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

<table>
<thead>
<tr>
<th>Time of oxidation</th>
<th>1,4-Eryt b</th>
<th>1-Eryt b</th>
<th>2,3-Man</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min a</td>
<td>—</td>
<td>—</td>
<td>0.37</td>
</tr>
<tr>
<td>30 min</td>
<td>0.35</td>
<td>0.16</td>
<td>0.37</td>
</tr>
<tr>
<td>90 min</td>
<td>0.24</td>
<td>0.26</td>
<td>0.42</td>
</tr>
<tr>
<td>3 h</td>
<td>0.33</td>
<td>0.37</td>
<td>0.43</td>
</tr>
<tr>
<td>5 h</td>
<td>0.33</td>
<td>0.45</td>
<td>0.43</td>
</tr>
<tr>
<td>24 h</td>
<td>0.43</td>
<td>0.62</td>
<td>0.42</td>
</tr>
<tr>
<td>30 h</td>
<td>0.50</td>
<td>0.68</td>
<td>0.45</td>
</tr>
<tr>
<td>48 h</td>
<td>0.95</td>
<td>0.67</td>
<td>0.45</td>
</tr>
</tbody>
</table>

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

are isolated, only unbranched D-mannose residues would be completely protected from oxidation. A methylation analysis of the oxidised and borohydride-reduced 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 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. For locust bean gum it increased from 0.37, for the starting material, to a constant value of about 0.45 (Table 1).

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Debromination of 1,2-Dibromides with Sodium Dithionite

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In connection with a current investigation of sulfonates, we have found that sodium dithionite can act as a debromination agent. Treatment of meso-a,a'-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 \textit{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 \textit{meso-} and \textit{racemic-2,3-dibromobutanes}. The butenes thus formed were collected and analysed by GLC. Both the \textit{meso-} and \textit{racemic-2,3-dibromobutanes} gave a mixture of \textit{cis-} and \textit{trans-2-butene} in the ratio 1:1 in about 65% of the theoretical yield.

Reduction reactions involving sodium dithionite can formally be considered to proceed via a nucleophilic attack of the dithionite anion followed by cleavage of the sulfur-sulfur bond to sulfur dioxide and an intermediate sulfinate or selenite ion transfers by sulfur dioxide radical anions (S\textsubscript{2}O\textsubscript{4}\textsuperscript{2-}).

The results obtained in the debromination reaction may be explained by assuming a nucleophilic attack of the dithionite anion via a common carboxylation intermediate to give a mixture of \textit{trans-2-bromo-1-methylpropene-sulfinate} and \textit{erythro-2-bromo-1-methylpropene-sulfinate}. The sulfinates should then decompose in a stereospecific manner to \textit{cis-} and \textit{trans-2-butene}, bromide ion and sulfur dioxide, respectively, according to a known reaction.

Available data, however, do not exclude a mechanism involving a nucleophilic attack of the sulfur dioxide radical anion (S\textsubscript{2}O\textsubscript{4}\textsuperscript{2-}) on an intermediate carboxylation from the vicinal dibromides. An alternative mechanism would be a one-electron transfer reaction, which lacks high stereospecificity. Electrochemical reductions of vicinal dibromides, however, proceed in a stereospecific manner, which may be due to experimental conditions.

\textbf{Experimental. Debromination of meso-\textit{a},\textit{a}'-dibromostilbene. meso-\textit{a},\textit{a}'-Dibromostilbene (13.6 g, 0.04 mol) and sodium dithionite (3.7 g, 0.05 mol) were dissolved in N\textsubscript{2}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 \textit{trans}-stilbene (6.5 g, yield 90%), identified by comparison with an authentic sample (m.p. and mixed m.p. 124°C).}

\textbf{Debromination of \textit{trans-1,2-dibromocyclohexane}. \textit{trans}-1,2-Dibromocyclohexane (6.0 g, 0.025 mol) and sodium dithionite (8.7 g, 0.05 mol) were dissolved in N\textsubscript{2}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.}

\textbf{Debromination of \textit{meso-} and \textit{racemic-2,3-dibromobutane}.} To a stirred mixture of sodium dithionite (17.5 g, 0.1 mol) in N\textsubscript{2}N-dimethylformamide (200 ml) at 140--145°C was added \textit{meso-} or \textit{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 \textit{meso-} and \textit{racemic-2,3-dibromobutanes} gave a mixture of \textit{cis-} and \textit{trans-2-butene} in the ratio 1:1 as shown by GLC analysis (column, 4.5 m x 3 mm, packed with 15% dimethylsulfone on Gas Chrom. RX 60/80 mesh, relative retention times \textit{trans-} and \textit{cis-2-butene} 1.00:1.08, column temperature 30°C).

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