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Plant Mucilages. VII.[1] Six Oligosaccharides obtained from Odoratan and Falcatan by Partial Acid Hydrolysis*

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The mucilage from the rhizome of *Polygonatum odoratum* Druce var. *japonicum* Hara named odoratan[2] and the mucilage from the rhizome of *Polygonatum falcatum* A. Gray named falcatan[3] were extracted and their properties investigated in this laboratory. Both substances are composed of D-fructose, D-mannose, D-glucose and D-galacturonic acid, although their molar ratios are different. Both polysaccharides show similar values of the specific rotation and of the viscosity, and it is interesting to note that they have similarly high molecular weight, while they contain many fructose residues as components. In this paper, the isolation and identification of six oligosaccharides as partial acid hydrolysates of both odoratan and falcatan are described, and data on the aldohexose chains in both polysaccharides are discussed.

Odoratan and falcatan were respectively hydrolyzed with 0.5N sulfuric acid at 90° for 2 hr, and the products were fractionated by active charcoal column chromatography. Then the fractions were applied to a column of Sephadex G-15, and when necessary, the

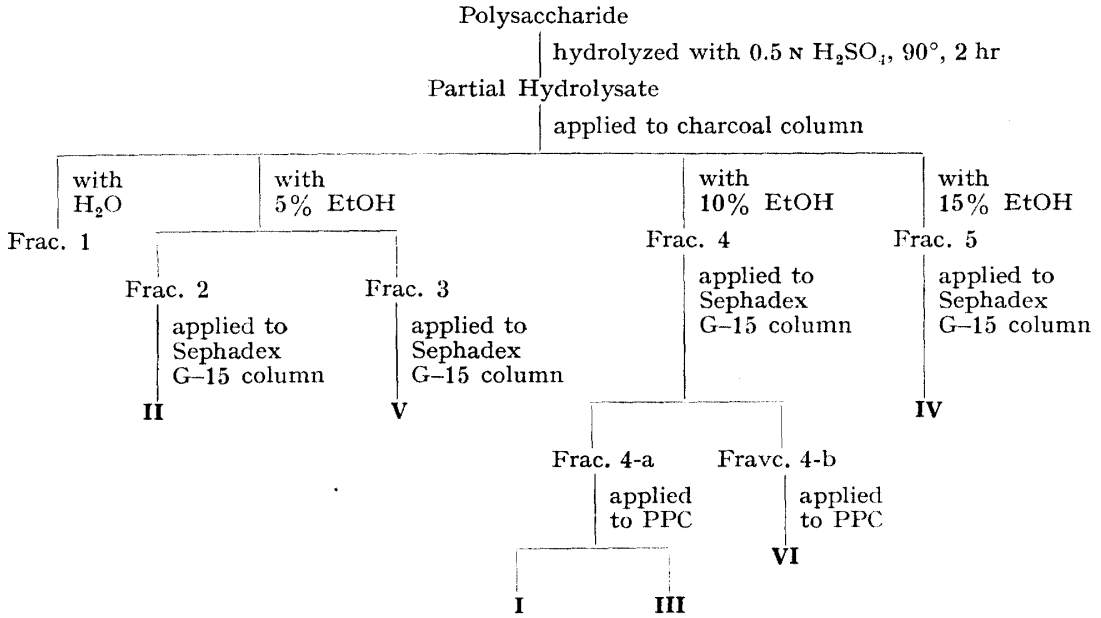

Chart 1. Isolation of Oligosaccharides

* 本報告は *Chem. Pharm. Bull.* (Tokyo), **21**, 2511 (1973) に発表.

1) Part VI: M. Tomoda and M. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **21**, 989 (1973).

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

3) M. Tomoda and S. Nakatsuka, *Chem. Pharm. Bull.* (Tokyo), **20**, 2491 (1972).

fractions obtained by gel chromatography were further purified by paper partition chromatography (PPC). Three disaccharides (**I**, **II**, and **III**), two trisaccharides (**IV** and **V**) and a tetrasaccharide (**VI**) were obtained from odoratan, and five oligosaccharides but **III** were obtained from falcatan. The outline of the preparation and isolation of the partial hydrolysates is shown on Chart 1.

The homogeneity of each oligosaccharide was checked by the cellulose thin-layer chromatography (TLC) and by the gas-liquid chromatography (GLC) of its trimethylsilyl derivative. Most of the trimethylsilyl derivatives of the oligosaccharides gave two anomeric peaks on GLC, but the trimethylsilyl derivatives of their reduction products showed single sharp peaks.

After recrystallization, **I** was obtained as hygroscopic colorless rodes (monohydrate), mp 134—136°, $[\alpha]_D^{23}$ +3.4° (H_2O, c=1.3); **II** was obtained as colorless rods, mp 204—205°, $[\alpha]_D^{27}$ −6.7° (H_2O, c=3.9); **IV** was obtained as colorless prisms, mp 161—163°, $[\alpha]_D^{23}$ −5.8° (H_2O, c=2.2); **V** was obtained as colorless prisms, mp 164—166°, $[\alpha]_D^{27}$ −20.9° (H_2O, c=2.3). Specific rotations of the other oligosaccharides were as follows: **III**, $[\alpha]_D^{23}$ +6.0° (H_2O, c=0.3); **VI**, $[\alpha]_D^{27}$ −25.9° (H_2O, c=1.6).

