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INVESTIGATIONS ON THE FIBERS OF PINEAPPLE [*Ananas comosus* (L.) MERR.] LEAVES: STRUCTURAL STUDY OF THE HEMICELLULOSE

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ABSTRACT

Investigations on the hemicellulose released from extractive-free, delignified pineapple [*Ananas comosus* (L.) Merr.] leaf fiber revealed that it consists of (1→4)-linked D-xylopyranosyl residues in the main chain, from which branches of 4-*O*-methyl-D-glucopyranosyluronic acid, D-xylopyranosyl, and L-arabinofuranosyl groups originate from O-2 of the D-xylosyl residues.

INTRODUCTION

In a previous communication[1], direct evidence of some ester linkages between the 4-*O*-methyl-D-glucosyluronic acid groups of the hemicellulose and the lignin components was adduced in the case of pineapple [*Ananas comosus* (L.) Merr.] leaf fiber. The structure of the aldobiouronic acid unit present in the hemicellulose was also established. It was, therefore, of interest to study further the structure of this hemicellulose.

RESULTS AND DISCUSSION

The extract obtained by treatment with 4% sodium hydroxide solution had $[\alpha]_D^{23}$ +10.5° (in M NaOH), and contained xylose, 4-*O*-methylglucuronic acid, arabinose, and galactose in the molar ratios of 148:40.2:7:5, and traces of rhamnose, mannose, and glucose. On purification[2,3], the hemicellulose fraction had $[\alpha]_D^{23}$ +12° (in M NaOH), and retained some arabinose and traces of the hexoses. The molar ratios of xylose:4-*O*-methylglucuronic acid:arabinose were now 152:41:8. It was found that the arabinosyl groups could be specifically removed by treatment with 10% formic acid for 2 h on a boiling-water bath; no other monosaccharide could then be found, indicating that these groups are labile, and might consist of α-L-arabinofuranosyl groups.

The hemicellulose fraction was now hydrolyzed with M sulfuric acid for 20 h on a boiling-water bath. After neutralization, and the usual treatments, the hydrolyzate was passed through columns of Dowex-50W X-8 (H^+) and Dowex-1 X-4

(HCO_3^-) resins. The eluate and washings were combined, concentrated to a small volume, and the sugars resolved on Whatman No. 3MM chromatography paper, and eluted from the corresponding zones. The solutions were then evaporated to dryness, and their specific rotations determined. The values of the specific rotations of the xylose (+18°) and the arabinose (+101°) proved that the xylose had the D, and the arabinose, the L configuration. The α-D configuration of the 4-*O*-methylglucuronic acid had already been established[1].

The pure hemicellulose was now permethylated[4-6], complete methylation being proved by the absence of OH bands from the i.r. spectrum. The product was first hydrolyzed with 85% formic acid, and, after removal of the formic acid, with 0.5M sulfuric acid; the acid was then neutralized with $BaCO_3$. Part of the hydrolyzate was converted into alditol acetates, and the mixture analyzed by g.l.c. The rest of the hydrolyzate was passed through a column of Dowex-50W X-8 (H^+) and then through one of Dowex-1 X-4 (HCO_3^-) resin. The eluate and washings were combined, and evaporated to a syrup. The mixture was resolved on paper, and the four partially methylated sugars were isolated, and characterized (see Table I). The acidic fraction was eluted from the column of Dowex-1 X-4 with 0.5M sulfuric acid, and the eluate was made neutral, decationized, the product converted into its methyl ester methyl glycoside, and this reduced with lithium aluminum hydride. The product was then hydrolyzed, and individual sugars were characterized after isolation from paper. The results are given in Table I.

The presence of a small proportion of 2,3,5-tri-*O*-methylarabinose indicates the existence of arabinofuranosyl groups as nonreducing end-groups, present to the extent of one such group for every 35 xylosyl residues in the main chain. The presence of 2,3,4-tri-*O*-methylxylose in the neutral fraction of the hydrolyzate, and of 2,3,4-

TABLE I

METHYL ETHERS OF SUGARS FROM THE HYDROLYZATE OF METHYLATED HEMICELLULOSE FROM THE LEAF FIBER OF *Ananas comosus* (L.) MERR.

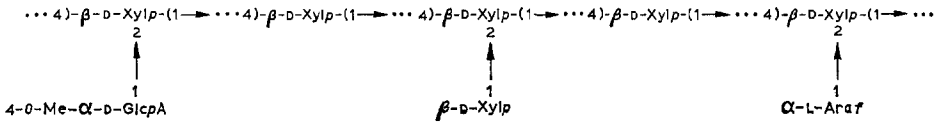
Sugars[a]	T[b]	*Approximate mole %*	*Properties of isolated sugars*		
			$[\alpha]_D^{23}$ *in water (degrees)*	*Derivative*	*M.p. of anilide (°C)*
2,3,5-Ara	0.42	2	—	—	—
2,3,4-Xyl	0.55	3	+19.5	anilide	97
2,3-Xyl	1.20	67	+23	anilide	120
3-Xyl	2.17	6	+15	anilide	136
Me-aldobiouronic acid		22	+146	—	—
2,3,4-Glc	2.23	—	+67.5	anilide	145
3-Xyl	2.17	—	+12	anilide	133

