Title	Isolation and characterization of fructans from polygonatum odoratum var. japonicum rhizomes
Sub Title	
Author	友田, 正司(Tomoda, Masashi) 佐藤, 訓子(Sato, Noriko) 杉山, 晶子(Sugiyama, Akiko)
Publisher	共立薬科大学
Publication year	1973
Jtitle	共立薬科大学研究年報 (The annual report of the Kyoritsu College of Pharmacy). No.18 (1973.) ,p.108- 110
JaLC DOI	
Abstract	
Notes	抄録
Genre	Technical Report
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000018-0108

No. 18 (1973)

Isolation and Characterization of Fructans from *Polygonatum odoratum* var. *japonicum* Rhizomes*

Masashi Tomoda, Noriko Satoh, and Akiko Sugiyama

友田正司，佐藤訓子，杉山晶子

As the constituents of the rhizome of *Polygonatum odoratum* Druce var. *japonicum* Hara (=*Polygonatum odoratum* Druce var. *pluriflorum* Ohwi), one of us has already reported the presences of a mucous polysaccharide, "odoratan," D-fructose, D-glucose, sucrose, and polysaccharides and oligosaccharides composed of fructose and glucose.[1] The characterization of odoratan was described in that paper. Now we report the isolation and characterization of four new fructans from the neutral polysaccharide fraction which was obtained in good yield, 17.7% from dehydrated weight of the material.

After extraction of the fresh rhizomes with hot methanol, the residue was extracted with hot water. The mucilage was precipitated from the water extract by addition of ethanol, and the supernatant was concentrated, then applied to a charcoal column. Five fractions were obtained by elution with water and stepwise increments of ethanol.

The fraction eluted with water contains fructose and glucose. The fraction eluted with 6% ethanol is sucrose, and the fraction eluted with 15% ethanol contains raffinose and oligosaccharides composed of fructose and glucose. But these fractions were obtained in low yields, and the major part of the whole eluate was occupied by the fractions eluted with 20% and 25% ethanol.

The last two fractions were combined and applied to a column of Sephadex G-25. The repeated gel chromatography gave new four non-reducing polysaccharides which showed respectively single spot on double ascending cellulose thin-layer chromatography (TLC). The names "Polygonatum-fructan O-A, O-B, O-C, and O-D" are proposed for the polysaccharides in order of molecular weight. They were obtained as white powder and easily soluble in water. Specific rotations of them were as follows: O-A, $[\alpha]_D^{20}$ −42.6° (H_2O, c=1), O-B, $[\alpha]_D^{20}$ −40.0° (H_2O, c=1), O-C, $[\alpha]_D^{20}$ −36.6° (H_2O, c=1) and O-D, $[\alpha]_D^{20}$ −33.3° (H_2O, c=1).

TLC of the hydrolysates of the polysaccharides and gas-liquid chromatography (GLC) of trimethylsilylated derivatives of the methanolysates revealed that the component sugars of them are fructose and glucose. Owing to the values of molecular weight obtained by the use of a vapor pressure osmometer and the results of quantitative determination of the component sugars of the polysaccharides, it is able to conclude that "O-A" is composed of twenty-nine fructose units and one glucose unit, "O-B" is composed of twenty-six fructose units and one glucose unit, "O-C" is composed of eighteen fructose units and one

* 本報告は *Chem. Pharm. Bull.* (Tokyo), **21**, 1806 (1973) に発表.

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

glucose unit, and "O–D" is composed of ten fructose units and one glucose unit.

As the results of periodate oxidation, the values of periodate consumption and formic acid liberation per one mole of the component anhydrosugar unit of the polysaccharides are given in Table I. The periodate-oxidized samples were reduced with sodium borohydride and the analysis of the mild hydrolysates of the products showed the presence of glycerol and no appearance of component hexose.

TABLE I. Mole Values of Periodate Consumption and Formic Acid Liberation per One Mole of Component Sugar Unit

	Periodate Consumption	Formic Acid Liberation
Polygonatum-fructan O–A	1.01	0.030
Polygonatum-fructan O–B	1.04	0.039
Polygonatum-fructan O–C	1.01	0.051
Polygonatum-fructan O–D	1.05	0.064

Methylations of the polysaccharides were performed with methyl iodide and silver oxide in dimethylformamide. After mild hydrolysis and methanolysis of the methylated products, the methanolysates were analyzed by TLC and GLC. In all cases, methyl 1,3,4,6-tetramethyl D-fructofuranoside, methyl 3,4,6-trimethyl D-fructofuranoside and methyl 2,3,4-trimethyl D-glucopyranoside were identified. The results of methylation study support the presumption that each fructose residue consumed one mole of periodate, while glucose residue consumed two moles of periodate with release of one mole of formic acid. By means of the digestion with β-fructofuranosidase, almost all glycosidic linkages of the polysaccharides were easily cleft. From these results, the structure illustrated in Chart 1 could be proposed to the four polysaccharides.

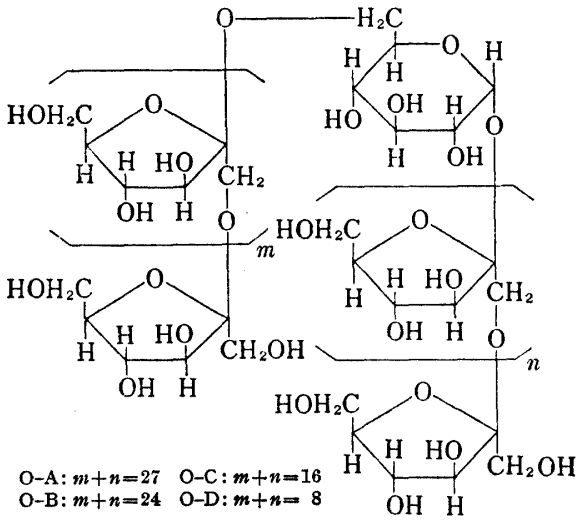

Chart 1

Fructans from various plants are divided into three groups.[2] The first is so-called inulin group which is characterised by chains of 2→1 linked β-D-fructofuranose residues. The second is phlean or levan group which has the main chain of 2→6 linked β-D-fructofuranose residues. The third group is made up of the fructans having branched structure in which both β-2→1 and β-2→6 linkages are present.

The fructans from *Polygonatum odoratum* var. *japonicum* rhizomes are linear chain non-reducing polysaccharides which are mostly composed of 2→1 linked β-D-fructofuranose residues, but they differ from typical inulin-type fructan in containing a D-glucopyranose residue in the middle of the molecule. They have not terminal non-reducing D-glucopyranose residues. The sole example of fructan having such a manner of glucose linkage in the molecule is the polysaccharide from the tubers of *Cordyline terminalis*.[3] But the latter is a highly branched fructan which contains both 2→1 and 2→6 linkages. Thus the four Polygonatum-fructans belong in a new class of natural fructan. O-β-D-Fructofuranosyl-(2—6)-O-α-D-glucopyranosyl-(1—2)-β-D-fructofuranoside (=*neo*-kestose) was found in the tubers of *Leucojum vernum* and *Leucojum aestivum*.[4] Polygonatum-fructans are structurally related to this trisaccharide, and the formation of the fructans may be interpreted as a transfructosylation starting from *neo*-kestose.

2) E. L. Hirst, *Proc. Chem. Soc.*, **1957**, 193.
3) L. A. Boggs and F. Smith, *J. Am. Chem. Soc.*, **78**, 1880 (1956).
4) H. Hammer, *Acta. Chem. Scand.*, **24**, 1294 (1970).