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Plant Mucilages. XXIV. The Structural Features of Althaea-mucilage O, a Representative Mucous Polysaccharide from the Roots of *Althaea officinalis**

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The isolation and properties of Althaea-mucilage O, the representative mucous substance obtained from the root of *Althaea officinalis* L., were reported in a previous paper of this series. The substance is an acidic polysaccharide composed of L-rhamnose, D-galactose, D-galacturonic acid, and D-glucuronic acid in a molar ratio of approximately 3 : 2 : 3 : 3. Methylation studies of the original and the carboxyl-reduced polysaccharides showed that the substance was composed of 1→2 linked L-rhamnopyranose units, 1→2 linked L-rhamnopyranose units having branches at position 4, D-galactopyranosyl-(1→4)-D-galactopyranose side chains, 1→4 linked D-galactopyranosyluronic acid units having branches at position 3, and terminal D-glucopyranosyluronic acid units in a ratio of approximately 2 : 1 : 1 : 3 : 3.

The purpose of this study was to examine the sequence of the component sugars and the configurations of the glycosidic linkages.

The mucilage was hydrolyzed with 1 N sulfuric acid at 100° for 2 hr, then neutralized and applied to a column of Dowex 50W-X8 (H^+). The eluate with water was applied to a column of DEAE-Sephadex A-25 (formate form), and five oligosaccharides (I to V) were obtained from the fractions by stepwise elution with dilute formic acid. Each of them was further purified by paper partition chromatography (PPC). The homogeneity of each oligosaccharide was checked by PPC and by paper electrophoresis.

Cellulose thin-layer chromatography (TLC) of the hydrolysates of the oligosaccharides was carried out to identify their component sugars. Quantitative determination of the component sugars was carried out by gas-liquid chromatography (GLC) of alditol acetates derived from the hydrolysates of the carboxyl-reduced oligosaccharides as described in the previous paper, and by colorimetric methods. All five oligosaccharides bear a L-rhamnose residue as a common reducing terminal.

Each carboxyl-reduced oligosaccharide was methylated with methylsulfinylmethyl sodium and methyl iodide in dimethyl sulfoxide. The fully methylated products were hydrolyzed and analyzed by gas-liquid chromatography-mass spectrometry (GLC-MS) after conversion into alditol acetates.

Based on the results of the methylation analysis, and by comparing their chromato-

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graphic properties, the proton magnetic resonance (^{1}H-NMR) spectra, and the values of specific rotation with those of authentic samples, I, II, and III were identified as *O*-α-(D-galactopyranosyluronic acid)-(1→2)-L-rhamnopyranose, *O*-β-(D-glucopyranosyluronic acid)-(1→3)-*O*-α-(D-galactopyranosyluronic acid)-(1→2)-L-rhamnopyranose, and *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, respectively.

Marked production of II was observed on partial hydrolysis of IV and V with 1 N sulfuric acid at 100° for 1 hr. The hydrolysate was analyzed by PPC and determined by GLC after conversion of the carboxyl-reduced derivatives into alditol acetates. The ratios of II, disaccharides, and monosaccharides were 7.5: 1.0: 2.3 in the hydrolysate from IV, and 7.8: 1.0: 2.2 in the hydrolysate from V. In addition, the formation of III was detected in the hydrolysates of IV and V by PPC and by paper electrophoresis.

Oligosaccharides IV and V were reduced with sodium borohydride. The ^{1}H-NMR spectra of the resulting alditols derived from IV and V showed four anomeric proton signals at δ 4.80 (3H, d, J=7 Hz), δ 5.20 (2H, d, J=2 Hz), δ 5.32 (1H, d, J=3 Hz), and δ 5.48 (2H, d, J=3 Hz), and a methyl signal at δ 1.30 (9H, d, J=6 Hz) in the non-reducing derivative from IV, and four anomeric proton signals at δ 4.80 (4H, d, J=7 Hz), δ 5.20 (3H, d, J=2 Hz), δ 5.31 (1H, d, J=3 Hz), and δ 5.47 (3H, d, J=3 Hz), and a methyl signal at δ 1.28 (12H, d, J=6 Hz) in the non-reducing derivative from V. These data

