Mass spectrometer for glucose/fructose mixing with maleic acid and AlCl₃.

**Figure S1. CAD on complex m/z 437**

Reaction condition: glucose/fructose (250 mM); maleic acid (100 mM); AlCl₃ (100 mM).

Temperature: 180°C; Reaction time: 1 min.

Complex assignment was studied by further collisionally activated dissociation (CAD) MS² and MS³ on m/z 437. For Figure S1a-c, MS² spectra on ions of m/z 437 were compared. In Figure S1a, before heating, glucose mixing with maleic acid and AlCl₃, ions of m/z 303 are formed upon CAD of ions of m/z 437 for [Al(Glucose)(C₄H₃O₄)₂]⁺. In Figure S1b, these are, however, not seen in CAD spectrum of ions of m/z 437 for [Al(Fructose)(C₄H₃O₄)₂]⁺. In Figure S1c, CAD of ions of m/z 437 in the reaction mixtures produces ions of m/z 303, confirming the presence of glucose in the m/z 437 adduct.

For Figure S1d-f, MS³ spectra on ions of m/z 321 obtained from CAD on m/z 437 were compared. These ions are [Al(Glucose)(C₄H₃O₄)₂]⁺, [Al(Fructose)(C₄H₃O₄)₂]⁺ and ions of m/z 437 obtained in the reaction mixture, respectively.

In Figure S1e, ions of m/z 285 are formed upon CAD of ions of m/z 321 in case of [Al(Fructose)(C₄H₃O₄)₂]⁺. These ions are, however, not seen in CAD spectrum of ions of m/z 321 for [Al(Glucose)(C₄H₃O₄)₂]⁺ from Figure S1d. In Figure S1f, all the ions peaks are detected. This confirms the presence of fructose in the in the m/z 437 adduct.

Overall, the m/z 437 represents the Al(Glucose)(maleic acid)₂ complex, moreover, the fructose can be detected by reacting glucose with maleic acid combined with AlCl₃, which supports the reaction mechanisms proposed in Figure 5c.

**Figure S1a.** CAD spectra of m/z 437 of Maleic acid+AlCl₃+Glucose before reaction
**Figure S1b.** CAD spectra of m/z 437 of Maleic acid+AlCl₃+Fructose before reaction

![CAD spectra of m/z 437 of Maleic acid+AlCl₃+Fructose before reaction](image)

**Figure S1c.** CAD spectra of m/z 437 of Maleic acid+AlCl₃+Glucose after reaction (180°C, 1min)

![CAD spectra of m/z 437 of Maleic acid+AlCl₃+Glucose after reaction (180°C, 1min)](image)

**Figure S1d.** CAD spectra of m/z 321 obtained from CAD on m/z 437 of Maleic acid+AlCl₃+Glucose before reaction

![MS³ 437 for [Al(Glucose)(C₄H₃O₄)₂]⁺](image)

**Figure S1e.** CAD spectra of m/z 321 obtained from CAD on m/z 437 of Maleic acid+AlCl₃+fructose

![CAD spectra of m/z 321 obtained from CAD on m/z 437 of Maleic acid+AlCl₃+fructose](image)
Figure S1f. CAD spectra of m/z 321 obtained from CAD on m/z 437 of Maleic acid+AlCl₃+Glucose after reaction (180°C, 1min).
<table>
<thead>
<tr>
<th>Signal (ppm)</th>
<th>Peak assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>93</td>
<td>C1 of α-D-glucose</td>
</tr>
<tr>
<td>97</td>
<td>C1 of β-D-glucose</td>
</tr>
<tr>
<td>131</td>
<td>C2 of maleic acid</td>
</tr>
<tr>
<td>170</td>
<td>C1 of maleic acid</td>
</tr>
<tr>
<td>189</td>
<td>C1 of open chain D-Glucose</td>
</tr>
</tbody>
</table>

Note: $^{13}$C-NMR peak assignment for glucose is based on Figure 3. $^{13}$C-NMR peak assignment for maleic acid is based on Figure 4(b).

Peaks present in range from 60 – 80 ppm represent signal of C2-C6 carbon atoms in D-glucose in D$_2$O.