Mass spectrometer for glucose/fructose mixing with maleic acid and $AlCl_3$.

Figure S1. CAD on complex m/z 437

Reaction condition: glucose/fructose (250 mM); maleic acid (100 mM); $AlCl_3$ (100 mM). Temperature: 180°C; Reaction time: 1min.

Complex assignment was studied by further collisionally activated dissociation (CAD) MS^2 and MS^3 on m/z 437. For Figure S1a-c, MS^2 spectra on ions of m/z 437 were compared. In Figure S1a, before heating, glucose mixing with maleic acid and $AlCl_3$, ions of m/z 303 are formed upon CAD of ions of m/z 437 for $[Al(Glucose)(C_4H_3O_4)_2]^+$. In Figure S1b, these are, however, not seen in CAD spectrum of ions of m/z 437 for $[Al(Fructose)(C_4H_3O_4)_2]^+$. 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, MS^3 spectra on ions of m/z 321 obtained from CAD on m/z 437 were compared. These ions are $[Al(Glucose)(C_4H_3O_4)_2]^+$, $[Al(Fructose)(C_4H_3O_4)_2]^+$ 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 $[Al(Fructose)(C_4H_3O_4)_2]^+$. These ions are, however, not seen in CAD spectrum of ions of m/z 321 for $[Al(Glucose)(C_4H_3O_4)_2]^+$ 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 $AlCl_3$, which supports the reaction mechanisms proposed in Figure 5c.

Figure S1a. CAD spectra of m/z 437 of Maleic acid+$AlCl_3$+Glucose before reaction

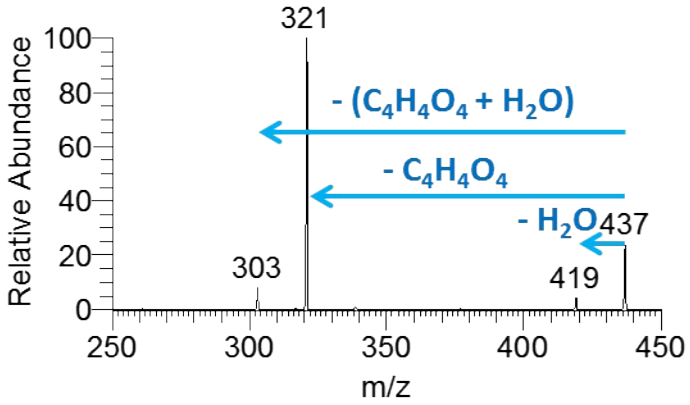

Figure S1b. CAD spectra of m/z 437 of Maleic acid+$AlCl_3$+Fructose before reaction

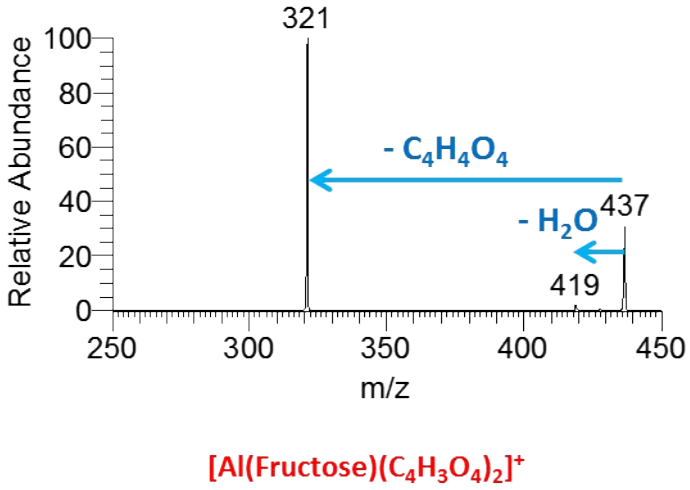

Figure S1c. CAD spectra of m/z 437 of Maleic acid+$AlCl_3$+Glucose after reaction (180^{o}C, 1min)

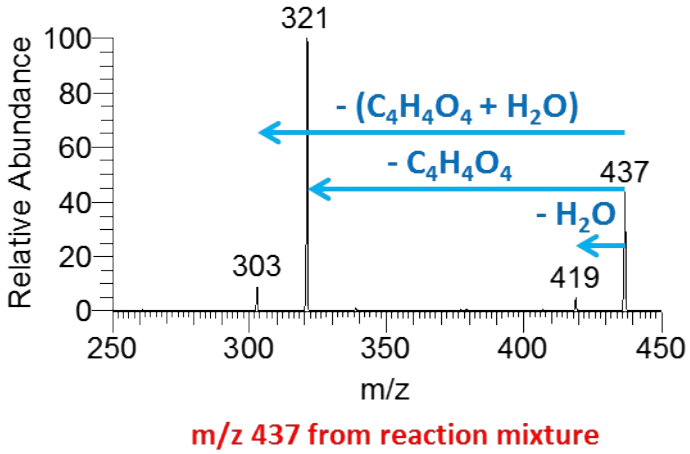

Figure S1d. CAD spectra of m/z 321 obtained from CAD on m/z 437 of Maleic acid+$AlCl_3$+Glucose before reaction

