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INVESTIGATION ON THE STRUCTURE OF THE HEMICELLULOSE OBTAINED FROM THE FIBER OF *Sansevieria trifasciata* LEAVES*

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ABSTRACT

Partial hydrolysis, with 0.5M sulfuric acid for 6 h at 100°, of a pure hemicellulose fraction released from the extractive-free, delignified fiber of *Sansevieria trifasciata* leaves by 4% alkali yielded several oligosaccharides, from which two acidic and two neutral oligosaccharide fractions could be isolated in good yields. These oligosaccharides were characterized. Analysis of the Smith degradation product of the hemicellulose fraction furnished additional evidence for the structure of the hemicellulose.

INTRODUCTION

In a previous communication[1], the general structural features of the hemicellulose from the fibers of *Sansevieria trifasciata* leaves were discussed. Further, corroborative evidence, from the results of methylation analysis, Smith degradation, and characterization of the oligosaccharides isolated from the hemicellulose, are reported herein.

RESULTS AND DISCUSSION

Optimum conditions for obtaining the highest proportion of oligosaccharides were ascertained by pilot experiments. The purified fraction of the hemicellulose (2 g) was then hydrolyzed with 0.5M sulfuric acid for 6 h at 100°. After the usual treatment, the product was resolved on several chromatographic papers, and two acidic [one of them, acidic oligosaccharide I, characterized[1] as 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-xylose] and two neutral oligosaccharide fractions were isolated.

*Part II. For Part I, see ref. 1.
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On hydrolysis, acidic oligosaccharide II (42.5 mg), $[\alpha]_D^{23}$ +59.5° (water) [lit.[2] +58°] and equivalent weight 464, yielded products that had the same respective, chromatographic mobility as those of xylose, 4-*O*-methylglucuronic acid, and acidic oligosaccharide I. The methyl ester methyl glycoside was reduced, and the product was methylated by the Kuhn method[3,4]. On hydrolysis, the product yielded, in the molar ratio of 1:1.9, 2,3,4,6-tetra-*O*-methylglucose and a di-*O*-methylxylose having R_t 1.20 in column (b) (either 2,3- or 3,4-di-*O*-methylxylose, or both). The di-*O*-methylxylose fraction could not be characterized through derivatization, but, from other results, including the value of the specific rotation, +59.5° (lit.[2] +58°), it seemed possible that the aldotriouronic acid was *O*-(4-*O*-methyl-α-D-glucopyranosyl-uronic acid)-(1→2)-*O*-β-D-xylopyranosyl-(1→4)-D-xylose.

Neutral oligosaccharide I, a syrup (65 mg), had $[\alpha]_D^{23}$ −25°, and R_{Xyl} 0.58 (in solvent *A*); on scrupulous drying, it crystallized from dry ethanol, m.p. 183–185°. It yielded only xylose on hydrolysis, and the molecular weight, as determined by the alkaline hypoiodite method[5], was 272, indicating the compound to be a xylobiose. The completely methylated xylobiose was hydrolyzed, affording, in equal proportions, two methyl sugars characterized as 2,3,4-tri- and 2,3-di-*O*-methyl-D-xylose through their crystalline anilides. The 2,3,4-tri-*O*-methyl-*N*-phenyl-D-xylosylamine had m.p. 96–98° (lit.[6] 97–98°), and the corresponding derivative of 2,3-di-*O*-methylxylose had m.p. 121–122°; lit.[6] m.p. 122°. Hence, the compound must have the structure 4-*O*-β-D-xylopyranosyl-D-xylose (lit.[7] $[\alpha]_D^{23}$ −32→−25.5° in water).

On thorough drying (dry ethanol), neutral oligosaccharide II gave a solid (37.5 mg), m.p. 202–205°, $[\alpha]_D^{23}$ −44° (water); R_{Xyl} 0.29. On hydrolysis, it yielded xylose only. The molecular weight of this oligosaccharide, as determined by the alkaline hypoiodite method[5], was 406, showing it to be a xylotriose. It was completely methylated by the Kuhn method[3,4], and the product hydrolyzed. After the usual treatment, the hydrolyzate was analyzed, as the alditol acetates, by g.l.c., which indicated the presence of 2,3,4-tri- and a di-*O*-methylxylose in the ratio of 1:1.88. The di-*O*-methylxylose was characterized as 2,3-di-*O*-methylxylose through preparation of its crystalline anilide, m.p. and mixed m.p. 121–122°; lit.[6] m.p. 122°. From these results, the structure of the xylotriose was *O*-β-D-xylopyranosyl-(1→4)-*O*-β-D-xylopyranosyl-(1→4)-D-xylopyranose; lit.[7] m.p. 205–206°, $[\alpha]_D^{23}$ −39.4→−47°.

Purified fraction 2 (10 mg) was oxidized with sodium metaperiodate, and the product was Smith-degraded[8]. Analysis of the Smith-degradation product showed that it contained mainly glycerol, along with xylose (~15%). This result further corroborated the results of methylation, as, upon Smith degradation, the (1→4)-linked xylopyranosyl residues should liberate glycerol, and the branch-point xylose residues, which are linked at O-1, O-2, and O-4, should be immune to periodate oxidation, and so should be liberated as free xylose.

