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Short Communications

The Distribution of the D-Galactose Residues in Guaran and Locust Bean Gum

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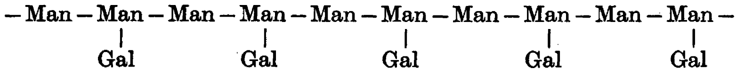
The galactomannans from the seeds of leguminous plants are composed of chains of (1→4)-linked β-D-mannopyranose residues, some of which are substituted at O-6 with an α-D-galactopyranosyl group.[1] The ratio of D-galactose to D-mannose in these polysaccharides varies with their origin, and in two of the most important, guaran and locust bean gum, it is about 1:2 and 1:4, respectively.[1]

X-Ray diffraction spectra of stretched films of guaran were interpreted many years ago[2] as indicating that the D-galactose residues were arranged along the chains in an alternating manner, as shown in (*1*). On the other hand, studies of the digestion of locust bean gum by (1→4)-β-D-mannanase[3] indicated that, whereas rather more than half of the D-galactose residues occupied isolated (non-contiguous) positions in the chains, the remainder was present in block-type structures, as shown in (*2*). The ability of locust bean gum to increase the strength of agar[4] and carrageenan[5] gels has been interpreted[6] as indicating the presence of blocks of contiguous, unsubstituted D-mannose residues, as in (*2*).

We recently studied the distribution of α-D-galactopyranosyl groups in guaran by a method based upon periodate oxidation.[7] It had previously been observed that the periodate oxidation of guaran, containing 36 % D-galactose residues, virtually stopped when about 58 % of the D-mannose residues had been oxidised.[8] For locust bean gum, containing 19 % D-galactose, we have now determined the corresponding value to be 80 %. Anomalous oxidation-limits are also observed for other polysaccharides, such as sodium alginate.[9,10] This effect was traced to the formation of inter-residue hemiacetal linkages between the aldehyde groups of oxidised residues and the hydroxyl groups of adjacent, unoxidised residues. When there is a free hydroxyl at C-6 in the oxidised residue, formation of intra-residue hemiacetals competes with the formation of inter-residue hemiacetals; protection of adjacent residues against periodate oxidation is then incomplete, and they are ultimately fully oxidised. When, however, OH-6 in an oxidised residue is blocked by substitution, the inter-residue hemiacetals are so stable that adjacent units become virtually resistant to subsequent attack by periodate.[8–10]

It follows that, for a galactomannan with an alternating structure (*1*), or any other structure in which all the D-galactose residues



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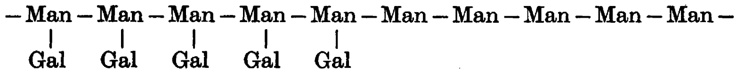

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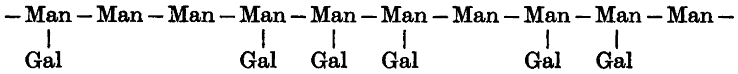

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Table 1. Methylation analysis of periodate oxidised – borohydride reduced locust bean gum. The experimental conditions have been repeated.[7,8] Components (area, of peak, relative to 2,3,6-Man = 1.00) on GLC, column SP 1000.

Time of oxidation	1,4-Eryt [b]	1-Eryt [b]	2,3-Man
0 min [a]	–	–	0.37
30 min	0.35	0.16	0.37
90 min	0.24	0.26	0.42
3 h	0.33	0.37	0.43
5 h	0.33	0.45	0.43
24 h	0.43	0.62	0.42
30 h	0.50	0.68	0.45
48 h	0.95	0.67	0.45

[a] In the analysis of unoxidised polysaccharide 2,3,4,6-tetra-*O*-methyl-D-galactose (20 %) was also detected. [b] These figures are inaccurate because the volatility of acetylated tetritol ethers leads to considerable losses during the evaporation of solutions.[7]

are isolated, only unbranched D-mannose residues would be completely protected from oxidation. A methylation analysis of the oxidised and borohydride-reduced[8,10] polysaccharide should therefore give 2,3,6-tri-*O*-methyl-D-mannose as the only hexose derivative in the hydrolysate. On the other hand, for a galactomannan in which all the D-galactose residues are contiguous, as in (*2*), it would be mostly 6-*O*-substituted D-mannose residues that were protected, and methylation analysis should give, almost exclusively, 2,3-di-*O*-methyl-D-mannose as the only hexose derivative.

For a perfectly random distribution of D-galactose residues, and an equal rate of oxidation of unsubstituted and substituted D-mannose residues, the ratio between 2,3-di-*O*-methyl- and 2,3,6-tri-*O*-methyl-D-mannose should be the same as in the methylation analysis of the original galactomannan. In fact, there is an indication[7] that the unsubstituted residues are oxidised somewhat faster than the substituted residues, so that the ratio should be a little higher for the oxidised than for the original polysaccharide.

For guaran, the above ratio for the oxidised material was approximately 2:1, on a molar basis, compared to 1.6:1 as observed for the starting material.[7] For locust bean gum it increased from 0.37, for the starting material, to a constant value of about 0.45 (Table 1).

It is evident, therefore, that simple, alternating structures (*1*) and simple, block structures (*2*) are excluded for both polysaccharides. The results are fully consistent with a near-random arrangement such as (*3*), which is the simplest interpretation of the present data. However, they are not in conflict with the kind of structure proposed by Courtois and Le Dizet[3] for locust bean gum, in which sequences such as (*1*) and (*2*) are both present, in a ratio (based upon D-mannose) of approximately 2:1.

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Debromination of 1,2-Dibromides with Sodium Dithionite *

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In connection with a current investigation of sulfinates,[1] we have found that sodium dithionite can act as a debromination agent.[2]

Treatment of *meso*-α,α'-dibromostilbene with an excess of anhydrous sodium dithionite in refluxing *N*,*N*-dimethylformamide afforded *trans*-stilbene almost quantitatively. The re-

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