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Plant Mucilages. III.[1] Smith Degradation Products of Plantasan.*

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The seed mucilage of *Plantago major* L. var. *asiatica* Decaisne named plantasan has been isolated and recognized as an acidic polysaccharide composed of D-xylose, L-arabinose, L-rhamnose, D-galactose, and D-galacturonic acid.[2] The previous investigation showed that the molar ratio of them was 15: 3: 2: 0.4: 4. This result suggests a high branched structure for the polysaccharide like the other many plant gums and mucilages,[3] and the evidences of it produced by Smith degradation[4] and following methylation and periodate oxidation studies of a product are described in the present paper.

Plantasan was subjected to periodate oxidation, and after stopping of the reaction by addition of ethylene glycol, the product was reduced with sodium borohydride. The controlled hydrolysis of acetal linkages was achieved with 1 N sulfuric acid at room temperature for two days. After neutralization, the solution was concentrated and dialyzed against water. The dialyzable fraction was converted into trimethylsilyl and trifluoro-

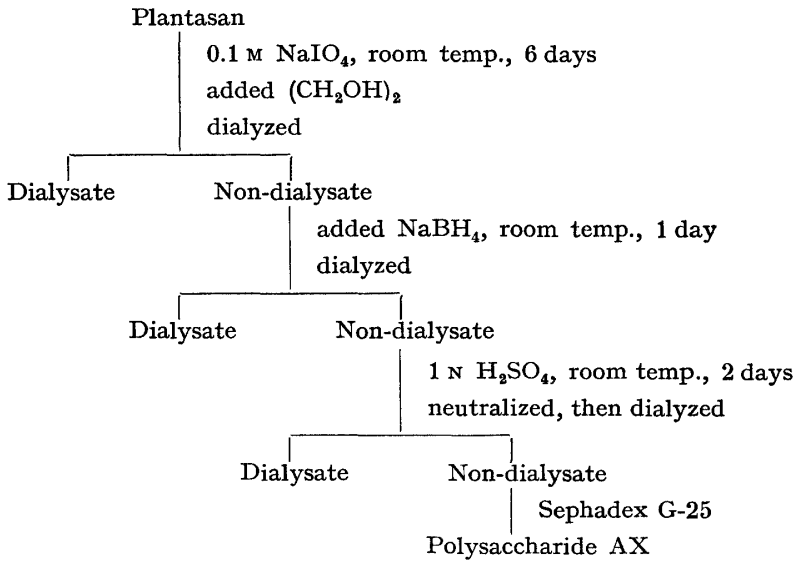

Chart 1. Smith Degradation of Plantasan.

* 本報告は *Chem. Pharm. Bull.* (Tokyo), **20**, 778 (1972) に発表.

1) Part II: M. Tomoda, Y. Yoshida, H. Tanaka, and M. Uno, *Chem. Pharm. Bull.* (Tokyo), **19**, 2173 (1971).

2) M. Tomoda and M. Uno, *Chem. Pharm. Bull.* (Tokyo), **19**, 1214 (1971).

3) a) F. Smith and R. Montgomery, "*Chemistry of Plant Gums and Mucilages*" (Reinhold, New York, 1959); b) G. O. Aspinall, "*The Carbohydrates, Chemistry and Biochemistry*" (ed. by W. Pigman and D. Horton), **IIB**, 515 (Academic Press, New York and London, 1970).

4) I. J. Goldstein, G. W. Hay, B. A. Lewis, and F. Smith, "*Methods in Carbohydrate Chemistry*" (ed. by R. L. Whistler), **V**, 361 (Academic Press, New York and London, 1965).

acetyl derivatives and analyzed by gas-liquid chromatography and thin-layer chromatography. The non-dialyzable fraction was applied to a column of Sephadex G-25, and a polysaccharide was obtained. The outline of the process is shown in Chart 1.

As the result of periodate oxidation, 1.35 mole of periodate per one mole of component anhydro sugar unit of plantasan was consumed with 0.81 mole of formic acid liberation. And Smith degradation of plantasan produced glycerol (11.6% of the dialysate), glycolaldehyde (5.6% of the dialysate), ethylene glycol (3.2% of the dialysate), D-xylose glycoside (42.8% of the dialysate), L-arabinose glycoside (23.3% of the dialysate), D-xylose (4.2% of the dialysate), and L-arabinose (12.5% of the dialysate), and a new polysaccharide (14.4% yield from plantasan). The glycosides are estimated to be compounds which pentose combines with C-2-substituted glycerol, and some of glycosidic bonds may be cleaved during hydrolysis of acetal linkages with cold dilute acid.