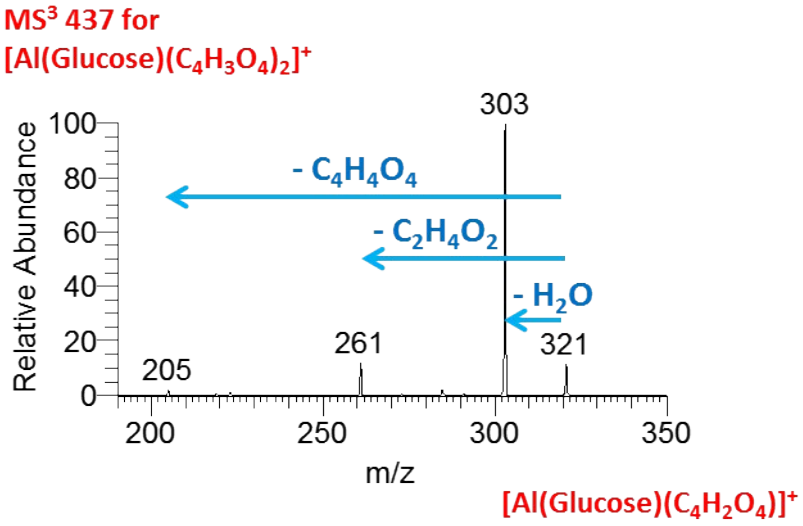

Figure S1e. CAD spectra of m/z 321 obtained from CAD on m/z 437 of Maleic acid+$AlCl_3$+fructose

before reaction

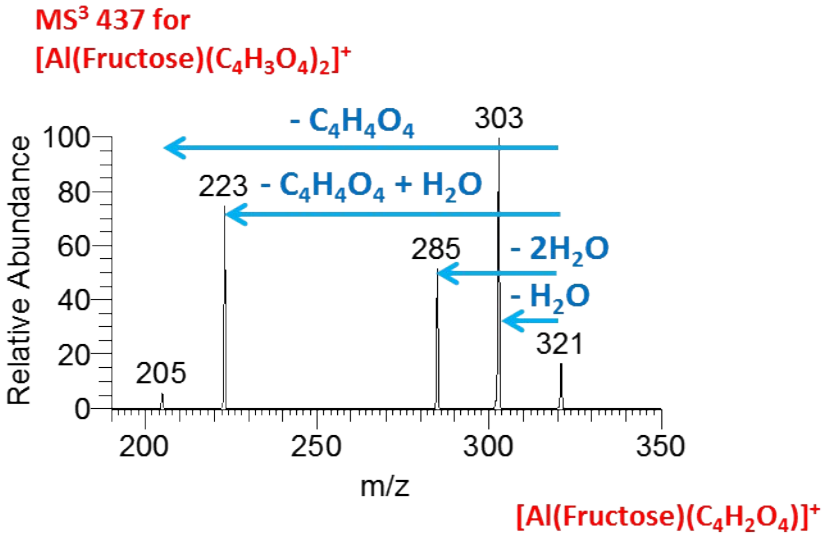

Figure S1f. CAD spectra of m/z 321 obtained from CAD on m/z 437 of Maleic acid+$AlCl_3$+Glucose after reaction (180°C, 1min).

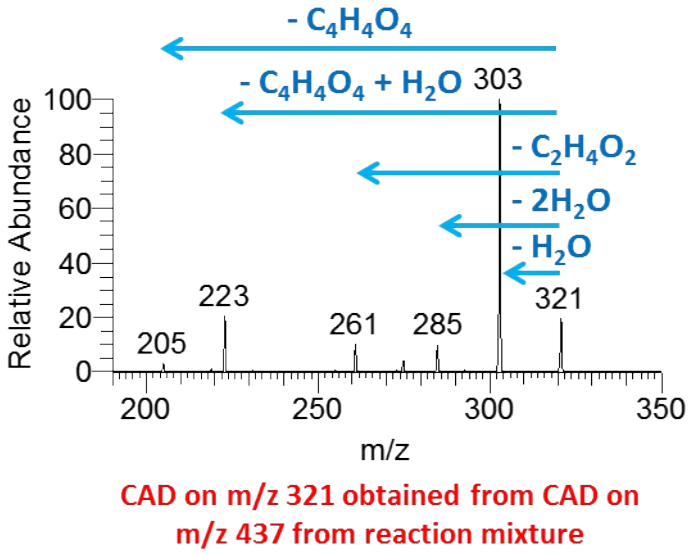

Table S1. ^{13}C-NMR peak assignment

Signal (ppm)	Peak assignment
93	C1 of α-D-glucose
97	C1 of β-D-glucose
131	C2 of maleic acid
170	C1 of maleic acid
189	C1 of open chain D-Glucose

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_2O.