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Preliminary communication

Regularity within the molecular structure of arabinogalactan from Western larch (*Larix occidentalis*)

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Extensive researches[1] into the molecular structure of the water-soluble arabinogalactan extracted from *Larix occidentalis* wood[2] have shown that (1→3)-linkages preponderate between the β-D-galactopyranosyl residues, and that there is extensive branching in which short chains of β-D-galactopyranosyl residues are joined (1→6). The proportion of constituent L-arabinose is low (~ 10%), the sugar being present as furanosyl and pyranosyl end-groups, and as (1→3)-linked furanosyl chain-units. The possible relationship between this arabinogalactan structure and that of the basal, branched framework of many plant-gum exudates has long been recognized[3]. No matter how complex the gums of *Acacia* species may be, they normally, after a single Smith-degradation[4] (periodate oxidation, borohydride reduction; controlled hydrolysis with acid), yield a monodisperse polymer of low molecular weight (essentially a galactan, with some pendant arabinosyl units)[5,6], or a mixture of polymers whose molecular weights are simply related[7]. Therefore it was of particular interest to examine the behaviour of the arabinogalactan from *Larix occidentalis* wood when subjected to Smith degradation. The fact that this arabinogalactan may occur as a mixture of components of widely disparate molecular weights[1,8], as do the *Acacia* gums, adds to the value of the experiment.

Shavings from *Larix occidentalis* wood were leached with warm water for 48 h, the extract was centrifuged, and the clear solution was concentrated *in vacuo*. Addition of ethanol and acetone (2 vol. of each) precipitated the arabinogalactan, which was then re-precipitated from aqueous solution and freeze-dried. The colourless, amorphous product had $[\alpha]_D$ +8° (*c* 2), was nitrogen-free, and was shown by gel-permeation chromatography to contain two components of molecular weight 78 000 (20%) and 18 000 (80%, by weight). The proportion of the latter component is much higher than has been reported for other samples[1,8]. Acid hydrolysis afforded galactose and arabinose (8:1), while partial hydrolysis (0.01M trifluoroacetic acid, 100°, 24 h) and paper chromatography showed clearly the production of (1→6)-linked galactose di- and tri-saccharides as well as a series of (1→3)-linked oligosaccharides. During the acid treatment, "phlobaphene" precipitated; however, the u.v. absorption of the arabinogalactan speci-

mens at 260 nm indicated that the flavan content was < 1%. Methylation analysis confirmed the presence of sugars linked as reported earlier[1].

The arabinogalactan reduced 7.8 mmol of periodate/g in 4 days, and, after removal of most of the periodate and iodate with barium acetate, sodium borohydride reduction, and borate removal, yielded a product that was then kept in aqueous M trifluoroacetic acid at room temperature. After 24 h, the degraded polysaccharide was shown by gel-permeation chromatography to consist of a single component of molecular weight 2200; this value was unaltered after acid treatment for a further 48 h. The product was worked-up, in the usual way[6], by freeze-drying the solution, extraction of soluble material from the residue with methanol–ether, and purification of the Smith-degraded polysaccharide by treatment in aqueous solution with ion-exchangers. The product, $[\alpha]_D$ +16° (*c* 1.3), contained galactosyl and arabinosyl residues in 8:1 ratio, and partial hydrolysis with acid showed that the majority of the inter-galactose linkages were (1→3).

There can be no doubt, therefore, that the arabinogalactan components of *Larix occidentalis* wood consist mainly of (1→3)-linked blocks of β-D-galactopyranosyl residues (~ 12) separated at regular intervals by sugar units vulnerable to periodate. Three such regions appear to exist in the component having molecular weight 18 000, and a correspondingly larger number in that having molecular weight 78 000. This structural concept parallels exactly that put forward for the gums of *Acacia podalyriaefolia* and *A. filicifolia*[6]; both gums, though polymolecular, yield a single polysaccharide component of similar molecular weight (2100) and $[\alpha]_D$ on Smith degradation.

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