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植物粘質物 (第2報) アマドコロの根茎から
粘質多糖類 Odoratan の単離と性質

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Plant Mucilages. II¹⁾. Isolation and Characterization of a
Mucous Polysaccharide, "Odoratan", from *Polygonatum*
odoratum var. *japonicum* Rhizomes*.

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The rhizome of *Polygonatum odoratum* DRUCE var. *japonicum* HARA (= *Polygonatum odoratum* DRUCE var. *pluriflorum* OHWI) has been used as a crude drug for the purpose of analeptic. We wish to report the isolation of a mucous polysaccharide from the rhizome of this plant and its properties are also described in the present paper. On the constituents of the rhizome of *Polygonatum odoratum* DRUCE (= *Polygonatum officinale* ALL.), presences of a mucilage²⁾ and an imino acid³⁾ have been reported until now. Gaal²⁾ has concluded that the mucilage is composed of D-fructose (81.7%), D-glucose and L-arabinose. But the new mucous polysaccharide obtained by us has different properties from it even in respect of component sugars.

The fresh rhizomes were extracted with hot methanol, then the residue was extracted with hot water. The methanol extract contains D-glucose, D-fructose and sucrose. The crude mucilages were precipitated from the water extract by addition of ethanol. The supernatant contains polysaccharides and oligosaccharides composed of D-fructose and D-glucose. The solution of the precipitate was applied to a DEAE-cellulose (acetate form) column, and a mucous polysaccharide was obtained from the eluate with water.

The polysaccharide was homogeneous on gel chromatography with Sephadex G-200 and gave one spot on glass-fiber paper electrophoresis in alkaline borate buffer. The name "odoratan" is proposed for the polysaccharide. It showed a negative specific rotation ($[\alpha]_D^{20} - 29.2^\circ$ in H₂O, c=0.3).

Although small amount of the other polysaccharide fraction was obtained from the DEAE-cellulose column with a gradient elution of sodium acetate solution, the result of glass-fiber paper electrophoresis showed that the fraction is a mixture of two polysaccharides. The outline of the fractionation is shown in Chart 1.

It was shown that the component sugars of odoratan are D-fructose, D-mannose, D-

* 本報告は *Chem. Pharm. Bull.* (Tokyo), **19**, 2173 (1971) に発表.

1) Part I: M. Tomoda and M. Uno, *Chem. Pharm. Bull.* (Tokyo), **19**, 1214 (1971).

2) B. Gaal, *Ber. ungar. pharm. Ges.*, **3**, 133 (1927).

3) a) A. I. Virtanen and P. Linko, *Acta. Chem. Scand.*, **9**, 551 (1955); b) A. I. Virtanen, *Nature*, **176**, 984 (1955).