The polysaccharide showed a negative specific rotation ($[\alpha]_D^{30}$ $-107.2°$ in H_2O, $c=0.9$), and it is homogeneous on a glass-fiber paper electrophoresis and gel chromatography. We named provisionally it polysaccharide AX. The number-average molecular weight of it was estimated from the calibration curve given by gel chromatography,[2] and the value of 9200 was obtained. The hydrolysis of it produced D-xylose and L-arabinose, and determination of them showed that the molar ratio was 9: 1.

After methylation of polysaccharide AX with sodium hydride and methyl iodide in dimethyl sulfoxide,[5] methylated product was methanolyzed and the methanolysate was analyzed by gas liquid chromatography and thin-layer chromatography. Methyl glycosides of 2,3-di-O-methyl D-xylose, 3-O-methyl D-xylose, and 2,3,5-tri-O-methyl L-arabinose were identified.

By periodate oxidation of polysaccharide AX, 0.73 mole of periodate per one mole of component anhydro sugar unit was consumed and no formic acid liberation was observed. Smith degradation of polysaccharide AX produced very small amounts of a xylan in addition to glycerol, glycolaldehyde, ethylene glycol, D-xylose glycoside, L-arabinose glycoside, D-xylose, and L-arabinose. Their yields in the dialysate were 35.0%, 0.7%, 0.2%, 25.4%, 0.6%, 1.2%, and 0.4%.

Thus, Smith degradation of plantasan removed all the D-galacturonic acid, L-rhamnose and D-galactose residues, together with some of D-xylose and L-arabinose. The methylation study provided the evidence that polysaccharide AX has a main chain of 1→4 linked D-xylopyranose units having a highly branched structure with 1→2 branch point. From the result of periodate oxidation, it is concluded that the molar ratio of the methyl glycosides of 2,3-di-O-methyl D-xylose, 3-O-methyl D-xylose, and 2,3,5-tri-O-methyl L-arabinose was approximately 6: 3: 1.

A possible structural unit shown in Chart 2 could be proposed to polysaccharide AX, although further detailed study is still necessary for the confirmation of branching posi-

5) S. Hakomori, *J. Biochem.*, **55**, 205 (1964).

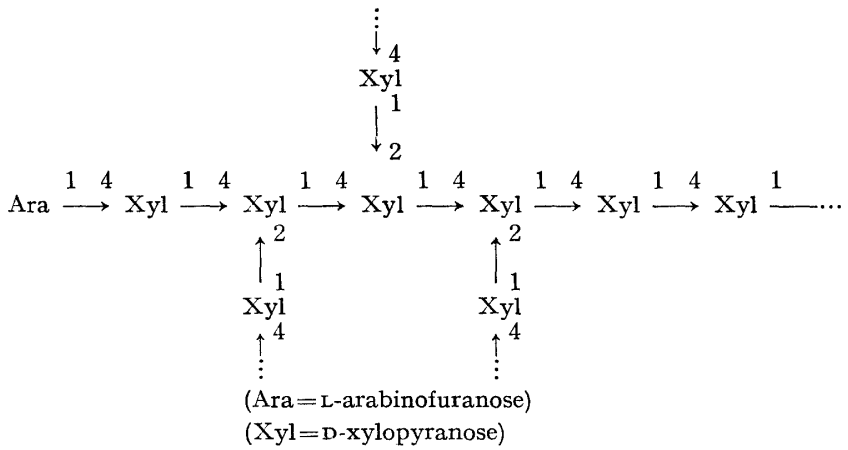

Chart 2. Possible Structural Unit of Polysaccharide AX.

tions. Of course, in the molecule of plantasan, all the D-xylose residues of polysaccharide AX must combine with short or long side-chains.

The results of present investigation indicated that D-galacturonic acid, L-rhamnose and D-galactose residues exist as linear chains or terminal residues in plantasan, on the other hand, D-xylose forms high branched backbone structure and a part of L-arabinose residue also occupy branching points. Further evidence obtained from partial hydrolysis for the proposed structure will be described in following papers.