

# Sustainable Conversion of Carbohydrates to Chemicals.

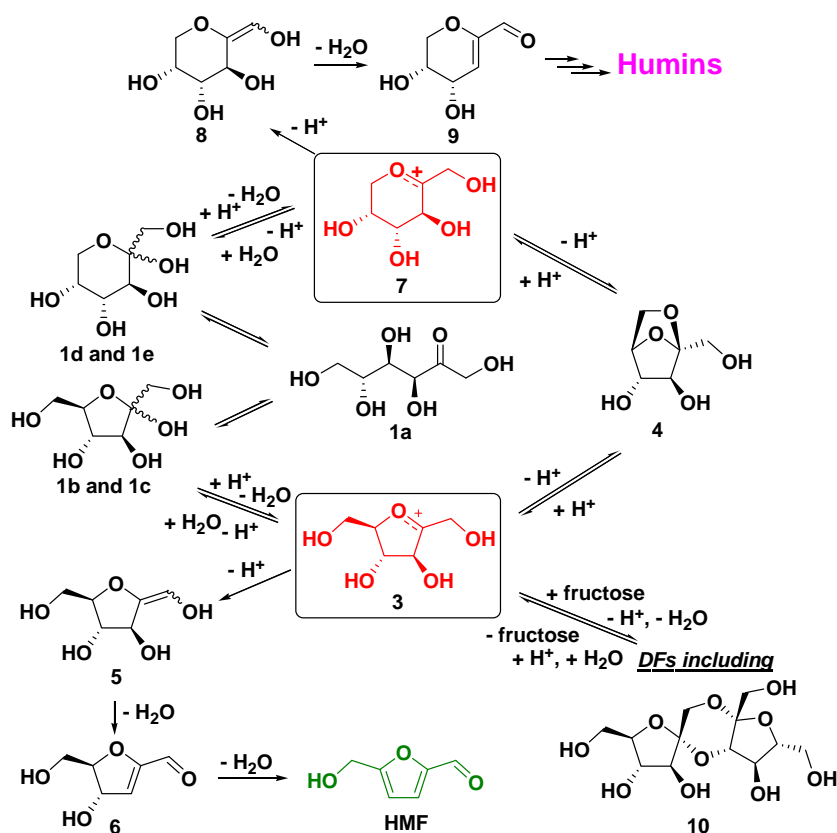
## *Do We Appreciate the Mechanistic Limitations?*

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Molecular level control of the conversion of biomass to chemicals including fuels is important for the sustainability of the chemical and pharmaceutical industry and to a lesser extent for the energy industry. Globally, the largest portion of biomass is composed of carbohydrates including C<sub>5</sub>- and C<sub>6</sub>-monosaccharides, which can be linked together by glycosidic bonds in various combinations to form di- and polysaccharides, which are key components of sugar, starch, lignocellulose, and even some algae. Depolymerization of the glycosidic bonds by catalytic hydrolysis can produce monosaccharides for subsequent conversions. A frequently underestimated complication of the conversion of glucose or fructose is that both have five molecular isomers in equilibria in solution. Their equilibrium concentrations and reactivity depend on the nature of the solvent, which could be affected by the presence of water.

The acid catalyzed conversion of fructose could lead to the formation of the desirable 5-(hydroxymethyl)-2-furaldehyde (HMF) and the side product humins. In situ NMR study and labelling experiments have revealed that the formation of HMF proceeds through different reaction steps (**1b,c**→**3**→**5**→**6**→HMF) than the formation of humins (**1d,e**→**7**→**8**→**9**→humins).



Interestingly, the reversible formation of 2,6-anhydro-β-D-fructofuranose (**4**) from **3** provides a mechanistic limitation on selective HMF synthesis by its protonation to form **7**, which can be readily converted to humins. Similar mechanistic routes are available for glucose and sucrose. Possible approaches to overcome of the various mechanistic limitations will be discussed.