Title	Plant mucilages. XV. the main structural features of the backbone chain of paniculatan
Sub Title	
Author	友田, 正司(Tomoda, Masashi) 佐藤, 訓子(Sato, Noriko) 鈴木, 陽子(Suzuki, Yoko)
Publisher	共立薬科大学
Publication year	1977
Jtitle	共立薬科大学研究年報 (The annual report of the Kyoritsu College of Pharmacy). No.22 (1977.) ,p.135- 136
JaLC DOI	
Abstract	
Notes	抄録
Genre	Technical Report
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000022-0135

Plant Mucilages. XV. The Main Structural Features of the Backbone Chain of Paniculatan*

MASASHI TOMODA NORIKO SATOH and YŌKO SUZUKI

友田正司, 佐藤訓子, 鈴木陽子

The representative mucous substance obtained from the inner bark of *Hydrangea paniculata* SIEB., named paniculatan, has been investigated in this laboratory. The substance is an acidic polysaccharide having a high branching structure. The present work was undertaken to perform the reduction and the methylation analysis of paniculatan, and the controlled Smith degradation product of the original polysaccharide was also studied by the reduction and the methylation analysis.

The carboxyl groups of uronic acid residues in the polysaccharide were reacted with a carbodiimide reagent, then reduced with sodium borohydride to the corresponding neutral sugar units. Quantitative determination of the component sugars of the carboxyl-reduced polysaccharide was carried out by gas-liquid chromatography (GLC) of alditol acetates derived from the hydrolyzate. The results showed that the sample contained rhamnose, galactose, glucose, and 4-*O*-methyl-glucose in the molar ratio of 4.0 : 7.6 : 2.3 : 5.0. The analysis of the component sugars of the original polysaccharide showed that the proportion of rhamnose : galactose : hexuronic acids was 4.0 : 4.1 : 10.3. The component sugars were also analyzed by cellulose thin-layer chromatography (TLC). From these results, it can be concluded that paniculatan is composed of L-rhamnose : D-galactose : D-galacturonic acid : D-glucuronic acid : 4-*O*-methyl D-glucuronic acid in the approximate molar ratio of 4 : 4 : 3 : 2 : 5.

The methylations of the original and the carboxyl-reduced polysaccharides were performed with methylsulfinylmethyl sodium and methyl iodide in dimethyl sulfoxide. The fully methylated products were successively hydrolyzed with formic acid and dilute sulfuric acid. The hydrolyzates were analyzed by gas-liquid chromatography-mass spectrometry (GLC-MS) after conversion to alditol acetates. The hydrolysis products of the fully methylated carboxy-reduced polysaccharide were identified as 3-mono-*O*-methyl-L-rhamnopyranose, 2,3,6-tri-*O*-methyl-D-galactopyranose, 2,6-di-*O*-methyl-D-galactopyranose, and 2,3,4,6-tetra-*O*-methyl-D-glucopyranose, and they were obtained in the molar ratio of 4.0 : 4.3 : 3.0 : 6.5. Methyl ethers of the hexuronic acids were removed from the hydrolyzate of methylated paniculatan by treatment with an anion-exchange resin, and the residual products were identified as 3-mono-*O*-methyl-L-rhamnopyranose, 2,3,6-tri-*O*-methyl-D-galactopyranose, and 2,6-di-*O*-methyl D-galactopyranose. They were obtained in the molar ratio of 4.0 : 3.2 : 1.2. These results suggested that the minimal repeating unit of paniculatan

* 本報告は *Chem. Pharm. Bull.* (Tokyo), **25**, 968 - 973 (1977) に発表

was composed of seven kinds of the component sugar unit.

Paniculatan was subjected to periodate oxidation, and after stopping the reaction by addition of ethylene glycol, the product was reduced with sodium borohydride. The selective cleavage of acetal linkages was achieved by mild hydrolysis with dilute sulfuric acid. The controlled Smith degradation product was isolated by the gel chromatography using Sephadex G-15. None of the component sugars was detected in the low molecular weight fraction. The controlled Smith degradation product gave single spot on glass-fiber paper electrophoresis in alkaline borate buffer, and it showed a positive specific rotation ($[\alpha]_D^{23}$ +3.7° in H_2O, c =2.4). The value of 10000 as the molecular weight of it was estimated from the calibration curve obtained by the gel chromatography using Sephadex G-200. Analysis of its hydrolyzate showed that the product was composed of rhamnose: galactose : galacturonic acid in the molar ratio of 2.0 : 0.6 : 1.0.

In addition, the product was reduced with sodium borohydride after treatment with methanol and Dowex 50W (H^+), and the carboxyl-reduced derivative was obtained. The controlled Smith degradation product and its carboxyl-reduced derivative were fully methylated and the hydrolyzates of them were analyzed by GLC-MS as described above. As the hydrolyzates of the carboxyl-reduced product, 3,4-di-*O*-methyl-L-rhamnopyranose, 3-mono-*O*-methyl-L-rhamnopyranose, 2,3,4,6-tetra-*O*-methyl-D-galactopyranose, 2,3,6-tri-*O*-methyl-D-galactopyranose, and 2,6-di-*O*-methyl-D-galactopyranose were identified and obtained in the molar ratio of 2.8 : 1.0 : 1.1 : 1.4 : 0.2. It is conceivable that the incomplete cleavage of acetal linkages in controlled Smith degradation caused the appearance of 2,6-dimethyl-galactose. The methyl ethers of the neutral sugar components of the methylated controlled Smith degardation product were also identified by GLC-MS to be 3,4-di-*O*-methyl-L-rhamnopyranose, 3-mono-*O*-methyl-L-rhamnopyranose, and 2,3,4,6-tetra-*O*-methyl--D-galactopyranose in the molar ratio of 2.7 : 1.0 : 1.2.

Owing to these results, it can be presumed that the backbone chain in the mucous polysaccharide is composed of rhamnose and galacturonic acid in the approximate molar ratio of 2 : 1. The chain must be composed of 1→2 linked L-rhamnopyranose residues and 1→4 linked D-galactopyranosyluronic acid residues, and it has branches at position 4 of each rhamnose and at position 3 of each galacturonic acid. On the other hand, all glucuronic acid and all 4-*O*-methyl-glucuronic acid units are located on the terminals of the molecule. All galactose and about one third of galacturonic acid units form the intermediates in the branching chains. About one fourth of galactose units must form the other branched points by 1→3 and 1→4 linkages, and these galactose units are present in part of the controlled Smith degradation product in addition to rhamnose and galacturonic acid units in the backbone chain. Thus paniculatan occupies a relatively unique position for its very high branching structure and for the presences of three kinds of hexuronic acids among the rest.