# The Location of 2-*O*-(β-D-Glucopyranosyluronic Acid)-D-mannose Units in Leiocarpan A

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SEVERAL plant gums[1] furnish the aldobiouronic acid, 2-*O*-(β-D-glucopyranosyluronic acid)-D-mannose (I), as a product of partial acid hydrolysis, but in no case has evidence been available to indicate from which part of the molecular structure this disaccharide originates. *Anogeissus leiocarpus* (formerly *A. schimperi*) gum[2] is an exudate which gives rise on partial hydrolysis to this aldobiouronic acid together with several neutral oligosaccharides containing D-galactose and L-arabinose residues. A further examination of this gum has shown it to contain two structurally related polysaccharides, leiocarpan A and leiocarpan B, which may be fractionated by graded precipitation from aqueous solution with cetyltrimethylammonium bromide. The major component, leiocarpan A, contains D-glucuronic acid (*ca.* 30%), D-mannose, D-xylose, and L-arabinose as the main constituent sugars. D-Galactose is only a minor constituent sugar and it is probable that the neutral oligosaccharides, which were isolated previously from the unfractionated gum, are formed mainly from leiocarpan B. We now report experiments which show that the main chains of leiocarpan A contain alternating 4-*O*-substituted β-D-glucopyranosyluronic acid and 2-*O*-substituted α-D-mannopyranosyl residues.

Autohydrolysis of leiocarpan A resulted in the formation of an arabinose-free degraded polysaccharide with complete removal of L-arabinofuranose and partial removal of D-xylopyranose residues. Reduction of methylated degraded leiocarpan A with lithium aluminium hydride followed by hydrolysis gave 2,3,4-tri-*O*-methyl-D-xylose, 2,3-di-*O*-methyl-D-glucose, 3,4,6-tri- and 3,4-di-*O*-methyl-D-mannose as the main products. Since the glucose derivative clearly arises from the reduction of the corresponding glucuronic acid residues, the following partial structure (II) for the degraded polysaccharide represents one of several possible variants.

Carboxyl-reduced leiocarpan A was prepared by

[1] F. Smith and R. Montgomery, "Chemistry of Plant Gums and Mucilages", Reinhold, New York, 1959.
[2] G. O. Aspinall and T. B. Christensen, *J. Chem. Soc.*, 1961, 3461.

treatment of acetylated leiocarpan A with diborane.[3] Acetolysis of acetylated carboxyl-reduced leiocarpan A, followed by deacetylation of the products, afforded a mixture of neutral oligosaccharides containing residues of D-glucose and D-mannose. Fractionation of this mixture gave two disaccharides, 2-*O*-β-D-glucopyranosyl-D-mannose (III) and 4-*O*-α-D-mannopyranosyl-D-glucose (IV), two trisaccharides (V and VI), and two tetrasaccharides (VII and VIII). The isolation of these oligosaccharides indicates that the main chains of leiocarpan A are composed of 4-*O*-substituted β-D-glucuronic acid and 2-*O*-substituted α-D-mannopyranose residues, and furthermore, in the absence from the mixture of oligosaccharides containing contiguous units of the same sugar, shows that the two types of sugar unit are present in a regularly alternating sequence as depicted in (II). Although there is some evidence to suggest that gum ghatti (from *Anogeissus latifolia*)[4] may also contain main chains of a similar type, leiocarpan A provides the first clearly defined example of this class of polysaccharide. Experiments are in progress to establish other structural features in leiocarpan A and related polysaccharides.

β-D-G*p*A 1 → 2 D-Man (I)

. . . 4 D-G*p*A 1 → 2 D-Man*p* 1 → 4 D-G*p*A 1 → 2 D-Man*p* 1 . . . (II)
6
↑
1
D-Xyl*p*

β-D-G*p* 1 → 2 D-Man (III)

α-D-Man*p* 1 → 4 D-G*p* (IV)

G*p* 1 → 2 Man*p* 1 → 4 G*p* (V)

Man*p* 1 → 4 G*p* 1 → 2 Man (VI)

G*p* 1 → 2 Man*p* 1 → 4 G*p* → 2 Man (VII)

Man*p* 1 → 4 G*p* 1 → 2 Man*p* 1 → 4 G*p* (VIII)

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[3] F. Smith and A. M. Stephen, *Tetrahedron Letters*, **1960**, No. 7, 17.
[4] G. O. Aspinall, V. P. Bhavanandan, and T. B. Christensen, *J. Chem. Soc.*, 1965, 2677.