Title	Constituents of the radix of asparagus cochinchinensis. I. isolation and characterization of oligosaccharides
Sub Title	
Author	友田, 正司(Tomoda, Masashi) 佐藤, 訓子(Sato, Noriko)
Publisher	共立薬科大学
Publication year	1974
Jtitle	共立薬科大学研究年報 (The annual report of the Kyoritsu College of Pharmacy). No.19 (1974.) ,p.75- 77
JaLC DOI	
Abstract	
Notes	抄録
Genre	Technical Report
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000019-0075

Constituents of the Radix of *Asparagus cochinchinensis*. I. Isolation and Characterization of Oligosaccharides*

MASASHI TOMODA and NORIKO SATOH

友田正司，佐藤訓子

The tuberous roots of *Asparagus cochinchinensis* MERR. have been used in Chinese crude drug for the purpose of analeptic, diuretic and cough medicine. On the constituents of this material, only a few substances, that is, β-sitosterol, glucose, and fructose[1] have been reported until present time. In this paper, the isolation and characterization of seven oligosaccharides composed of fructose and glucose in addition to sucrose from the fresh roots of this plant are described.

The material roots were extracted with hot methanol, and the extract was applied to a column of Dowex 50 W for the separation into neutral and amino acid fractions. From the latter, nineteen amino acids were found and determined, and the detail will be reported in the following paper.

The neutral fraction was applied to a charcoal column, and six fractions were obtained by elution with water and stepwise increments of ethanol. The fraction eluted with water contains fructose and glucose, and the fractions eluted with 20% and 25% ethanol were obtained in low yields.

The major part of the whole eluate was occupied by the fractions eluted with 5%, 10% and 15% ethanol. The each of these three fractions was applied to a column of Sephadex G-15. The repeated gel chromatography gave seven non-reducing oligosaccharides, which showed respectively single spot on thin-layer chromatography (TLC), in addition to sucrose.

TLC of the hydrolysates and gas-liquid chromatography (GLC) of the trimethylsilyl derivatives of the methanolysates of the oligosaccharides revealed that the component sugars of them are fructose and glucose. The results of quantitative determination of the component sugars and the values of molecular weight obtained by the use of a vapor pressure osmometer showed that they are a trisaccharide (**I**), a tetrasaccharide (**II**), a pentasaccharide (**III**), a hexasaccharide (**IV**), an octasaccharide (**V**), a nonasaccharide (**VI**), and a decasaccharide (**VII**). The homogeneity of **I** was also checked by the GLC of its trimethylsilyl derivative. Specific rotations of them in water were as follows : **I**, $[\alpha]_D^{24}+16.9°$; **II**, $[\alpha]_D^{20}-3.4°$; **III**, $[\alpha]_D^{20}-8.4°$; **IV**, $[\alpha]_D^{20}-15.1°$; **V**, $[\alpha]_D^{20}-17.4°$; **VI**, $[\alpha]_D^{20}-20.2°$; **VII**, $[\alpha]_D^{20}-22.4°$.

* 本報告は *Chem. Pharm. Bull.* (Tokyo), **22**, 2306 (1974) に発表.

1) T. Kobayashi, T. Tomimori, T. Nakajima and N. Yahagi, *Yakugaku Kenkyū*, **30**, 477 (1958).

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 oligosaccharides are given in Table I.

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

	Periodate consumption	Formic acid liberation
Oligosaccharide I	1.26	0.38
Oligosaccharide II	1.20	0.27
Oligosaccharide III	1.04	0.20
Oligosaccharide IV	0.92	0.16
Oligosaccharide V	0.89	0.12
Oligosaccharide VI	0.90	0.11
Oligosaccharide VII	0.94	0.10

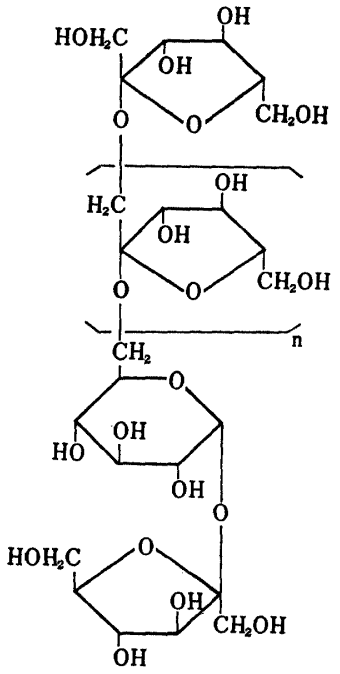
The oligosaccharides were methylated with methyl iodide and silver oxide in dimethylformamide.[2] After mild hydrolysis and methanolysis of the methylated products, the methanolysates were analyzed by GLC. In all cases but **I**, methyl 1, 3, 4, 6-tetramethyl D-fructofuranoside, methyl 3, 4, 6-trimethyl D-fructofuranoside, and methyl 2, 3, 4-trimethyl D-glucopyranoside were identified. It was revealed that the methanolysate obtained from methylated **I** is composed of the glycosides of 1, 3, 4, 6-tetramethyl D-fructofuranose and 2, 3, 4-trimethyl D-glucopyranose.

From these results, it is able to conclude that each oligosaccharide contains a D-glucopyranose residue, which consumes two moles of periodate with release of one mole of formic acid, in the middle of the molecule. And in addition to this aldohexose, there are two fructose units in **I**, three fructose units in **II**, four fructose units in **III**, five fructose units in **IV**, seven fructose units in **V**, eight fructose units in **VI**, and nine fructose units in **VII**. The values of specific rotation and the rapid rates of enzymic hydrolysis with β-fructofuranosidase strongly suggest that fructofuranose units are connected by β-D-glycosidic linkages. Thus **I** must be *O*-β-D-fructofuranosyl-(2→6)-*O*-α-D-glucopyranosyl-(1→2)-β-D-fructofuranoside, namely *neo*-kestose, and the other oligosaccharides possess the linear structures in which chains of 2→1 linked β-D-fructofuranose residues are joined with a *neo*-kestose unit.

Controlled acid hydrolysis of the oligosaccharides except **I** liberated fructose and yielded a trisaccharide which was identified with *neo*-kestose (**I**) by TLC

2) R. Kuhn, H. Trischmann and I. Löw, *Angew. Chem.*, **67**, 32 (1955).

and GLC. Sucrose was also found in the products, but neither iso-kestose nor glucose were able to be detected. Owing to these results, the structure illustrated in Chart 1 could be proposed to Asparagus-oligosaccharides. Thus the chain of 2→1 linked D-fructofuranose residues is combined with position 6 of D-glucopyranose in sucrose unit on the end of the molecule.



II : n=1
III : n=2
IV : n=3
V : n=5
VI : n=6
VII : n=7

(Chart 1)

Although it may have been a mixture of two substances, the presence of a tetrasaccharide corresponding to II in the tubers of *Leucojum vernum* and *Leucojum aestivum* was reported.[3] But none of the other oligosaccharides or polysaccharides composed of a linear structure containing *neo*-kestose unit in the molecule was found in these plants. However, four new fructans having such a structural type have been obtained from the rhizomes of *Polygonatum odoratum* var. *japonicum* in our laboratory.[4] Thus Asparagus-oligosaccharides described in this report occupy the positions in the region between Polygonatum-fructans and *neo*-kestose.

3) H. Hammer, *Acta Chem. Scand.*, **24**, 1294 (1970).
4) M. Tomoda, N. Satoh and A. Sugiyama, *Chem. Pharm. Bull.* (Tokyo), **21**, 1806 (1973).