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Water-soluble Carbohydrates of Zizyphi Fructus. II.[1] Isolation of Two Polysaccharides and Structure of an Arabinan*

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The dried fruits of *Zizyphus* genus (*Rhamnaceae*) have long been used as a crude drug for the purpose of analeptic and palliative. On the constituents of this crude drug, the presences of the much amounts of D-fructose, D-glucose and oligosaccharides composed of fructose and glucose were described in the previous paper.[1] As already reported, some polysaccharides were also found in the material, and the yield of them was higher in Japanese Zizyphi Fructus than in Chinese one. We have now isolated two polysaccharides from Japanese Zizyphi Fructus, that is, the dried fruits of *Zizyphus vulgaris* Lamarck var. *inermis* Bunge, and the structure of a neutral polysaccharide is described in the present paper.

The material was extracted with hot water, and the extract was treated repeatedly on a Sephadex G-25 column. Then the solution of crude polysaccharide fraction was applied to a DEAE-cellulose (acetate form) column, and a neutral polysaccharide and an acidic polysaccharide were obtained respectively from the eluate with water and with potassium acetate solution.

Both polysaccharides gave respectively single spot on glass-fiber paper electrophoresis in alkaline borate buffer. The neutral polysaccharide was homogeneous on gel chromatography with Sephadex G-200 and the acidic polysaccharide also showed one peak on gel chromatography, but the elution volume of the latter was very near to the void volume of the Sephadex G-200 column. Gel chromatography of standard dextran fractions of known molecular weights on Sephadex G-200 has given the calibration curve, and the molecular weight of the neutral polysaccharide thus estimated was 22000.

It was shown that the neutral polysaccharide is almost composed of L-arabinose, but small amount of D-galactose is also contained as its component sugar. The acidic polysaccharide is composed of D-galacturonic acid, L-rhamnose, L-arabinose, D-xylose and D-galactose.

Quantitative determination of the components of the neutral polysaccharide, named Zizyphus-arabinan (**I**), showed that the molar ratio of arabinose to galactose was about 30: 1. It gave a negative specific rotation ($[\alpha]_D^{20}$ −142.2° in H_2O, c=1.15).

After methylation of **I** with sodium hydride and methyl iodide in dimethyl sulfoxide, the fully methylated **I** was methanolyzed and the methanolysate was analyzed by gas-liquid chromatography (GLC). Methyl glycosides of 2,3,5-tri-O-methyl L-arabinofuranose,

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1) Part I: M. Tomoda, H. Asakura, and A. Iida, *Shōyakugaku Zasshi*, **23**, 45 (1969).

2,3-di-O-methyl L-arabinose and 3-O-methyl L-arabinose were produced in a molar ratio of 1: 4.3: 3.6.

The high negative rotation of **I** coupled with its rapid rate of acid hydrolysis strongly suggests that arabinose units are furanose type and are connected by α-L-glycosidic linkages. From the observation of methylation study, it is able to conclude that **I** has a chain of 1→5 linked α-L-arabinofuranose units having a branched structure with 1→2 branch point.

As the result of periodate oxidation, 0.6 mole of periodate per one mole of component anhydro sugar unit in **I** was consumed with the liberation of 0.03 mole of formic acid. Smith degradation of **I** produced glycerol and arabinose in a molar ratio of 3: 2.

Both the non-reducing terminal arabinose units and the non-branching intermediate arabinose units of **I** ought to consume one mole of periodate and produce one mole of glycerol as a Smith degradation product per one mole of component sugar. On the contrary, arabinose units at branching positions in **I** are not attacked with periodate oxidation. Therefore the periodate oxidation study shows the presences of two branching units per five arabinose units of **I**, and the fact that the production rate of formic acid is equivalent to the galactose content in **I** suggests that thirty units of L-arabinose residue possess one unit of D-galactose.

It has been reported that arabinans which occure as components of pectic substances possess branched-chain structures composed of 1→5 and 1→3 linked α-L-arabinofuranose residues. Thus **I** has different branching points from those of ordinary arabinans in pectic substances, although it possesses similar properties to them on the high branched structure composed of α-L-arabinofuranose units and on the relatively low molecular weight.