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 struc-

ture 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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action appeared to be fast and was complete in about 15 min. Similar treatment of *trans*-1,2-dibromocyclohexane gave cyclohexene, which distilled during the debromination. The formation of cyclohexene was complete after 30 min with an overall 60 % yield.

The reaction was not stereospecific as shown by an investigation of the debromination of *meso*- and *racemic*-2,3-dibromobutanes. The butenes thus formed were collected and analysed by GLC. Both the *meso*- and *racemic*-2,3-dibromobutanes gave a mixture of *cis*- and *trans*-2-butenes in the ratio 1:1 in about 65 % of the theoretical yield.

Reduction reactions involving sodium dithionite can formally be considered to proceed *via* nucleophilic attack of the dithionite anion followed by cleavage of the sulfur-sulfur bond to sulfur dioxide and an intermediate sulfinate [3-7] or *via* electron transfers by sulfur dioxide radical anions ($SO_2^{\cdot-}$).[8-12]

The results obtained in the debromination reaction may be explained by assuming a nucleophilic attack of the dithionite anion *via* a common carbocation intermediate to give a mixture of *threo*-2-bromo-1-methylpropanesulfinate and *erythro*-2-bromo-1-methylpropanesulfinate. The sulfinates should then decompose in a stereospecific manner to *cis*- and *trans*-2-butene, bromide ion and sulfur dioxide, respectively, according to a known reaction.[1]

Available data, however, do not exclude a mechanism involving a nucleophilic attack of the sulfur dioxide radical anion ($SO_2^{\cdot-}$) on an intermediate carbocation from the vicinal dibromides. An alternative mechanism would be a one-electron transfer reaction, which lacks high stereospecificity.[13] Electrochemical reductions of vicinal dibromides, however, proceed in a stereospecific manner,[14] which may be due to experimental conditions.

Experimental. Debromination of meso-α,α'-dibromostilbene. *meso*-α,α'-Dibromostilbene (13.6 g, 0.04 mol) and sodium dithionite (8.7 g, 0.05 mol) were dissolved in *N,N*-dimethylformamide (100 ml). The reaction mixture was heated for 15 min at 140 – 145 °C and then poured into water (1000 ml). The stilbene precipitate was filtered off. Recrystallization from ethanol yielded *trans*-stilbene (6.5 g, yield 90 %), identified by comparison with an authentic sample (m.p. and mixed m.p. 124 °C).

Debromination of trans-*1,2-dibromocyclohexane*. *trans*-1,2-Dibromocyclohexane (6.0 g, 0.025 mol) and sodium dithionite (8.7 g, 0.05 mol) were dissolved in *N,N*-dimethylformamide (50 ml). The reaction mixture was heated for 1 h at 140 – 145 °C. The cyclohexene thus formed was continuously distilled from the reaction mixture (1,2 g, b.p. 83 °C/760 mmHg, yield 60 %) and characterized by comparison with an authentic sample.

Debromination of meso- *and* racemic-*2,3-dibromobutane*. To a stirred mixture of sodium dithionite (17.5 g, 0.1 mol) in *N,N*-dimethyl-

formamide (200 ml) at 140 – 145 °C was added *meso*- or *racemic*-2,3-dibromobutane (10.8 g, 0.05 mol) over 10 min. The gaseous butenes were formed immediately and collected in about 60 – 65 % yield in a graduated cylinder *via* a washing bottle containing 2 M aqueous sodium hydroxide. Both the *meso*- and *racemic*-2,3-dibromobutanes gave a mixture of *cis*- and *trans*-2-butenes in the ratio 1:1 as shown by GLC analysis (column, 4.5 m × 3 mm, packed with 15 % dimethylsulfolane on Gas Chrom. RZ 60/80 mesh, relative retention times *trans*- and *cis*-2-butene 1.00:1.08, column temperature 30 °C).

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