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**Pectic Substances. III. The Major Pectin from the Roots of
*Angelica acutiloba****

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Angelicae Radix (Japanese name, Tohki) is a well-known Oriental crude drug used mainly in the treatment of gynecological diseases. The root of *Angelica acutiloba* KITAGAWA is the representative source for this crude drug in Japan. We have now isolated a pure acidic polysaccharide from the roots of this plant. This substance was recognized as an indication for the identification method described above. Its properties and structural features are reported in the present paper.

The polysaccharide gave a single spot on both cellulose acetate membrane and glass-fiber paper electrophoresis. In addition, it gave a single peak on gel chromatography with Cellulofine GCL-90M. It had a high positive specific rotation ($[\alpha]_D^{25} + 235^\circ$). Gel chromatography gave a value of 20800 for the molecular weight. Quantitative determination showed that the polysaccharide contained 87.5% galacturonic acid, 2.7% rhamnose, 1.9% arabinose, 1.3% galactose, and 0.8% glucose. The molar ratio of galacturonic acid : rhamnose : arabinose : galactose : glucose is 80.0 : 3.0 : 2.3 : 1.2 : 0.7.

The $^1\text{H-NMR}$ spectrum of the polysaccharide shows signals at δ 2.07 and 3.74. They suggest the presence of *O*-acetyl groups and *O*-methyl groups as carboxylic acid methyl esters. The presence of these groups was confirmed by GC of the hydrolyzate, and the acetyl and the methoxyl contents were determined to be 5.0 and 7.3%, respectively. Thus 19 per 40 galacturonic acid residues in the polysaccharide exist as methyl esters. The name "Angelica-pectin A" is proposed for this major acidic polysaccharide.

The carboxyl groups of galacturonic acids in the pectin were reduced to give the corresponding neutral sugar residues. Methylation of the carboxyl-reduced derivative was performed with methylsulfinyl carbanion and methyl iodide in dimethyl sulfoxide. The methylated product was hydrolyzed, and the hydrolyzates were converted into the partially methylated alditol acetates. GLC-MS revealed derivatives of 2,3,5-tri-*O*-methyl-L-arabinose, 2,3-di-*O*-methyl-L-arabinose, 2-*O*-methyl-L-arabinose, 3,4-di-*O*-methyl-L-rhamnose, 3-*O*-methyl-L-rhamnose, 2,3,4,6-tetra-*O*-methyl-D-glucose, 2,3,4,6-tetra-*O*-methyl-D-galactose, and 2,3,6-tri-*O*-methyl-D-galactose as the products in a molar ratio of 2.0 : 1.1 : 1.0 : 2.2 : 1.8 : 1.0 : 1.1 : 33.0. This result suggests that fairly large amounts of galacturonic acid residues were lost during the process of carboxyl reduction. The attempt of methylation of the original pectin ended in failure because of the poor solubility of it in dimethyl

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sulfoxide.

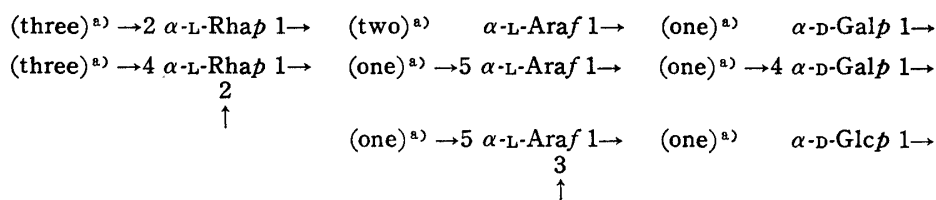
The pectin was subjected to periodate oxidation followed by reduction with sodium borohydride. The product contained 1.3% rhamnose, 0.5% arabinose, and 7.7% galactose. Neither galacturonic acid nor glucose was found in it. After deacetylation with alkali, the product was subjected to a second periodate oxidation followed by reduction. No change in the contents of rhamnose and arabinose in the product was found after the second periodate oxidation, while all the galactose residues were decomposed by this treatment. The results of periodate oxidation indicate that the survival of rhamnose and arabinose is based on the existence of branching residues. It is conceivable that the appearance of a large excess of galactose in the first product, compared with the original pectin, is due to the reduction of partially acetylated galacturonic acid methyl ester residues with sodium borohydride.

The high positive value of the specific rotation suggests that D-galacturonic acid residues in the pectin are α -linked. For the determination of the configuration of neutral sugar linkages, the pectin was acetylated, then oxidized with chromium trioxide in acetic acid. The recoveries of L-rhamnose, L-arabinose, D-galactose, and D-glucose were 100, 100, 89, and 100% after 1 h, respectively. These results indicate that these neutral sugar residues are α -linked.

Based on the accumulated evidence described above, it can be concluded that the main backbone chain in Angelica-pectin A is largely composed of α -1 \rightarrow 4-linked D-galactopyranosyluronic acid residues having a degree of methyl esterification of 47.5%. The minimal component neutral sugar units of the pectin per about 160 galacturonic acid residues are shown in Chart 1.

Based on the ratio of structural units (Chart 1), it is conceivable that the side chain are linked to position 4 of the rhamnose residues in the back bone.

In addition to L-rhamnose, L-arabinose and D-galactose, D-xylose and D-fucose have been also known as the component neutral sugars in some kinds of pectins. The presence of D-glucose as one of the neutral components is thus characteristic of Angelica-pectin A.



Rhap, rhamnopyranose ; Araf, arabinofuranose ; Galp, galactopyranose ; Glcp, Glucopyranose
 Chart 1. Component Neutral Sugar Residues in the Minimal Unit in the Structure of Angelica-pectin A

a) Number of residues