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Plant Mucilages. XXXVII. A Representative Mucilage, "Althaea-mucilage RL", from the Leaves of *Althaea rosea**

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Recently, we have obtained a representative mucilage, "Althaea-mucilage R", from the roots of *Althaea rosea* CAVAILLES (hollyhock), and its structural features have been reported. The root has been utilized as a crude drug with emollient and demulcent actions. In addition, the leaves of this plant have been used similarly. The leaves contain relatively large amounts of mucilages, but no structural study on the mucilages has been reported so far. The present paper deals with the isolation and structural features of a new representative mucilage from the leaves of *Althaea rosea*.

The fresh leaves were homogenized and extracted with cold water. The crude mucilage was obtained from the extract by addition of ethanol. The solution of the crude mucilage was applied to a column of DEAE-Sephadex A-25 (carbonate form). After elution with 0.2 M ammonium carbonate, a pure mucilage was obtained from the eluate with 0.5 M ammonium carbonate.

The mucilage was homogeneous as examined by ultracentrifugal analysis, cellulose acetate membrane electrophoresis, glass-fiber paper electrophoresis, and gel chromatography with Sephacryl S-400.

The mucilage showed a positive specific rotation ($[\alpha]_D^{24}+60.7°$ in H_2O, $c=0.1$), and its solution in water gave the high intrinsic viscosity value of 32.5 at 30°C. The relative viscosity of the solution of the pure mucilage was about 5.6 times that of the crude mucilage. From both this result and the yield, it seems reasonable to assume that the pure mucilage is the representative mucous substance in the water extract from the leaves. Gel chromatography gave a value of about 1800000 for the molecular weight. The name "Althaea-mucilage RL" is proposed for this substance.

The mucilage was found to consist of L-rhamnose, D-galactose, D-galacturonic acid, D-glucuronic acid, *O*-acetyl groups, and protein. Quantitative determination showed that the mucilage contained 31.4% rhamnose, 1.8% galactose, 29.5% galacturonic acid, and 29.5% glucuronic acid, and that their molar ratio was 20.4 : 1.0 : 16.0 : 16.0. The acetyl content of the mucilage was determined to be 4.3%. The determination of protein content was carried out by the method of Lowry *et al.*, and a value of 4.4% was obtained.

Methylation of the carboxyl-reduced mucilage was performed with methyl-sulfinyl

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carbanion and methyl iodide in dimethyl sulfoxide. The fully methylated derivative was hydrolyzed with dilute sulfuric acid in acetic acid. The products were analyzed by GLC-MS after conversion into alditol acetates. 3,4-Di-*O*-methyl-L-rhamnopyranose, 3-*O*-methyl-L-rhamnopyranose, 2,3,4,6-tetra-*O*-methyl-D-glucopyranose, 2,3,4,6-tetra-*O*-methyl-D-galactopyranose, and 2,6-di-*O*-methyl-D-galactopyranose were identified as their alditol acetates in a molar ratio of 18.4 : 1.0 : 16.0 : 1.3 : 16.8.

The ^{1}H-NMR spectrum of the mucilage showed four anomeric proton signals at δ 4.59 (bs), δ 4.70 (bs), δ 5.01 (d, J=2 Hz), and δ 5.26 (d, J=2 Hz), and their integral ratio was 16 : 1 : 20 : 16. In addition, a methyl signal of rhamnose at δ 1.23 (d, J=5 Hz) and an acetyl signal at δ 1.89 (s) were observed. The signals at δ 4.59, 5.01, and 5.26 are due to β-D-glucuronic acid, α-L-rhamnose, and α-D-galacturonic acid residues, respectively. The signal at δ 4.70 suggests that the D-galactose residues in the mucilage are β-linked.

The mucilage was hydrolyzed with 1 N sulfuric acid for 2 h, then neutralized and applied to a column of Dowex 50 W (H^+). The eluate with water was applied to a column of DEAE-Sephadex A-25 (formate form). Six oligosaccharides (I to VI) were obtained by stepwise elution with dilute formic acid and purified by rechromatography. Based on the results of component sugar analysis and a comparison of their chromatographic properties, the ^{1}H-NMR apectra, and the values of specific rotation with those of authentic samples, I to V were identified.

Oligosaccharide VI was composed of L-rhamnose and D-galacturonic acid in a molar ratio of 1 : 1. The determination of the reducing terminal was carried out by analysis of the hydrolysate of the corresponding alditol, and the result indicated that VI has an L-rhamnose residue as a reducing terminal. The oligosaccharide was converted into the corresponding carboxyl-reduced derivative by reduction of the methyl ester methyl glycoside with sodium borohydride. Methylation of the carboxyl-reduced derivative of VI was performed, and the product was hydrolyzed as described above. The hydrolysate was analyzed by GLC-MS after conversion into alditol acetates ; 3,4-di-*O*-methyl-L-rhamnopyranose, 2,3,4,6-tetra-*O*-methyl-D-galactopyranose, and 2,3,6-tri-*O*-methyl-D-galactopyranose were identified as their alditol acetates in a molar ratio of 1.8 : 1.0 : 1.1. In addition, VI produced rhamnose, galacturonic acid, and oligosaccharide I on partial hydrolysis with 1 N sulfuric acid for 1 h. Based on the evidence described above, VI was identified as *O*-α-(D-galactopyranosyluronic acid)-(1→2)-*O*-α-L-rhamnopyranosyl-(1→4)-*O*-α-(D-galactopyranosyluronic acid) -(1→2)-L-rhamnopyranose.

All galactose residues were liberated from the mucilage under the partial hydrolysis conditions described above.

In conjunction with the results of methylation analysis, this finding suggests that a twentieth of the rhamnose residues in the backbone chain possesses a galactose residue at position 4.

Based on the accumulated evidence described above, it can be concluded that the

polysaccharide moiety of the mucilage contains the units shown in Chart 1.

The presence of only one galactose unit as neutral side units in Althaea-mucilage RL is unique, compared with the other mucilage which have been isolated from Malvaceae plants. In addition, Althaea-mucilage RL has the lowest degree of branching at rhamnose residues among all the mucilages having similar neutral sugar side chains.

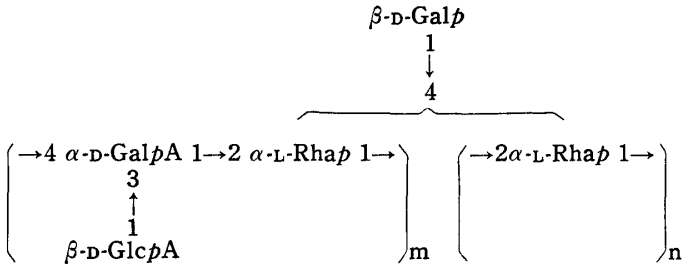

Chart 1. A Possible Structural Fragment of the Polysaccharide Moiety of Althaea-Mucilage RL
Galp, Galactopyranose
m+n=20; m:n=4:1