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Plant Mucilages. XVII. Partial Hydrolysis and a Possible Structure of Paniculatan*

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The mucous polysaccharide from the inner bark of *Hydrangea paniculata* SIEB., named paniculatan, has been isolated and investigated in this laboratory. The substance is composed of L-rhamnose, D-galactose, D-galacturonic acid, D-glucuronic acid, and 4-O-methyl D-glucuronic acid in the approximate molar ratio of 4 : 4 : 3 : 2 : 5. The reduction of carboxyl groups, controlled Smith degradation and methylation studies revealed that its backbone chain was composed of 1→2 linked L-rhamnopyranose residues having branches at position 4 and 1→4 linked D-galactopyranosyluronic acid residues having branches at position 3 in the approximate molar ratio of 2 : 1. In addition, it was confirmed that all D-glucuronic acid and all 4-O-methyl-D-glucuronic acid units were located on the terminals of the molecule, and that all D-galactose and about one third of D-galacturonic acid moieties formed the intermediates in the branching chains.

In this paper, the isolations and characterizations of five oligosaccharides as partial acid hydrolyzates of the mucilage are described, and a possible structure of paniculatan is proposed.

Paniculatan was hydrolyzed with 0.5 N sulfuric acid for 2 hr, and the residue was filtered off. The filtrate was neutralized and applied to a column of Sephadex G-15. The polysaccharide fraction obtained by this chromatography and the insoluble material at the first hydrolysis were combined and hydrolyzed again with 1 N sulfuric acid for 2 hr. The products and the low molecular weight fraction obtained by the first hydrolysis were applied individually to a column of DEAE-Sephadex A-25 (formate form), and when necessary, the fractions obtained by the stepwise elution with dilute formic acid were further purified by paper partition chromatography (PPC). Five oligosaccharides (I to V) were isolated. The outline of the preparation of the partial hydrolyzates is shown on Chart 1.

The homogeneity of each oligosaccharide was checked by cellulose thin-layer chromatography (TLC) and by paper electrophoresis. The TLC of the hydrolyzates of the oligosaccharides showed their component sugars. Quantitative determinations of the component sugars were carried out by gas-liquid chromatography (GLC) of alditol acetates derived from the hydrolyzate and by a colorimetric method.

The oligosaccharides were converted to the corresponding neutral oligosaccharides by the reductions of the methyl esters of the methyl glycosides with sodium borohydride. The methylations of the carboxyl-reduced oligosaccharides were performed with met-

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hysulfynilmethyl 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.

