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Plant Mucilages. XXXIV. The Location of *O*-Acetyl Groups and the Structural Features of Plantago-mucilage A, the Mucous Polysaccharide from the Seeds of *Plantago major* var. *asiatica**

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In a previous paper, Tomoda *et al.* have reported the isolation and the characterization of Plantago-mucilage A, a representative mucous polysaccharide from the seeds of *Plantago major* L. var. *asiatica* DECAISNE (=*Plantago asiatica* L.). The mucilage has the main chain composed of highly branched β-1→4-linked D-xylopyranose residues, β-D-xylopyranosyl side chains, and two kinds of aldobiouronic acid side chains. In addition, the mucilage contains 4.8% *O*-acetyl groups. The present work was undertaken to elucidate the location of the *O*-acetyl groups. This paper also reports the revision of some previously proposed structural features of Plantago-mucilage A.

The analytical data showed that the molar ratio of L-arabinose : D-xylose : D-glucuronic acid : D-galacturonic acid : *O*-acetyl group was 4.0 : 14.5 : 3.3 : 0.7 : 3.7 in Plantago-mucilage A. As reported previously, the controlled Smith degradation product was obtained from the original mucilage by periodate oxidation and reduction followed by mild hydrolysis. The product was composed of L-arabinose, D-xylose, and *O*-acetyl group in a molar ration of 4.0 : 9.0 : 2.0.

Both the mucilage and the controlled Smith degradation product were exhaustively treated with methyl vinyl ether, as a protective reagent for the free hydroxyl groups, in the presence of *p*-toluenesulfonic acid as a catalyst in dimethyl sulfoxide. After conversion of the free hydroxyl groups to 1-methoxyethyl ethers, the derivatives were deacetylated, then methylated with methyl iodide and silver oxide in *N,N*-dimethylformamide. The resultant products were subjected to acid hydrolysis, and the final products were analyzed by gas-liquid chromatography-mass spectrometry (GLC-MS) after conversion into alditol acetates. 2-*O*-Methyl-L-arabinose and 2-*O*-methyl-D-xylose were detected and identified in a molar ratio of 1.0 : 3.0 in the product derived from Plantago-mucilage A. On the other hand, both 2-*O*-methyl-L-arabinose and 2-*O*-methyl-D-xylose were also identified in the product derived from the controlled Smith degradation product, but their molar ratio was 1.0 : 1.0.

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These results indicate that 2-*O*-acetyl-L-arabinose and 2-*O*-acetyl-D-xylose units are present in the mucilage in a molar ratio of 1 : 3. Two-thirds of the 2-*O*-acetyl-D-xylose units must be located at the terminals in the mucilage because of their disappearance after periodate oxidation. On the basis of the molar ratio of *O*-acetyl groups to component sugars, it can be concluded that hexuronic acid residues do not possess *O*-acetyl groups.

Reinvestigations of the methylation analysis of the mucilage and the controlled Smith degradation product were carried out. Methylation was performed with methylsulfinyl carbanion and methyl iodide in dimethyl sulfoxide. The fully methylated products were hydrolyzed, reduced, and acetylated. The products were analyzed by GLC–MS as described above ; 2,5-di-*O*-methyl-D-arabinose, 2,3,4-tri-*O*-methyl-D-xylose, 2-*O*-methyl-D-xylose, 2,3,4,6-tetra-*O*-methyl-D-glucose, and 2,3,4,6-tetra-*O*-methyl-D-galactose were identified in a molar ratio of 4.0 : 5.3 : 9.2 : 3.4 : 0.6 in the product derived from the carboxyl-reduced mucilage. In the previous work, the alditol acetates of 2-*O*-methyl and 3-*O*-methyl D-xyloses were not separated from each other under the conditions used. In the present study, we used different conditions with a 0.3% OV 275+0.4% XF 1150 column for GLC and GLC–MS, and the mass fragmentation pattern of the corresponding peak indicated that 2-*O*-methyl D-xylose was the sole monomethyl xylose in the methylation products. In the case of methylation analysis of the controlled Smith degradation product, 2,3,5-tri-*O*-methyl-L-arabinose, 2,3-di-*O*-methyl-D-xylose, and 2-*O*-methyl-D-xylose were identified as the partially methylated alditol acetates in a molar ratio of 4.3 : 5.0 : 4.1 by GLC–MS.