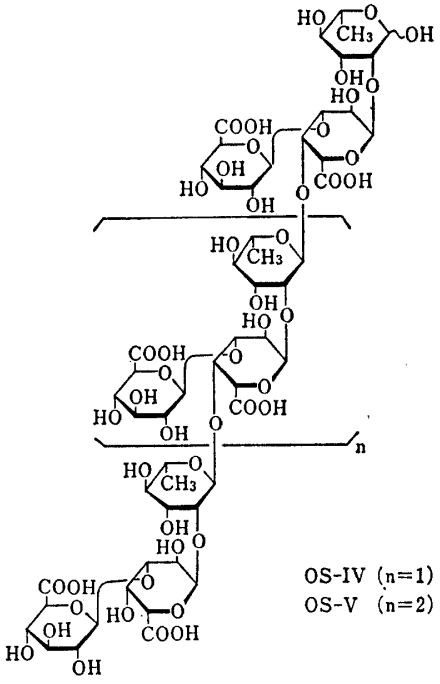

Chart 1. Structures of Oligosaccharides IV and V
(OS=oligosaccharide)

suggest that the D-glucuronic acid residues in IV and V are β-linked, and that the L-rhamnose and D-galacturonic acid residues in IV and V are α-linked.

Based on the accumulated evidence described above, IV and V were identified as a nonasaccharide and a dodecasaccharide composed of a repeating unit having the structure II (Chart 1).

The combined yields of II, III, IV and V went up to over 60% of the total mono- and oligosaccharides obtained from the partial hydrolysate of the mucilage. Consequently, it can be concluded that these oligosaccharides do represent the structural features of the main chain in Althaea-mucilage O.

The glycosidic linkage of the D-galactose residue is much more easily cleaved than those of the other component sugars in the mucilage. Therefore, no oligosaccharide having D-galactose as a component was obtained by partial acid hydrolysis. The results of partial hydrolysis of the mucilage during the carboxyl-reducing reaction and the methylation studies, however, indicate that branches composed of 4-*O*-D-galactopyranosyl D-galactopyranose are attached to position 4 of about one-third of the L-rhamnose moieties in the main chain.

Oxidation of the acetylated mucilage with chromium trioxide in acetic acid resulted in zero recovery of D-galactose after 1 hr. This result indicates that the D-galactose residues in the mucilage are β-linked.

The mucilage was subjected to periodate oxidation followed by reduction with sodium borohydride. As a result of the oxidation, 1.18 mol of periodate was consumed per mol of component anhydro sugar units with the liberation of 0.16 mol of formic acid. The reduction product was isolated and selective cleavage of the acetal linkages was achieved by mild hydrolysis with dilute sulfuric acid. After reduction, the controlled Smith degradation products were separated by gel chromatography on Sephadex G-15. In addition to galacturonic acid-(1→2)-glycerol (=product d), three products (a to c) containing galacturonic acid, rhamnose, and glycerol were obtained. Analysis revealed that the molar ratios of galacturonic acid: rhamnose: glycerol in the products were 4: 3: 1 in product a, 3: 2: 1 in product b, 2: 1: 1 in product c. The molecular weights were 1200 for a, 910 for b, 590 for c, and 260 for d. The ratio of the yields of the products a, b, c, and galacturonic acid-(1→2)-glycerol was 1.5: 1.0: 1.2: 1.7.

Based on the results of controlled Smith degradation, we concluded that there are three types of the positions of the galactosyl galactose side chains linking to rhamnose residues in the main chain. The branching seems to be rather random. In the two types which produce the controlled Smith degradation products a and b, the side chains are linked to neighboring rhamnose residues. In the simplest part, Althaea-mucilage O contains the following undecasaccharide repeating unit (Chart 2).

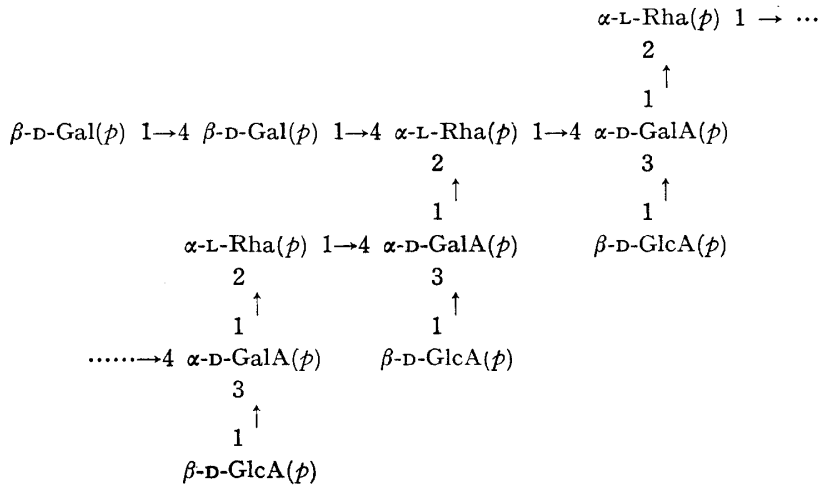

Chart 2. A Possible Structural Fragment of Althaea-mucilage O