The TLC of the hydrolysates and the GLC of the trimethylsilyl derivatives of the methanolysates of the oligosaccharides showed that **I**, **III**, and **IV** are composed of mannose and glucose, and that **II**, **V**, and **VI** are composed of mannose. After reduction of the oligosaccharides with sodium borohydride, the products were methanolyzed, then the identification of the methanolysates was carried out by GLC after trimethylsilylation. The results revealed that **I** is D-glucosyl D-mannose, **II** is D-mannosyl D-mannose, **III** is D-mannosyl D-glucose, **IV** is D-mannosyl D-glucosyl D-mannose, **V** is D-mannosyl D-mannosyl D-mannose, and **VI** is D-mannosyl D-mannosyl D-mannosyl D-mannose.

After periodate oxidation, the values of periodate consumption, formic acid and formaldehyde liberations per one mole were established for each oligosaccharide and the data suggest the presence of 1→2 or 1→4 glycosidic linkages for the two trisaccharides and the tetrasaccharide, while the possibility of 1→3 glycosidic linkage in addition to 1→2 and 1→4 linkages also should be taken into consideration for the three disaccharides.

On the other hand, the oligosaccharides were subjected to oxidation with bromine followed by mild periodate oxidation and Smith degradation. Trimethylsilyl derivatives of the products were analyzed by GLC, and the results showed that all the samples yielded glycolic acid, glycerol and erythritol. These results support the presumption that all the disaccharides and trisaccharides have only a 1→4 glycosidic linkage. According to these results, it is also conceivable that the tetrasaccharide is composed of 1→4 linked D-mannopyranose residues and in this case the coexistence of a 1→2 linkage is not inconsistent.

Finally, methylation provided evidences which confirm the presence of 1→4 glycosidic linkages in all the oligosaccharides. The samples were methylated with sodium hydride and methyl iodide in dimethyl sulfoxide. The fully methylated products were

methanolyzed and the methanolysates were analyzed by GLC. The methyl glycosides of 2,3,4,6-tetra-O-methyl D-glucose and 2,3,6-tri-O-methyl D-mannose were identified from **I**. The methyl glycosides of 2,3,4,6-tetra-O-methyl D-mannose and 2,3,6-tri-O-methyl D-mannose were identified from **II, V,** and **VI**. And the methyl glycosides of 2,3,4,6-tetra-O-methyl D-mannose and 2,3,6-tri-O-methyl D-glucose were identified from **III**. In the case of **IV**, methyl 2,3,4,6-tetra-O-methyl D-mannoside was identified, but it was observed that the methyl glycosides of 2,3,6-tri-O-methyl D-glucose and of 2,3,6-tri-O-methyl D-mannose interfere with each other on GLC. The structure of **IV** was demonstrated by the results of its partial hydrolysis.

IV, V, and **VI** were hydrolyzed with 0.5N sulfuric acid at 90° for 1 hr and the resulting products were identified by the TLC and the GLC of their trimethylsilyl derivatives. As the results of this treatment, the partial hydrolysates obtained were **I** and **III** from **IV**, **II** from **V**, and **II** and **V** from **VI**, in addition to monosaccharides.

The values of the specific rotation and of the melting point of **I, II** and **V** coincide with those given in the literature for O-β-D-glucopyranosyl-(1→4)-D-mannopyranose, O-β-D-mannopyranosyl-(1→4)-D-mannopyranose and O-β-D-mannopyranosyl-(1→4)-O-β-D-mannopyranosyl-(1→4)-D-mannopyranose. These results gave the evidence that all oligosaccharides have β-glycosidic linkages of D-mannopyranose and D-glucopyranose.

The present study has made clear that the configuration of the glycosidic linkages of all the D-mannopyranose and D-glucopyranose residues in odoratan and falcatan is of the β-type, and elucidated the fact that most of the D-mannopyranose and D-glucopyranose are connected one another by β-1→4 glycosidic linkages. At least, both polysaccharides have two kinds of aldohexose chain unit, which are, O-β-D-mannopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→4)-D-mannopyranose and O-β-D-mannopyranosyl-(1→4)-O-β-D-mannopyranosyl-(1→4)-O-β-D-mannopyranosyl-(1→4)-D-mannopyranose.

As the result of the Smith degradation of falcatan,[3] mannose was detected as one of the resulting products in addition to glycerol and erythritol; a similar result was also obtained by the Smith degradation of odoratan. From the results stated above, it can be put forward that in the present investigation no other oligosaccharides than those showing a 1→4 glycosidic linkage have been found, which dose not exclude the possibility of a part of D-mannopyranose residues of both polysaccharides occupying branching position or part of D-mannopyranose residues having 1→3 glycosidic linkages. Therefore, it will be necessary to apply different conditions for partial hydrolysis in order to elucidate further the structure of these compounds.