As already reported in a previous paper, *O*-β-D-xylopyranosyl-(1→3)-D-xylopyranose, *O*-β-D-xylopyranosyl-(1→4)-D-xylopyranose, *O*-α-(D-glucopyranosyluronic acid)-(1→3)-L-arabinofuranose, and *O*-α-(D-galactopyranosyluronic acid)-(1→3)-L-arabinofuranose were obtained and identified as partial hydrolysates from the mucilage. In addition, the presence of α-glycosidic linkages of L-arabinofuranose units in the mucilage was already proved on the basis of the ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectrum of the controlled Smith degradation product.

Based on the accumulated evidence described above, it can be concluded that Plantago-mucilage A contains the units shown in Chart 1.

On the basis of these results, we concluded that the molar ratios of D-xylopyranose and 2-*O*-acetyl-D-xylopyranose are approximately 3 : 2 in the terminal units and approximately 8 : 1 in the intermediate units, and that the molar ratio of L-arabinofuranose and 2-*O*-acetyl-L-arabinofuranose is approximately 3 : 1.

The present report is the first to describe the presence of *O*-acetyl groups and the lacation of them in mucilages obtained from plants of the Plantago genus. The native water-soluble glucomannans obtained from the bulbs of plants in the Liliaceae and Amaryllidaceae families possess *O*-acetyl groups, and deacetylation causes insolubility of the products in water. In contrast to these neutral polysaccharides, the deacetylation

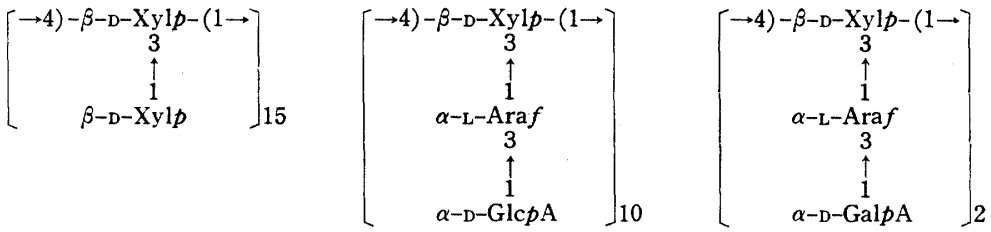

Chart 1. Minimal Component Units in the Structure of Plantago-mucilage A

The terminal xylose units consist of D-Xyl*p* : 2-Ac-D-Xyl*p* (3 : 2), and the intermediate xylose units consist of D-Xyl*p* : 2-Ac-D-Xyl*p* (8 : 1).
The intermediate arabinose units consist of L-Ara*f* : 2-Ac-L-Ara*f* (3 : 1).
Abbreviations : Xyl*p*, xylopyranose ; Ara*f*, arabinofuranose ; Glc*p*A, glucopyranosyluronic acid ; Gal*p*A, galactopyranosyluronic acid ; Ac, acetyl.

of paniculatan, the acidic polysaccharide composed of 4-*O*-methyl-D-glucuronic acid, D-glucuronic acid, D-galacturonic acid, D-galactose, L-rhamnose, and 3-*O*-acetyl-L-rhamnose, isolated from the inner barks of *Hydrangea paniculata* (Saxifragaceae), increases the solubility in water. In the case of Plantago-micilage A, increase of water solubility and lowering of the molecular weight and viscosity in aqueous solution were observed upon deacetylation, as in the case of paniculatan. However, the effects were less marked than in the case of paniculatan.

Several studies on the properties and structures of the mucilages obtained from the seeds of plants in the *Plantago* genus have been reported. As components of the seed mucilages, D-xylose, D-galactose, and D-galacturonic acid in *Plantago lanceolata*, D-xylose, L-arabinose, L-rhamnose, and D-galacturonic acid in *Plantago ovata*, and D-xylose, L-arabinose, D-galactose, L-rhamnose, and D-galacturonic acid in *Plantago arenaria* were reported. In the cases of mucilages from the seeds of *Plantago ovata* and *P. arenaria*, the presence of *O*-α-(D-galacturonic acid)-(1→2)-L-rhamnose units as side chains was reported. In Plantago-mucilage A, however, neither D-galactose nor L-rhamnose was found as a component, and there were two kinds of aldobiouronic acid side chains, namely *O*-α-(D-glucopyranosyluronic acid)-(1→3)-L-arabinofuranose as the major one and *O*-α-(D-galactopyranosyluronic acid)-(1→3)-L-arabinofuranose as the minor one, in addition to β-D-xylose side chains. Thus, Plantago-mucilage A has characteristic side chains and location of *O*-acetyl groups, although the main chain, composed of β-1→4-linked D-xylose residues, is similar to those of the seed mucilages from other plants in the *Plantago* genus.