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Note

An arabinoxylan from the mucilage of the leaves of *Litsea polyantha*

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The plant *Litsea polyantha* grows abundantly in India. It has some medicinal uses[1]. The highly viscous water extract of the leaves is used by village people as a purgative and laxative. Isolation and characterisation of an arabinoxylan from the same leaves has already been published[2]. The present chemical investigation was performed on another arabinoxylan from the leaves of *Litsea polyantha*.

RESULTS AND DISCUSSION

From dried and powdered leaves, the crude polysaccharide was isolated as reported earlier[2]. During purification of the crude polysaccharides via the "Cetavlon" complexes, one arabinoxylan[2] formed an insoluble complex with "Cetavlon" and another remained in solution.

The present studies† were performed on the arabinoxylan that did not form an insoluble complex. After separating the complex by centrifugation, the clear supernatant solution was exhaustively dialysed and lyophilised. Gel filtration of the residue through a column of Sephadex G-100 yielded a single peak when eluted with water; the material had $[\alpha]_D^{27}$ −120°, contained D-xylose and L-arabinose in 1:2 molar ratio, and was found to be paper-electrophoretically homogeneous (borate buffer, pH 9.5).

Graded hydrolysis of the arabinoxylan with oxalic acid gave L-arabinose and D-xylose plus three oligosaccharides. The oligosaccharides were isolated and purified by preparative p.c. and characterised as follows.

Oligosaccharide I, $[\alpha]_D^{27}$ −36°, gave L-arabinose and D-xylose in almost equimolar proportions. Methylation analysis (Table I, column D) showed the presence of 2,3,5-tri-*O*-methylarabinose and 2,4-di-*O*-methylxylose in the molar ratio of 1:1, indicating that arabinose was the non-reducing end-group, (1→3)-

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†Experimental procedures were as described in ref. 2

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linked to xylose. The oligosaccharide was assigned as 3-*O*-L-arabinofuranosyl-D-xylose.

Oligosaccharide II, $[\alpha]_D^{27}$ −15°, contained L-arabinose and D-xylose in 1:2 molar ratio. Hydrolysis of the permethylated derivative yielded 2,3,5-tri-*O*-methylarabinose, and 2,3-, and 2,4-di-*O*-methylxylose in almost equimolar proportions. The structure was assigned as *O*-L-arabinofuranosyl-(1→3)-*O*-β-D-xylo pyranosyl-(1→4)-D-xylose.

Oligosaccharide[3] III, $[\alpha]_D^{27}$ −44.9°, contained xylose only. The permethylated derivative yielded 2,3,4-tri- and 2,3-di-*O*-methylxylopyranose in 1:2 molar ratio. The structure of the oligosaccharide was assigned as *O*-D-xylopyranosyl-(1→4)-*O*-D-xylopyranosyl-(1→4)-D-xylopyranose.

The polysaccharide was fully methylated by the Hakomori method[3] followed by the Purdie method[4]. The permethylated polysaccharide was hydrolysed with 85% formic acid and then with 0.25M sulphuric acid. The alditol acetates[5] of the methylated hydrolysate were identified and their relative mol proportions determined by g.l.c. (Table I).

Methylation analysis of the arabinoxylan gave 2,3,5-tri-*O*-methyl-L-arabinose, 2,5-di-*O*-methyl-L-arabinose, 2-*O*-methyl-D-xylose, and D-xylose in the molar ratios 3.1:1.0:1.1:1.0. The formation of a high proportion of 2,3,5-tri-*O*-methyl-L-arabinose indicated that the majority of the L-arabinose residues are present as terminal, non-reducing, furanosyl groups. The presence of D-xylose in the hydrolysate of the methylated polysaccharide and the formation of *O*-D-xylopyranosyl-(1→4)-*O*-D-xylopyranosyl-(1→4)-D-xylopyranose indicated that the arabinoxylan contains a (1→4)-linked xylan backbone that is highly branched. Formation of 2-*O*-methyl-D-xylose and 2,5-di-*O*-methyl-L-arabinose, and the isolation of 3-*O*-L-arabinofuranosyl-D-xylose by partial hydrolysis suggested that some of the D-xylose residues in the main chain are substituted at O-3 by L-

TABLE I

METHYLATION STUDIES OF A, NATIVE POLYSACCHARIDES, B, DEGRADED POLYSACCHARIDE AND C, SMITH-DEGRADED PRODUCT, D, OLIGOSACCHARIDES I, II, AND III

