

## The Structure of Guaran

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The galactomannans from seeds of leguminous plants consist of chains of 1,4-linked  $\beta$ -D-mannose residues, part of which carry an  $\alpha$ -D-galactopyranose residue linked to O-6. Studies by Courtois and Le Dizet,<sup>1</sup> using enzymatic methods, indicate that these polysaccharides are essentially block polymers, in which highly branched regions alternate with regions having a low degree of branching. Recent results from periodate-oxidation studies of guaran<sup>2</sup> have indicated the possibility of studying this problem by chemical methods, and we now report such studies.

In guaran the ratio of D-mannose to D-galactose residues is about 2:1. On periodate oxidation, however, the Malapradian oxidation limit of 1.33 mol of periodate per hexose residue was not observed. The consumption of periodate virtually stopped when 58 % of the mannose residues had been oxidized.<sup>2</sup> It has been demonstrated<sup>3,4</sup> that this inhibition of periodate oxidation is due to the formation of inter-residue hemiacetals between the aldehyde groups of oxidized residues and hydroxyl groups in unoxidized, adjacent residues. When there is a free hydroxyl at C-6,

formation of intra-residue hemiacetals competes with the formation of inter-residue hemiacetals and the protection of adjacent residues against periodate oxidation is incomplete. Even if the rate is reduced, it is then practically possible to obtain the Malapradian oxidation limit. If guaran were a block polymer, only 6-substituted D-mannose residues should be completely protected. If the 6-substituents were randomly distributed, however, both unsubstituted and 6-substituted residues should be completely protected. This has now been investigated by methylation analysis of a number of samples, which have been subjected to periodate oxidation and borohydride reduction (Table 1). Hydrolysates of the methylated products were analysed, as the alditol acetates, by GLC-MS.<sup>5</sup> The two components with  $T=0.20$  and  $0.35$  are the acetates of 1,4-di-O-methyl-D-erythritol and 1-O-methyl-D-erythritol, respectively, derived from oxidized D-mannose residues without and with a substituent at O-6. These components are volatile and considerable parts of them have most probably been lost during concentration of solutions. The ratio between 2,3-di-O-methyl-D-mannose and 2,3,6-tri-O-methyl-D-mannose is not very accurate but is consistently somewhat higher for the oxidized samples than for the original polysaccharide. If guaran were a block polymer, however, this ratio should have been much higher. The small increase observed may be due to a somewhat faster oxidation of unsubstituted than of 6-O-substituted D-mannose residues. This is also indicated by the higher ratio of di- to mono-O-methyl-D-erythritol obtained from the samples which had only been oxidized for a short time. In conclusion, therefore, the present results are consistent with a random distribution of the terminal  $\alpha$ -D-galactopyranose residues in guaran.

**Experimental.** The preparation of the modified guaran samples has been reported.<sup>2</sup> The samples were methylated according to Hakomori, hydrolysed, reduced, acetylated and analysed by GLC-MS as previously described.<sup>5</sup> A glass-column (200  $\times$  0.3 cm) containing 3 % (w/w) of OV-225 on Chromosorb G (80–100 mesh) at 180 °C was used for GLC.

Table 1. Methylation analysis of periodate oxidized-borohydride reduced guaran.

Time of oxidation	Components (area of peak, relative to 2,3,6-Man = 1.00)			
	1,4-Eryt	1-Eryt	2,3,4,6-Gal	2,3-Man
0 min	—	—	1.44	1.61
2 min	—	—	1.11	1.94
3 min	—	—	1.03	1.57
5 min	0.12	0.15	0.73	1.74
10 min	0.21	0.20	0.53	1.90
15 min	0.25	0.34	0.26	2.01
20 min	0.25	0.51	0.20	2.01
35 min	0.37	0.64	0.18	1.63
1.5 h	0.43	0.92	—	1.66
3.5 h	0.36	1.99	—	2.16
5 h	0.14	1.37	—	2.26
9 h	0.64	1.70	—	1.97
11 h	1.05	1.85	—	1.96
13.5 h	0.83	2.17	—	2.35
20 h	0.63	1.94	—	2.13
24 h	0.77	1.67	—	2.09
30 h	1.03	2.25	—	2.49

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