

Title	Plant mucilages. VI. three disaccharides obtained from plantasan by partial acid hydrolysis
Sub Title	
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Publisher	共立薬科大学
Publication year	1973
Jtitle	共立薬科大学研究年報 (The annual report of the Kyoritsu College of Pharmacy). No.18 (1973.) ,p.105- 107
JaLC DOI	
Abstract	
Notes	抄録
Genre	Technical Report
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000018-0105

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Plant Mucilages. VI.¹⁾ Three Disaccharides obtained from
Plantasan by Partial Acid Hydrolysis*

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The previous structural investigation²⁾ of plantasan, the seed mucilage of *Plantago major* L. var. *asiatica* DECAISNE, provided the evidence that the acidic polysaccharide has a high branched structure and D-xylose forms its backbone chain. In this paper, the isolations and characterizations of three disaccharides as partial acid hydrolysates of plantasan are described, and informations on the main part of the acidic polysaccharide having a complicated structure are discussed.

According to a variety of glycosidic linkages which are cleaved on acid hydrolysis at remarkably different rates, the partial hydrolysis was carried out in two conditions. At each condition, the products were fractionated by active charcoal column chromatography, then oligosaccharides were isolated from the fractions by the means of paper partition chromatography (PPC). Two neutral disaccharides (**I** and **II**) and an acidic disaccharide (**III**) were obtained from the hydrolysate with 0.1N sulfuric acid at 90° for 2 hr. The acidic disaccharide **III** was also isolated in better yield from the hydrolysate with 1N sulfuric acid at 90° for 3 hr.

The homogeneity of the each disaccharide was proved by cellulose thin-layer chromatography (TLC) and by gas-liquid chromatography (GLC) of its trimethylsilyl derivative. The trimethylsilyl derivative of **III** gave anomeric two peaks on GLC, but the trimethylsilyl derivative of the reduction product of **III** showed a single sharp peak.

Neutral disaccharide **I** and **II** showed negative specific rotations, and contrarily, acidic disaccharide **III** showed a high positive specific rotation as follows: **I**, $[\alpha]_D^{20} -28.9^\circ$ ($c=0.7$, H₂O); **II**, $[\alpha]_D^{20} -5.2^\circ$ ($c=0.7$, H₂O); **III**, $[\alpha]_D^{20} +148.8^\circ$ ($c=1.0$, H₂O).

TLC of the hydrolysates and GLC of trimethylsilyl derivatives of the methanolysates of disaccharides showed that **I** and **II** are composed of D-xylose, and **III** is composed of L-arabinose and D-glucuronic acid. As the result of reexamination on the component sugar of plantasan by TLC of hydrolysate and by GLC of trimethylsilyl derivative of the methanolysate, it was confirmed that hexuronic acid in plantasan is not D-galacturonic acid, but D-glucuronic acid.

After reduction of the disaccharides with sodium borohydride, the products were methanolized, then determinations of the methanolysates were carried out by GLC after trimethylsilylation. The results revealed that **I** and **II** are D-xylosyl D-xylose, and

* 本報告は *Chem. Pharm. Bull.* (Tokyo), **21**, 989 (1973) に発表.

1) Part V: M. Tomoda and S. Nakatsuka, *Chem. Pharm. Bull.* (Tokyo), **20**, 2491 (1972).

2) M. Tomoda and M. Uno, *Chem. Pharm. Bull.* (Tokyo), **20**, 778 (1972).

III is an aldobiouronic acid, that is, *D*-glucuronosyl *L*-arabinose.

As the results of periodate oxidation, mole values of consumed periodate, liberated formic acid and formaldehyde per one mole of the each disaccharide suggest the presences of 1→2 or 1→3 glycosidic linkage for **I**, 1→4 glycosidic linkage for **II**, and 1→5 glycosidic linkage for **III**.

On the other hand, the disaccharides were subjected to oxidation with bromine followed by mild periodate oxidation and Smith degradation. Trimethylsilyl derivatives of the products were analyzed by GLC, and the results showed that **I** produced glyceric acid and ethylene glycol, and **II** produced glycolic acid, glycerol and ethylene glycol. These results show the presences of glycosidic linkage of 1→2 type for **I** and 1→4 type for **II**. By the same treatment, **III** produced glycolic acid, glycerol and glyceric acid. But the analysis of Smith degradation product of fully periodate-oxidized **III** revealed the presence of ethylene glycol instead of glycerol, so the appearance of glycerol in the product of the former mild periodate oxidation followed by Smith degradation is probably due to incomplete oxidation. This result supports the presence of 1→5 glycosidic linkage for **III**.

