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Author	友田, 正司(Tomoda, Masashi) 鈴木, 陽子(Suzuki, Yoko) 佐藤, 訓子(Sato, Noriko)
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Plant Mucilages. XXIII. Partial Hydrolysis of Abelmoschus-mucilage M and the Structural Features of Its Polysaccharide Moiety*

Masashi Tomoda, Yōko Suzuki and Noriko Satoh

友田正司，鈴木陽子，佐藤訓子

The representative mucous substance obtained from the root of *Abelmoschus manihot* Medicus (=*Hibiscus manihot* L.), named Abelmoschus-mucilage M, has been isolated and investigated in this laboratory. The substance is a complex of carbohydrate and peptide, and 82% consists of an acidic polysaccharide. The polysaccharide moiety is composed of L-rhamnose, D-galacturonic acid, and D-glucuronic acid in approximately equimolecular ratios. The reduction of carboxyl groups and methylation studies showed that the polysaccharide was composed of 1→2-linked L-rhamnopyranose units and 1→4-linked D-galactopyranosyluronic acid units having D-glucopyranosyluronic acid residues at position 3.

The present work was undertaken to isolate and identify three oligosaccharides obtained as the main products of partial hydrolysis of Abelmoschus-mucilage M. The structural features of the polysaccharide moiety are discussed.

The mucilage was hydrolyzed with 1 N sulfuric acid for 2 hr, then neutralized and applied to a column of Dowex 50W (H^+). The eluate with water was applied to a column of DEAE-Sephadex A-25 (formate form), and three oligosaccharides (I to III) were obtained from the main fractions by stepwise elution with dilute formic acid. Among them, I was purified by rechromatography under the same conditions.

The homogeneity of each oligosaccharide was checked by PPC and by paper electrophoresis.

Cellulose TLC of the hydrolysates of the oligosaccharides was carried out to identify their component sugars. The oligosaccharides were converted into the corresponding carboxyl-reduced oligosaccharides by reduction of the methyl ester methyl glycosides with sodium borohydride. Quantitative determination of the component sugars was carried out by GLC of alditol acetates derived from the hydrolysates of the carboxyl-reduced oligosaccharides and by colorimetric methods. All three oligosaccharides bear a L-rhamnose residue as a common reducing terminal.

Methylation of each carboxyl-reduced oligosaccharide was performed with methylsulfinylmethyl sodium and methyl iodide in dimethyl sulfoxide. The fully methylated products were hydrolyzed and the hydrolysates were analyzed by GLC-MS after conversion into alditol acetates.

The reducing terminal rhamnose unit of each oligosaccharide was converted into the

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corresponding alditol by reduction with sodium borohydride. The PMR spectra of the resulting non-reducing oligosaccharides showed an anomeric proton signal at δ 5.36 (1H, d, J=3 Hz) and a methyl signal of rhamnitol at δ 1.24 (3H, d, J=6 Hz) in the non-reducing derivative from I; two anomeric proton signals at δ 4.78 (1H, d, J=7 Hz) and δ 5.36 (1H, d, J=3 Hz), and a methyl signal at δ 1.22 (3H, d, J=6 Hz) in the non-reducing derivative from II; and four anomeric proton signals at δ 4.78 (2H, d, J=7 Hz), δ 5.20 (1H, d, J= 2 Hz), δ 5.36 (1H, d, J=3 Hz), and δ 5.49 (1H, d, J=3 Hz), and a methyl signal at δ 1.22 (6H, d, J=6 Hz) in the non-reducing derivative from III. On the other hand, the mucilage was degraded by periodate oxidation followed by reduction with sodium borohydride. The product had $[\alpha]_D^{19}$ +84.7° (in H_2O, c=2.3), and showed an anomeric proton signal of D-galacturonic acid at branching points at δ 5.47 (1H, d, J=3 Hz). Neither L-rhamnose nor D-glucuronic acid was detected in the product. These data suggest that D-galacturonic acid residues in I, II, and III are α-linked (the signals at δ 5.36 [due to terminal and chain residues] and δ 5.49 [due to a branching point] in the PMR spectra), that D-glucuronic acid residues in II and III are β-linked (the signal at δ 4.78 in the PMR spectra), and that the intermediate L-rhamnose residue in III is α-linked (the signal at δ 5.20 in the PMR spectrum).

Based on the results of the methylation analysis and PMR spectra, we concluded that I and II are *O*-α-(D-galactopyranosyluronic acid)-(1→2)-L-rhamnopyranose and *O*-β-(D-glucopyranosyluronic acid)-(1→3)-*O*-α-(D-galactopyranosyluronic acid)-(1→2)-L-rhamnopyranose, respectively. The specific rotation of I agreed with the reported value. II was identified with the trisaccharide obtained by the partial hydrolysis of paniculatan, the mucous polysaccharide from the inner bark of *Hydrangea paniculata*, on the basis of chromatographic behavior, PMR spectra, and specific rotation.

Marked production of II was observed on partial hydrolysis of III with 1 N sulfuric acid for 1 hr. The hydrolysate was analyzed by PPC and determined by GLC after conversion of the carboxyl-reduced derivatives into alditol acetates. In addition to II, the component monosaccharides, I, and *O*-β-(D-glucopyranosyluronic acid)-(1→3)-D-galactopyranosyluronic acid were produced, but II was the only trisaccharide in the product. The ratio of the yields of II, disaccharides, and monosaccharides was 5.2: 1.0: 2.2.

Based on the accumulated evidence described above, III was identified as *O*-β-(D-glucopyranosyluronic acid)-(1→3)-*O*-α-(D-galactopyranosyluronic acid)-(1→2)-*O*-α-L-rhamnopyranosyl-(1→4)-[*O*-β-(D-glucopyranosyluronic acid)-(1→3)]-*O*-α-(D-galactopyranosyluronic acid)-(1→2)-L-rhamnopyranose.

The combined yields of II and III were more than half of the total mono- and oligosaccharides obtained from a partial hydrolysate of Abelmoschus-mucilage M. Consequently, it can be concluded that the structure of III represents the fundamental unit of the polysaccharide moiety of the mucilage. This conclusion is supported by the results of methylation analysis of the original mucilage as described in the previous report. The present

work has thus elucidated the sequence of the component sugars and the configurations of the glycosidic linkages.

The component unit having the structure II is common in the mucilages from the roots of *Abelmoschus manihot* and *Althaea officinalis* and the inner barks of *Hydrangea paniculata*. However, only Abelmoschus-mucilage M possesses a simple repeating structure in its polysaccharide moiety.