[a]2,3,4-Xyl = 2,3,4-tri-*O*-methylxylose, etc.; Me-aldobiouronic acid = 3-*O*-methyl-2-*O*-(2,3,4-tri-*O*-methyl-α-D-glucopyranosyluronic acid)-D-xylose. [b]Retention times of the corresponding alditol acetates, relative to that of 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methyl-D-glucose as unity, in column *b*.

tri-*O*-methylglucose in the hydrolyzate of the reduced methyl (methyl aldobiosid)-uronate fraction indicated that xylopyranosyl and 4-*O*-methylglucopyranosyluronic acid groups are also present as nonreducing end-groups. The back-bone chain, however, consists of (1→4)-linked xylosyl residues, as was evident from the presence of a large proportion of 2,3-di-*O*-methylxylose in the hydrolyzate. The nonreducing end-units are attached to O-2 of the xylose residues, as is evident from the characterization of 3-*O*-methylxylose in the hydrolyzate. As no other hexose derivatives could be found in the hydrolyzate, they possibly make no contribution to the structure of the hemicellulose. However, the presence of the arabinofuranosyl groups as nonreducing end-groups, small though the proportion might be, could not be ignored.

The purified hemicellulose fraction was subjected to Smith degradation[7], and, after the usual treatment, the product was analyzed by g.l.c. It mainly showed peaks of glycerol, and a small proportion of xylose. The results of the methylation analysis were thus corroborated by this experiment; a large proportion of glycerol would be obtained from (1→4)-linked xylosyl residues, and the 1,2,4-linked xylosyl residues at the branch points would be immune to periodate oxidation, and the sugar, as such, would be liberated free.

From a consideration of the results of sugar analysis, methylation analysis, and Smith degradation of the hemicellulose, the general structure **1** may be assigned to the hemicellulose.



1

For every 4 to 5 D-xylopyranosyl residues in the main chain, there is one uronic acid group; for ~28 such D-xylopyranosyl residues, there is one D-xylopyranosyl group; and, for ~35 such D-xylopyranosyl residues, there is one L-arabinofuranosyl group.

Because the hemicellulose has a low, positive rotation, the polymer is likely to contain both α and β anomeric configurations. As the configuration of the 4-*O*-methylglucosyluronic acid groups had already been established[1] as α, and as the arabinosyl groups are likely to have the α-L configuration (see earlier), the D-xylopyranosyl groups are, therefore, likely to have the β configuration. Other fiber hemicelluloses, *viz.*, those of jute[8], roselle[9], mesta[10], agave[11], sisal[12], and sansevieria[13], contain D-xylopyranosyl groups in the β configuration.

When compared to the hemicellulose of *Sansevieria trifasciata* leaf-fiber[13], or that of jute fiber, that of pineapple fiber shows a much smaller peak at 1740–1730 cm^{-1}, indicating a smaller proportion of carbonyl groups present in the system.

EXPERIMENTAL

General. — All general methods, and isolation of the hemicellulose, were conducted as described earlier[1]. The hemicellulose (9 g) was purified by complexing with Fehling solution[2,3]; yield 7 g.

Methylation analysis of the purified hemicellulose. — The pure hemicellulose (5 g) was methylated *via* acetylation, as described earlier[13]; yield 4.05 g; $[\alpha]_D^{23}$ −22° (c 1.25, chloroform). The methylated hemicellulose (4 g) was dissolved in chloroform, and fractionated with petroleum ether; three fractions (fraction a, 0.7 g, $[\alpha]_D^{23}$ −18°; fraction b, 2.85 g, $[\alpha]_D^{23}$ −28°; fraction c, 0.35 g, $[\alpha]_D^{23}$ −25°) were isolated. The major fraction b was hydrolyzed, first with 85% formic acid for 2 h at 100°, and then (after removal of formic acid by codistillation with water) with 0.5M sulfuric acid for 16 h at 100°. For identification of the different, partially methylated sugars, they were resolved on paper, using solvents[13] *A* and *B*, and then suitable derivatives were prepared.

Smith degradation of the purified hemicellulose. — The purified hemicellulose (10 mg) was dispersed in 0.25M sodium metaperiodate (2 mL), and kept in the dark for 48 h at 15°, with occasional shaking. Saturated barium hydroxide solution was gradually added (to pH 6), and the mixture was filtered; to the clear filtrate was added sodium borohydride (50 mg), and it was kept for 4 h at room temperature, acidified with glacial acetic acid (to pH 6), and evaporated to dryness. Small portions of methanol were added and evaporated (5 times). The solid residue was hydrolyzed with 2M sulfuric acid for 20 h at 100°, and, after the usual treatment, was examined by g.l.c. in column[1] *a*.

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