Methylations of the disaccharides were performed with sodium hydride and methyl iodide in dimethyl sulfoxide. The fully methylated products were methanolized, then analyzed by GLC. Methyl glycosides of 2,3,4-tri-*O*-methyl *D*-xylose and 3,4-di-*O*-methyl *D*-xylose were identified from **I**. Methyl glycosides of 2,3,4-tri-*O*-methyl *D*-xylose and 2,3-di-*O*-methyl *D*-xylose were identified from **II**. And methyl glycosides of 2,3,4-tri-*O*-methyl *D*-glucuronic acid methyl ester and 2,3-di-*O*-methyl *L*-arabinose were identified from **III**. Thus in addition to the data on periodate oxidation studies, the results of methylation study proved finally that **I** is *D*-xylopyranosyl-(1→2)-*D*-xylopyranose, **II** is *D*-xylopyranosyl-(1→4)-*D*-xylopyranose, and **III** is *D*-glucuronopyranosyl-(1→5)-*L*-arabinofuranose.

To confirm the configurations of glycosidic linkages, **I** was digested with β -xylan xylanohydrolase and 13% of xylose was liberated after incubation for one day. **II** was digested with β -1,4-xylan xylanohydrolase and 97% of xylose was liberated after incubation for one day. And **III** was treated with β -*D*-glucuronide glucuronohydrolase and 99% of glucuronic acid was liberated after incubation for one day. These results of enzymic action gave the evidence that the three disaccharides have β -glycosidic linkages, and the values of specific rotations also support this conclusion. The structures of the three disaccharides are shown in Chart 1. Disaccharides **I** and **III** are new compounds, but **II** is a known one and it was identified on TLC and GLC by comparison with β -1,4-*D*-xylobiose prepared from corncob xylan.

The fact that *D*-xylobioses having 1→2 and 1→4 glycosidic linkages were obtained from plantasan as its partial hydrolysates supports the result²⁾ of study on the backbone structure of the acidic polysaccharide by Smith degradation, and the present investigation added the evidence that the configuration of linkages among all *D*-xylose residues

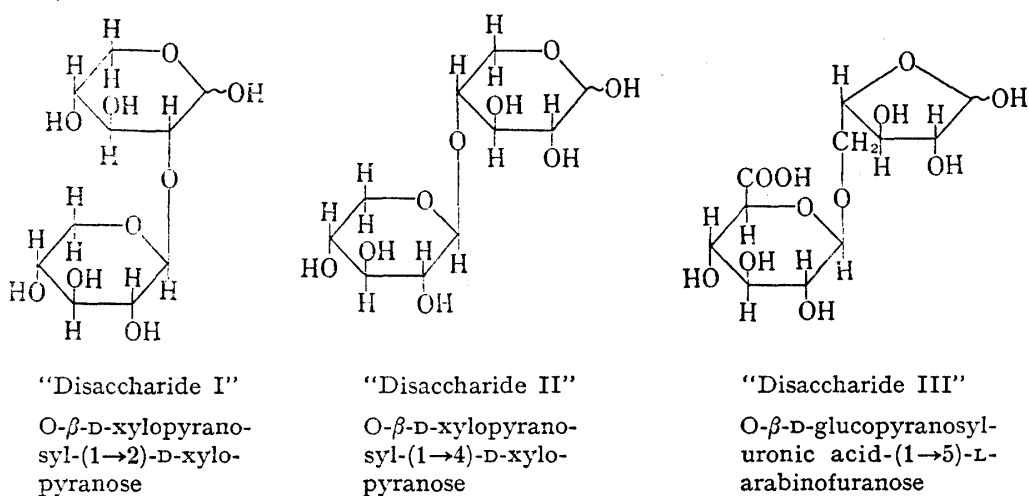


Chart 1. Structures of Disaccharides

is β -type. The isolation and the structural determination of an acidic disaccharide elucidated the fact that D-glucuronic acid in plantasan links with L-arabinofuranose by β -1→5 glycosidic linkage. As described in the previous report,²⁾ we have already known that L-arabinofuranose links with D-xylopyranose residues in the backbone chain. Any oligosaccharides composed of two or more hexuronic acid residues were not found in the partial acid hydrolysates, so it is conceivable that D-glucuronic acid exists as terminal residues.