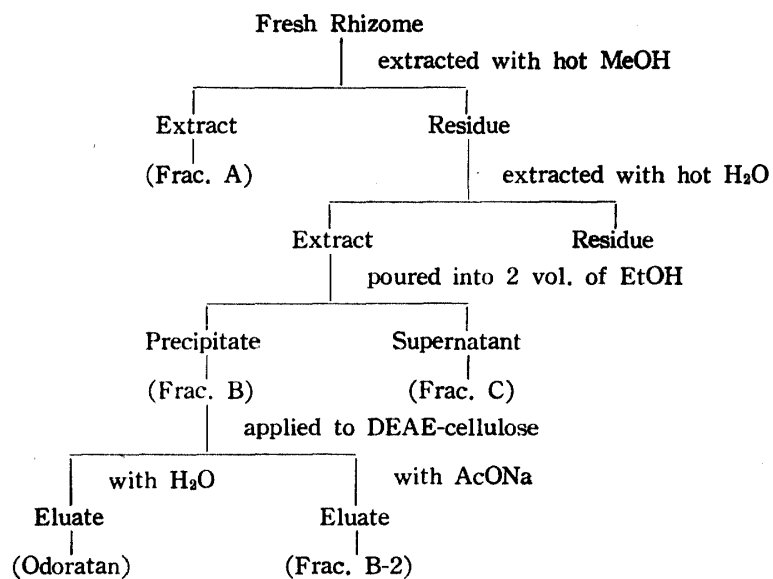
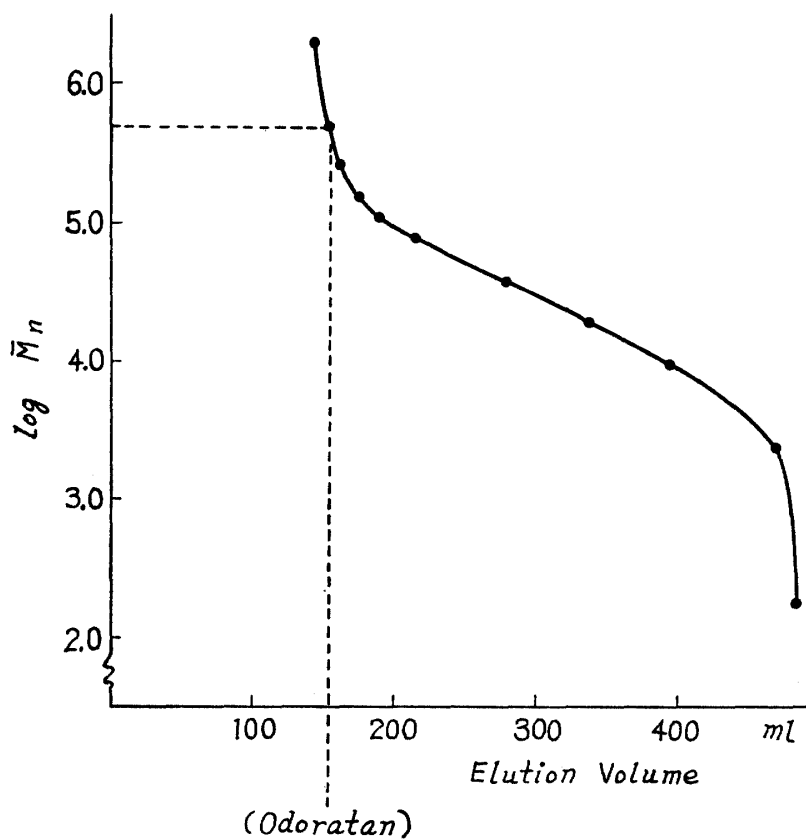


Chart 1. Isolation and Fractionation of Water-soluble Constituents.

Fig. 1 Plot of Elution Volume against $\log \bar{M}_n$ for Dextran Fractions on Sephadex G-200 with 0.1 M Ammonium Formate.

glucose and D-galacturonic acid by means of cellulose thin-layer chromatography of the hydrolysate and gas-liquid chromatography of its trimethylsilyl derivative. The fraction B-2 of Chart 1 contains L-rhamnose, D-xylose, L-arabinose and D-galactose in addition to D-fructose, D-mannose, D-glucose and D-galacturonic acid as its component sugars.

Molecular-sieve chromatography of standard dextran fractions of known molecular weights on Sephadex G-200 has given the calibration curve shown in Fig. 1. The number-average molecular weight, \bar{M}_n , of odoratan thus estimated was *ca.* 500000. This value must be regarded as approximate, but it was supported by the result of molecular-sieve chromatography of an enzymatic degradation product obtained from odoratan.

Quantitative determinations of the sugar components of odoratan showed that the molar ratio of them was as follows; D-fructose: D-mannose: D-glucose: D-galacturonic acid was about 6: 3: 1: 1.5. The water solution of odoratan gave the intrinsic viscosity value of 2.2 at 20°. On the other hand, the fraction B of Chart 1, the source of odoratan, gave the intrinsic viscosity value of 3.5 in its water solution. This result suggests the presence of the other unknown mucous substance in the fraction B. Fractions A, B-2 and C of Chart 1 showed very low or no viscosity in their water solution.

By means of the digestion with β -fructofuranosidase, 93.6% of D-fructose was liberated from odoratan. And the ketohexose was the single carbohydrate of low molecular weight produced by the enzymatic action. The residue after liberation of D-fructose was homogeneous on molecular-sieve chromatography and its molecular weight was estimated as *ca.* 250000.

As the result of periodate oxidation, 0.715 mole of periodate per one mole of the average component anhydrosugar of odoratan was consumed with 0.037 mole of formic acid liberation.

From the results of enzymatic degradation and periodate oxidation, it is conceivable that D-fructofuranose composes linear units, and on the average, odoratan contains 27 units per end group. This presumption is due to the fact that the presence of 1→6 linear linkage is denied by very low formic acid liberation. The detail of the structure of odoratan will be discussed in following papers.