Sugars[a]	T[b]		*Approximate mol %*			*D*			*Structural unit deduced*
	1	*2*	*A*	*B*	*C*	*I*	*II*	*III*	
2,3,5-Ara	0.49	0.44	48	34	32	52	34		Ara*f*-(1-
2,3,4-Xyl	0.67	0.54						32	Xyl*p*-(1-
2,5-Ara	1.11	0.89	17						3)-Ara*f*-(1-
2,4-Xyl	1 35	1.06				46	32		3)-Xyl*p*-(1-
2,3-Xyl	1.55	1 22		32	33		32	65	4)-Xyl*p*-(1-
2-Xyl	2.98	2 20	16	33	34				3,4)-Xyl*p*-(1-
Xyl			16						2,3,4)-Xyl*p*-(1-

[a]2,3,5-Ara = 2,3,5-tri-*O*-methyl-L-arabinose, etc [b]Retention times of the corresponding alditol acetates, relative to that of 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methylglucitol

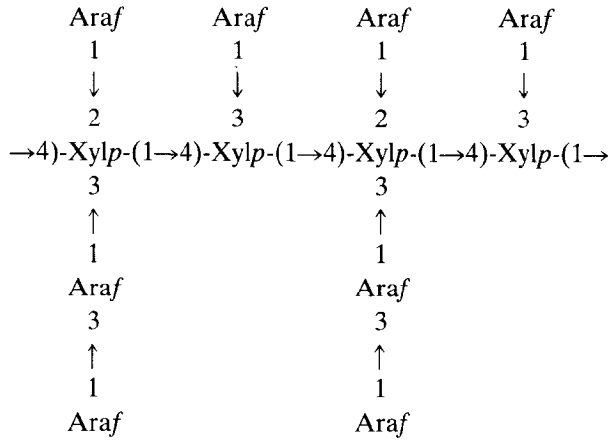
arabinose residues, some of which are further substituted at O-3 by L-arabinose residues.

A degraded polysaccharide was prepared by heating a solution of the polysaccharide in 15mM trifluoroacetic acid for 45 min at 100°. The degraded polysaccharide had $[\alpha]_D^{27}$ −95°, was electrophoretically homogeneous, and contained D-xylose and L-arabinose in the molar ratio of 2:1. Permethylation of this degraded arabinoxylan yielded 2,3,5-tri-*O*-methyl-L-arabinose, 2,3-di-*O*-methylxylose, and 2-*O*-methyl-D-xylose in the molar ratio of 1:1:1. These results show that the polysaccharide contained a (1→4)-linked xylan backbone; on average alternate xylose residues are substituted at O-3 by an L-arabinofuranosyl group.

Periodate oxidation of the native and degraded polysaccharides showed periodate consumptions of 0.55 and 0.68 mol of pentosyl residue, respectively; there was almost negligible liberation of formic acid as estimated by the method of Hirst *et al.*[6,7]. The theoretical values for periodate consumption and formic acid liberation, calculated on the basis of the results of the methylation studies, are 0.50 and 0.66 mol, with no formic acid. Thus the periodate-oxidation studies are in good agreement with methylation studies. Smith degradation[8] gave a polysaccharide that on hydrolysis yielded D-xylose and L-arabinose in 2:1 molar ratio. The degraded polysaccharide, on methylation, yielded 2,3,5-tri-*O*-methyl-L-arabinose, 2,3-di-*O*-methyl-D-xylose, and 2-*O*-methylxylose in the molar ratio of 1:1:1, indicating that all of the xylose residues are resistant to periodate oxidation and that the rest of the arabinose residues are non-reducing end-groups after the first periodate oxidation.

The product from the first Smith degradation contained D-xylose and L-arabinose in 2:1 ratio. Further periodate oxidation and subsequent $NaBH_4$ reduction yielded a product containing ~32% of xylose; in other words, all of the arabinose and half of the xylose in the product from first Smith degradation, had been oxidised. The results of Smith degradation are in good agreement with the results obtained by methylation, periodate-oxidation, and graded hydrolysis studies. The observed specific rotations indicate that most of the anomeric linkages are β.

From all of these data, it is possible to outline the structural features of the arabinoxylan from the mucilage of the leaves of *Litsea polyantha* as follows:



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