides were determined from the results of controlled acid hydrolysis of them. Thus VII, VIII, IX, XI, XIII and XIV are O- β -D-glucopyranosyl-(1 $\rightarrow$ 4)-O- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-D-mannopyranose, O- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-O- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-D-glucopyranose, O- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-O- β -D-glucopyranosyl-(1 $\rightarrow$ 4)-D-glucopyranose, O- β -D-glucopyranosyl-(1 $\rightarrow$ 4)-O- β -D-glucopyranosyl-(1 $\rightarrow$ 4)-D-mannopyranose, O- β -D-glucopyranosyl-(1 $\rightarrow$ 4)-O- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-O- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-D-mannopyranose and O- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-O- β -D-glucopyranosyl-(1 $\rightarrow$ 4)-O- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-D-mannopyranose, respectively.

The polysaccharide possesses these diverse component aldohexose units having β -1 $\rightarrow$ 4 glycosidic linkages. On the other hand, neither partial acid hydrolysis nor partial acetolysis gave pure oligosaccharides having 1 $\rightarrow$ 2 glycosidic linkage. From these results it is able to presume that 1 $\rightarrow$ 2 glycosidic linkages in the glucomannan are cleft much more easily than 1 $\rightarrow$ 4 glycosidic linkages by the action of acid.

The results of component sugar determination and methylation analysis and the value of the specific rotation indicated that oligosaccharide II is O- α -D-mannopyranosyl-(1 $\rightarrow$ 4)-D-mannopyranose. To make sure whether α -glycosidic linkage is essentially present in the polysaccharide or not, authentic mannotetraose (XII) having only β -1 $\rightarrow$ 4 glycosidic linkage was undergone the similar partial acetolysis, and after deacetylation, the products were analyzed by TLC and GLC. The results showed the formation of a slight amount of II in addition to abundant mannose, I and VI. In partial acid hydrolysates of the glucomannan or mannotetraose (XII), II was entirely absent. From these facts and the low yield (less than 0.2%) of II, it is conceivable that II is not the substance showing an essential component unit in Bletilla-glucomannan, but the artifact produced during the reaction of acetolysis.