+ 16.5°, m.p. 61–62°, undepressed on admixture with a sample obtained from the methylated *Scarcina* mannan,[1] and 2,3,4,6-tetra-*O*-methyl-D-glucose, $[\alpha]_D$ + 80°, m.p. and mixed m.p. 93–95°. Both ethers behaved similarly to reference samples on gas-liquid, paper, and thin layer chromatography.

A lactone of the aldobiouronic acid (R_{Glu} 1.20) was also obtained. It yielded mannose, glucuronic acid and its γ-lactone on acid hydrolysis. When a solution of either the aldobiouronic acid or its lactone was heated in aqueous acetic acid, the same equilibrium mixture was obtained.

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Polysaccharides in Pollen

III. The Acidic Arabinogalactan in Mountain Pine Pollen

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The acidic arabinogalactan from Mountain Pine pollen has previously been shown to be made up from L-arabinose, D-galactose, L-rhamnose and glucuronic acid,[1] and a brief examination by methylation and by partial hydrolysis is now reported. The properties of two samples obtained in the fractionation series described in Part II[2] are given in Table 1. Sample A was eluted by 0.05–0.16 M and sample B by 0.13–0.34 M potassium acetate. Mild acid hydrolysis gave, besides monomeric sugars and a polymeric fraction, a disaccharide with $[\alpha]$ + 139° (*c*, 1.2) and R_{Gal} 0.67 (solvent B, Ref. 2), giving on hydrolysis galactose and arabinose and after reduction only galactose. Its mobilities on electrophoresis (M_G) in borate (pH 10), germanate (pH 10.5)[3] and sulphonated benzene boronic acid (pH 6.8)[4] buffers were, respectively, 0.86, 1.61, and 3.8, whilst those of 3-*O*-β-L-arabinopyranosyl-L-arabinose, obtained from larch arabinogalactan, were 0.87, 1.61, and 3.5, respectively. It is therefore 3-*O*-α-D-galactopyranosyl-β-arabinose which has previously been isolated, *e.g.* by Smith from gum arabic.[5] The ease of formation of the disaccharide shows the arabinose to be present in the furanosidic form in the polysaccharide. A mixture of two acid-labile arabinobioses with R_{Gal} 1.08 and 1.18 and $[\alpha]$ + 55° was also obtained. The electrophoretic mobilities of the two were, in borate 0.28 and 0.52, in germanate 0.53 and 1.34 and in sulphonated benzeneboronic acid 0.3 and 3.3. This indicates one to have a (1→2)- and the other to have a (1→3)-linkage. The optical rotation of the mixture gives no clear indication of the configuration of these linkages. Hydrolysis of the above polymeric fraction gave galactose and rhamnose as the main products, and an aldobiouronic acid with $[\alpha]$ + 7° (*c*, 1.7), shown by methylation to be 6-*O*-β-D-glucopyranuronosyl-D-galactose, which is commonly obtained from plant gums of the present type.

For methylation a fraction isolated by ethanolamine-extraction of pollen was used. The resulting product, which showed no hydroxyl band on IR, still contained some unmethylated arabinose residues which did not, by chromatography of hydrolysed samples, decrease on further methylation. The hydrolysed methylated polysaccharide was fractionated on a carbon-Celite column and on thick filter papers to give the ethers shown in the experimental section. The complexity of the mixture allowed only a semi-quantitative determination of its composition.

The results indicate a highly branched structure where D-galactose, L-rhamnose and D-glucuronic acid[1] make up a backbone that represents about 20 % of the molecule. To this chains of L-arabinose residues are joined, the linkages combining the arabinose residues being (1→2), (1→3), as well as (1→5). The significant fraction of unmethylated arabinose indicates triple branching. D-Galactose occurs also to a large extent in the exterior part of the molecule as non-reducing terminal groups

Table 1. Properties of the pollen arabinogalactan fractions.

	$[\alpha]_{578}$	% Uronic anhydride	Neutral sugars % Gal	Arab	Xyl	Rhamn	IO_4^- * consumed	Formic acid * formed
A	−89°	8.9	21.4	75.0	2.2	1.4	0.049	0.0080
B	−66°	11.4	34.9	59.0	0.5	5.7	0.043	0.0082

* mmoles/10 mg.

combined *via* (1→3)-α-linkages to L-arabinose residues. From the upward shift in the optical rotation of the unhydrolysed part on hydrolytic removal of the L-arabinosyl residues, these appear to be present mainly in the α-form.

From the present results the pine pollen arabinogalactan appears to be related to the arabinogalactan-type gums represented, *e.g.*, by the *Acacia* gums [6] and by the arabinogalactan from gum tragacanth.[7]

Experimental. General procedures used in this investigation are those previously described.[2]

Sample B (1.78 g) was hydrolysed twice for 3 h in 0.01 M hydrochloric acid at 100° with intermediate removal of low-molecular weight products. These gave, on passing through a Sephadex G-25 column, a fraction (192 mg) that was resolved on thick filter papers into a galactosyl-arabinose and a mixture of two arabinobioses. The high-molecular weight residue (332 mg, 19 %) was hydrolysed for 16 h in 0.25 M sulphuric acid at 100° giving in a similar way 103 mg of crude aldobiouronic acid. After purification on thick filter paper, it was transferred into the reduced, fully methylated methyl glycoside which on hydrolysis and fractionation of the hydrolysate on thick filter paper gave 2,3,4-tri-*O*-methyl-D-galactose, [α] + 103°, m.p. and mixed m.p. of aniline derivative 164—165°, and 2,3,4,6-tetra-*O*-methyl-D-glucose, [α] + 69°, m.p. and mixed m.p. of aniline derivative 136—138°.

The methylated polysaccharide afforded the following ethers, listed according to the approximate yields:

3—5 % yield: L-*Arabinose*, m.p. 158—160°, [α] + 105° (*c*, 1); *2-O-methyl-L-arabinose*, M_G 0.36; *3-O-methyl-L-arabinose*, [α] + 105° (*c*, 1), M_G 0.67, m.p. of corresponding lactone 80—81.5°; *2,4-di-O-methyl-D-galactose*, m.p. 97°, m.p. and mixed m.p. of aniline derivative 210—212°; *2,4,6-tri-O-methyl-D-galactose*, m.p. and mixed m.p. of aniline derivative 170—172°; *4-O-methyl-L-rhamnose*, [α] + 36° (*c*, 0.4), M_G 0.33, m.p. 120—122°, product of demethylation, rhamnose.

5—10 % yield: *2,5-di-O-methyl-L-arabinose*, [α] −1° (*c*, 1), m.p. and mixed m.p. of amide 134—135°.

10—20 % yield: *2,3,4,6-tetra-O-methyl-D-galactose*, m.p. and mixed m.p. of aniline derivative 199—200°.

> 20 % yield: *2,3-di-O-methyl-L-arabinose*, [α] + 102° (*c*, 1), m.p. of corresponding amide 157.5—158°; *2,3,5-tri-O-methyl-L-arabinose*, [α] −40° (*c*, 2), m.p. and mixed m.p. of corresponding amide 139—140°.

The identity of the 2- and 3-*O*-methyl-L-arabinoses was deduced from the conformity of their M_G-values (borate buffer) with those of the corresponding methyl-D-galactoses.[8] The acidic fraction was not examined.

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