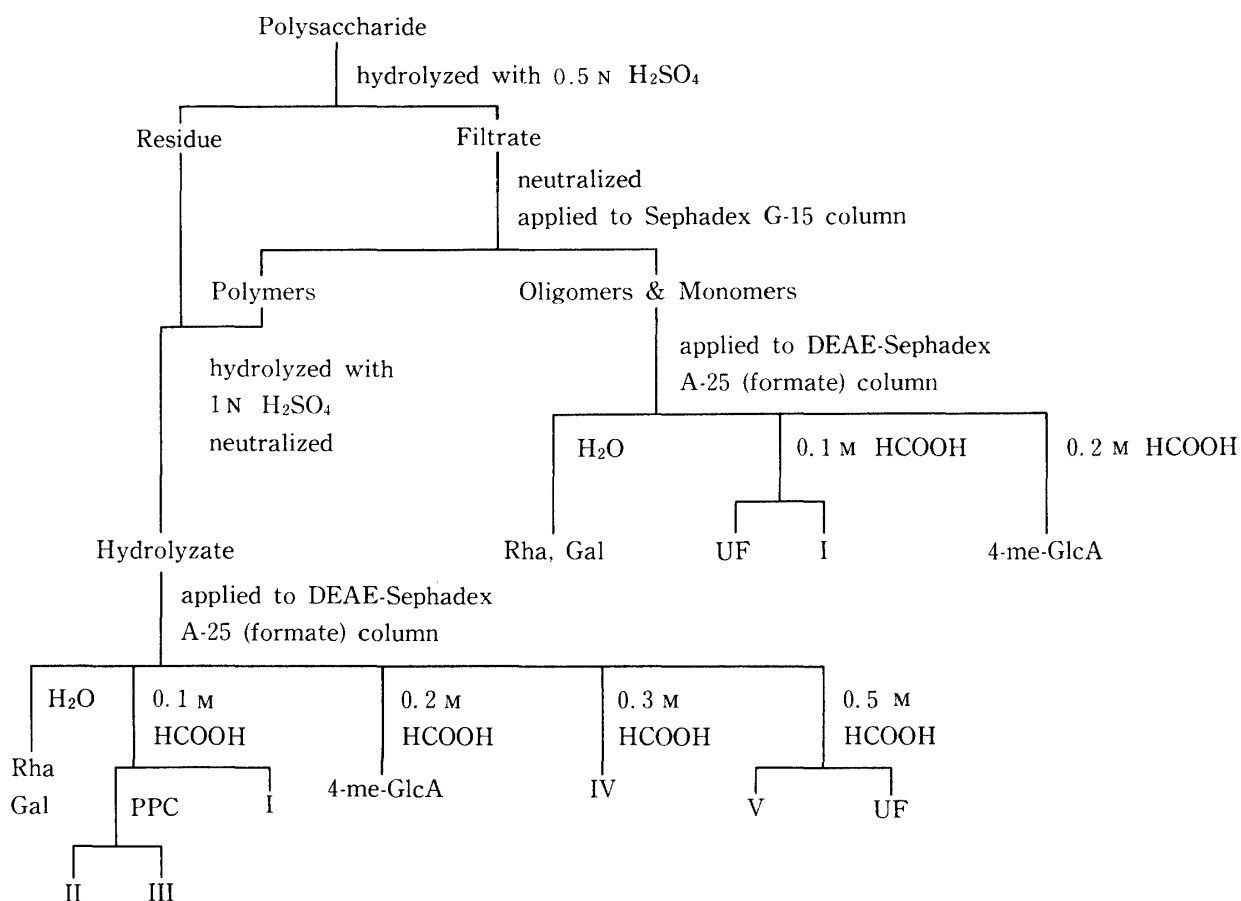


Chart 1. Isolation of Oligosaccharides

abbreviations: Rha = rhamnose; Gal = galactose; 4-me-GlcA = 4-*O*-methyl-glucuronic acid; UF = unidentified fractions

From the results of the methylation analysis and the values of specific rotation, it can be concluded that I, II, and V are *O*- α -(4-*O*-methyl-D-glucopyranosyluronic acid)-(1 \rightarrow 4)-D-galactopyranose, *O*- α -(D-galactopyranosyluronic acid)-(1 \rightarrow 2)-L-rhamnopyranose, and *O*- α -(D-glucopyranosyluronic acid)-(1 \rightarrow 3)-*O*- α -(D-galactopyranosyluronic acid)-(1 \rightarrow 2)-L-rhamnopyranose.

Partial hydrolysis of III and IV, and of the controlled Smith degradation product with 1 N sulfuric acid gave II in addition to their component monosaccharides. No other oligosaccharide was detected. Consequently, III and IV are *O*- α -(D-galactopyranosyluronic acid)-

(1 \rightarrow 2)-O- α -L-rhamnopyranosyl-(1 \rightarrow 2)-L-rhamnopyranose and O- α -(D-galactopyranosyluronic acid)-(1 \rightarrow 2)-O- α -L-rhamnopyranosyl-(1 \rightarrow 4)-O- α -(D-galactopyranosyluronic acid)-(1 \rightarrow 2)-L-rhamnopyranose, and no adjacent unit of galacturonic acid exist in the backbone chain of paniculatan. On the basis of the principle of optical superposition, the low value of specific rotation of the controlled Smith degradation product led us to express the anomeric configuration in L-rhamnose moiety as α -glycosidic and that in D-galactose moiety as β -glycosidic. The controlled Smith degradation product showed three anomeric proton signals at δ 4.80 (1H, d, J =7 Hz), δ 5.14 (4H, d, J =2 Hz), and δ 5.32 (2H, d, J =3.5 Hz) in its proton magnetic resonance spectrum. This result indicates that D-galactose residues are β -linked, and that both L-rhamnose and D-galacturonic acid residues are α -linked.

