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## Water-soluble Carbohydrates of *Zizyphi Fructus*. II.<sup>1)</sup> 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.<sup>1)</sup> 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 ( $[\alpha]_D^{20}$   $-142.2^\circ$  in  $H_2O$ ,  $c=1.15$ ).

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

\* 本報告は *Chem. Pharm. Bull.* (Tokyo), **21**, 707 (1973) に発表.

1) Part I: M. Tomoda, H. Asakura, and A. Iida, *Shōyākugaku 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  $\alpha$ -L-glycosidic linkages. From the observation of methylation study, it is able to conclude that **I** has a chain of 1 $\rightarrow$ 5 linked  $\alpha$ -L-arabinofuranose units having a branched structure with 1 $\rightarrow$ 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 occur as components of pectic substances possess branched-chain structures composed of 1 $\rightarrow$ 5 and 1 $\rightarrow$ 3 linked  $\alpha$ -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  $\alpha$ -L-arabinofuranose units and on the relatively low molecular weight.