In a separate, Smith-degradation experiment, the borohydride-reduced product was hydrolyzed at various intervals of time (2, 5, 8, 10, and 15 h). In none of these hydrolyzates could even a trace of a xylobiose be detected; this indicated that, at least, there

are no two branch points (either of 4-*O*-methylglucuronic acid, or of xylose) in succession. They possibly occur randomly.

The i.r. spectra of the defatted fibers of *Sansevieria trifasciata* and jute (*Corchorus capsularis*) are almost identical. The only noticeable difference was that the band at 1740–1730 cm^{-1}, due to ester stretching-vibrations, was relatively much larger in the spectrum of *Sansevieria trifasciata* than in that of jute fiber.

EXPERIMENTAL

General. — All values of specific rotation are equilibrium values, and were measured with a Perkin–Elmer Model 241 MC spectropolarimeter at 23 ±1° and 589.6 nm. All evaporations were conducted under diminished pressure at bath temperatures below 40°. Paper partition-chromatography was performed on Whatman No. 1 paper, and, for preparative purpose, on 3 MM papers, with the following solvent systems: (*A*) 8:2:1 ethyl acetate–pyridine–water, (*B*) 5:5:1:3 ethyl acetate–pyridine–acetic acid–water, (*C*) 9:2:2 ethyl acetate–acetic acid–water, and (*D*) 4:1:5 1-butanol–acetic acid–water, upper layer. The spray reagents used for developing the chromatograms were: (*1*) alkaline silver nitrate, and (*2*) a saturated solution of aniline hydrogenoxalate in water. For gas–liquid chromatography, a Hewlett–Packard 4730A gas–liquid chromatograph with flame-ionization detector was used. Resolutions were performed in glass columns (1.83 m × 6 mm) containing (*a*) 3% of ECNSS-M on Gas-Chrom Q (100–200 mesh) at 190° (for alditol acetates of sugars), and (*b*) 1% of OV-225 on Gas-Chrom Q (80–100 mesh) at 170° (for alditol acetates of partially methylated sugars). Chloroform solutions of the alditol acetates[9] were injected into the g.l.c. apparatus.

Graded hydrolysis of purified fraction 2. — A pilot experiment was conducted with purified[1] fraction 2 (10 mg). This was dispersed in 0.5M sulfuric acid (2 mL), and the solution heated at 100° in a standard-joint flask. Portions (0.1 mL) of the hydrolyzate were withdrawn from the flask at 1-h intervals, up to 10 h. After the usual treatment, the hydrolysis products were analyzed by paper chromatography. Hydrolysis with 0.5M sulfuric acid for 6 h was found to be optimal for obtaining the highest proportions of oligosaccharides. Pure hemicellulose fraction 2 (2 g) was therefore hydrolyzed under these conditions, and, after the usual treatment, the hydrolyzate was concentrated to a small volume, and the oligosaccharides were resolved by preparative, paper chromatography using solvent *C*.

Hydrolysis of oligosaccharides. — All of the pure oligosaccharides obtained from paper partition-chromatography (1 mg each) were hydrolyzed with M sulfuric acid for 6 h at 100°, and, after the usual treatment, the hydrolyzates were examined by paper partition-chromatography using solvent *A*, and also, as their alditol acetates, by g.l.c. in column (*a*).

Methylation and hydrolysis of oligosaccharides[3,4]. — The oligosaccharide (20 mg) was dissolved in *N*,*N*-dimethylformamide (10 mL), silver oxide (6 g) and Drierite (4 g) were added to the solution, and the suspension was stirred. Methyl

iodide (5 mL) was then added, and stirring was continued for 40 h in the dark. The mixture was filtered, and the insoluble materials were washed with *N,N*-dimethylformamide. The filtrate and washings were combined, and concentrated to a small volume under diminished pressure. Chloroform (50 mL) was added, and the mixture was filtered through a bed of Celite. The filtrate was washed with water (4 times), dried (sodium sulfate), and evaporated to dryness. The resulting product was further methylated by the Purdie method[9] (4 times), whereupon the product did not show any OH absorption band in the i.r. spectrum. The methylation product was hydrolyzed with 0.5M sulfuric acid for 16 h at 100°, and, after the usual treatment, part of the hydrolyzate was analyzed as the alditol acetates by g.l.c. in column (*b*), and part was resolved on paper.

Smith degradation of purified fraction 2. — The purified fraction 2 (10 mg) was dispersed in 0.25M sodium metaperiodate (2 mL), and kept in the dark for 48 h at 15°, with occasional shaking. To it was added a saturated solution of barium hydroxide to pH 6, the suspension filtered, the filtrate concentrated to a small volume, and sodium borohydride (50 mg) added. The solution was kept for 4 h at room temperature, and, after acidification with glacial acetic acid to pH 6, was evaporated to dryness. Methanol (~1 mL) was 5 times added to, and evaporated from, the solid, which was then hydrolyzed with M sulfuric acid for 20 h at 100°, and, after the usual treatment, examined by g.l.c. in column *a*.

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