Title	Pectic substances. II. the location of O-acetyl groups and the Smith degradation of zizyphus-pectin A
Sub Title	
Author	友田, 正司(Tomoda, Masashi) 清水, 訓子(Shimizu, Noriko) 権田, 良子(Gonda, Ryoko)
Publisher	共立薬科大学
Publication year	1985
Jtitle	共立薬科大学研究年報 (The annual report of the Kyoritsu College of Pharmacy). No.30 (1985.) ,p.62- 63
JaLC DOI	
Abstract	
Notes	抄録
Genre	Technical Report
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000030-0062

Pectic Substances. II. The Location of *O*-Acetyl Groups and the Smith Degradation of Zizyphus-pectin A*

Masashi TOMODA, Noriko SHIMIZU and Ryoko GONDA

友田正司，清水訓子，権田良子

The isolation and structural features of the major pectic substance, named Zizyphus-pectin A, from the fruit of *Zizyphus jujuba* MILLER var. *inermis* REHD. (Rhamnaceae) have been reported in the first paper of this series. This material is a well-known oriental crude drug. *O*-Acetyl groups were identified in Zizyphus-pectin A, and the content amounted to 2.3%. The present work was undertaken to elucidate the location of the *O*-acetyl groups. This paper also deals with the results of controlled Smith degradation of the pectin.

The pectin was exhaustively treated with methyl vinyl ether, as a protective reagent for free hydroxyl groups, in the presence of *p*-toluenesulfonic acid in dimethyl sulfoxide. After conversion of the free hydroxyl groups to 1-methoxyethyl ethers, the derivative was deacetylated, then methylated with methylsulfinyl carbanion and methyl iodide in dimethyl sulfoxide, followed by methylation with methyl iodide and silver oxide in *N,N*-dimethylformamide. The resultant product was subjected to acid hydrolysis, and the final products were analyzed by GLC–MS after conversion into alditol acetates. 1,4,5-Tri-*O*-acetyl-2,3,6-tri-*O*-methyl-D-galactitol was detected and identified. This result indicates that 2,3,6-tri-*O*-acetyl D-galactose units are present in the side chains of Zizyphus-pectin A.

The pectin was subjected to periodate oxidation followed by reduction with sodium borohydride. The original polysaccharide was composed of D-galacturonic acid, L-rhamnose, D-galactose, and L-arabinose in the molar ratio of 35 : 1 : 1 : 4. After periodate oxidation, all the D-galacturonic acid residues were decomposed, and the proportions of surviving rhamnose, galactose, and arabinose residues were 70%, 85%, and 28%, respectively. After deacetylation with alkali, the product was subjected to a second periodate oxidation followed by reduction. No change in the contents of L-rhamnose and L-arabinose in the product was found after the second periodate oxidation, while 92% of D-galactose residues were decomposed by this treatment. The reduction product obtained after the second periodate oxidation was treated with 1 N sulfuric acid for 44 h at room temperature. After neutralization and dialysis, the controlled Smith degradation products were isolated by gel chromatography on Sephadex G-15. From the low molecular weight fraction, three products (I, II, III) composed of L-arabinose and

* 本報告は *Chem. Pharm. Bull.*, **33**, 4017—4020 (1985) に発表

glycerol were obtained. The products were methylated with methylsulfinyl carbanion and methyl iodide in dimethyl sulfoxide. The fully methylated products were hydrolyzed and analyzed by GLC–MS after conversion into alditol acetates. Methylation analysis indicated the production of 2,3,5-tri-*O*-methyl arabinitol acetate from I, and that of 2,3,5-tri-O-methyl arabinitol acetate and 2,3-di-*O*-methyl arabinitol acetate in molar ratios of 1 : 1 from II, and 1 : 2 from III. Based on these results and the structure of the original pectin, I, II, and III were identified as *α*-L-arabinofuranosyl glycerol, *O*-*α*-L-arabinofuranosyl-(1→5)-*α*-L-arabinofuranosyl glycerol, and *O*-*α*-L-arabinofuranosyl-(1→5)-*O*-*α*-L-arabinofuranosyl-(1→5)-*α*-L-arabinofuranosyl glycerol. Rhamnose, galactose, and arabinose were detected in the hydrolysate of the relatively high molecular weight fraction, but no structural analysis of this fraction was done because of its low yield and insufficient purity.

The results of periodate oxidation indicate that the galacturonic acid residues possess no acetyl group. From the results of the second periodate oxidation, it can be concluded that the survival of rhamnose and arabinose is based on the existence of branching residues.

Based on both the acetyl content in the pectin and the result of the first periodate oxidation, we concluded that most of the galactosyl side chain is composed of 2,3,6-tri-*O*-acetyl-D-galactopyranose residues. The incomplete decomposition of galactose units by the second periodate oxidation of the deacetylated product may be attributable to steric hindrance.

Plant pectic polymers generally have backbones consisting of rhamnogalacturonan and side chains, such as a branched arabinan and a linear 1→4-linked galactan. However, little is known about the presence of *O*-acetyl groups in pectic substances. The present report is the first to describe the presence of 2,3,6-tri-*O*-acetylated D-galactopyranosyl units in the side chains of pectic substances.