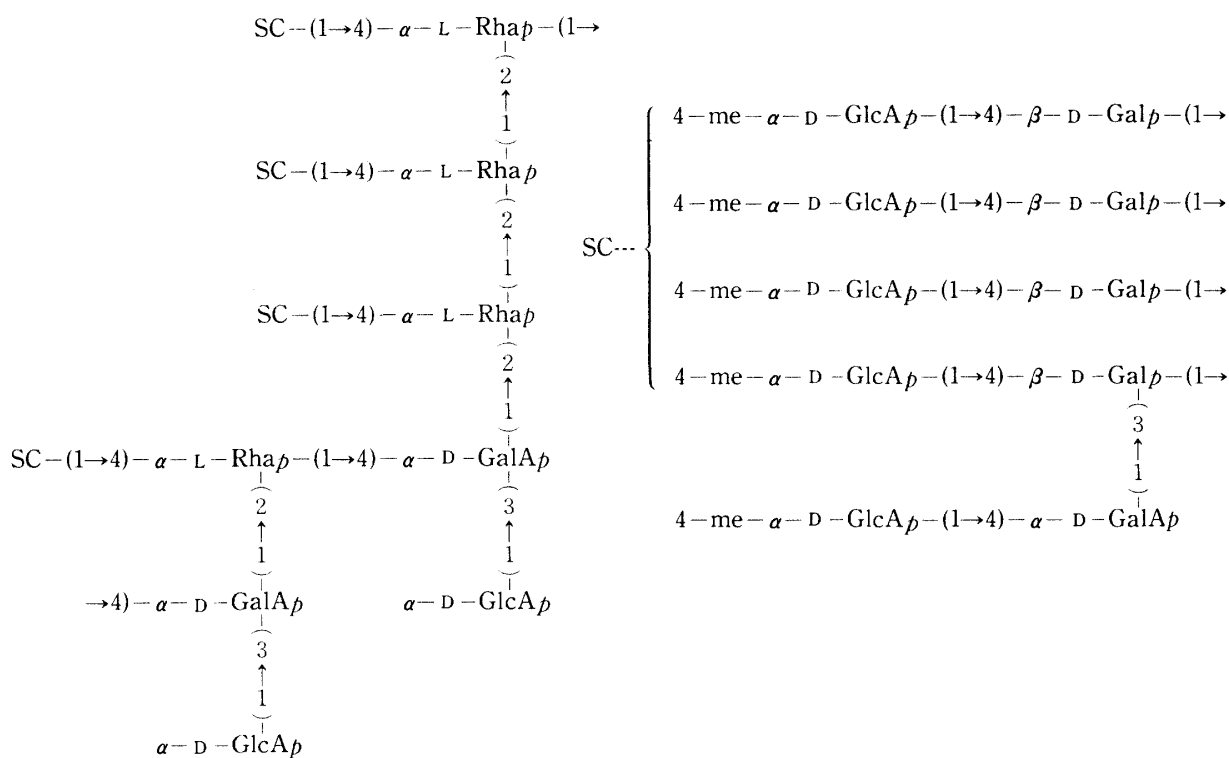


Chart 2. A Possible Structural Fragment of Paniculatan
 abbreviation: SC = side chains

These results indicate that D-glucuronic acid residues combine to position 3 of D-galacturonic acid moieties in the backbone chain of the mucilage. Therefore, the chain is composed of 1→2 linked L-rhamnose units having branches at position 4 and 1→4 linked D-galacturonic acid units having D-glucuronic acid residues at position 3 in the approximate molar ratio of 2:1. It can be presumed that the side chains composed of 4-O-α-(4-O-methyl-D-glucuronic acid)-D-galactose attach to position 4 of L-rhamnose units in the back-

bone chain. Owing to the results of methylation analysis and Smith degradation of the whole polysaccharide, it seems most probable, although not actually proved, that the branches composed of 4-*O*- α -(4-*O*-methyl-D-glucuronic acid)-D-galacturonic acid attach to position 3 of about one fourth of D-galactose moieties in the side chains. The present study also demonstrates that the residues of L-rhamnopyranose, D-galactopyranosyluronic acid, D-glucopyranosyluronic acid and 4-*O*-methyl-D-glucopyranosyluronic acid are α -linked, and that D-galactopyranosyl residue is β -linked. From the accumulated evidence, a possible structure of paniculatan can be shown in chart 2.