

Value Added Chemicals from Sugar Feedstocks

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Department of Chemistry



Based on

“Top Value Added Chemical from Biomass
Vol. 1: Results of Screening for Potential
Candidates from Sugars and Synthesis Gas”

Eds. T. Werpy and G. Petersen

Pacific Northwest Laboratory

And

National Renewable Energy Laboratory

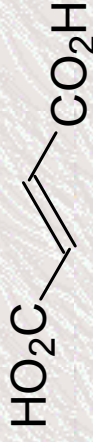
Criteria for Selecting Chemicals

- Obtainable from sugars derived from cellulose, hemicellulose, or starch
- At least two functional groups
- [Potentially] convertible to high value chemicals
- Data on [potential] market value
- Potential to become super-commodity chemicals

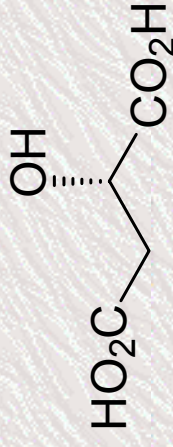
The Winners



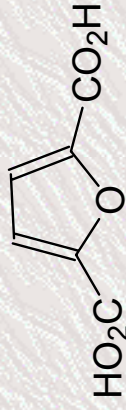
Succinic acid



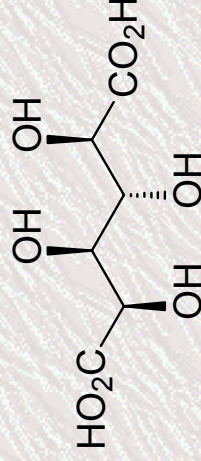
Fumaric acid



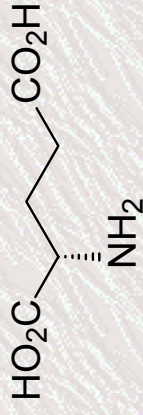
(S)-Malic acid



Furan dicarboxylic acid

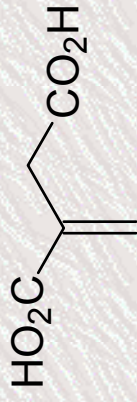


Glucaric acid

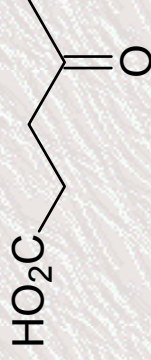


Glutamic acid

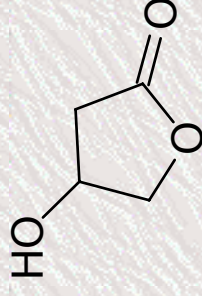
The Winners



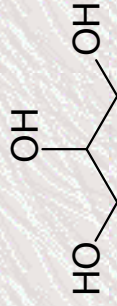
Itaconic acid



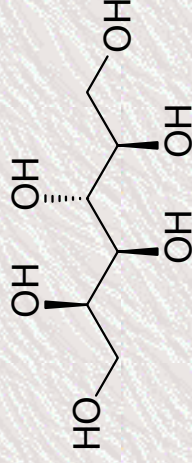
Levulinic acid



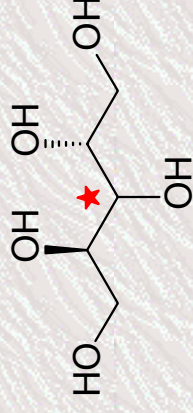
Hydroxybutyrolactone



Glycerol

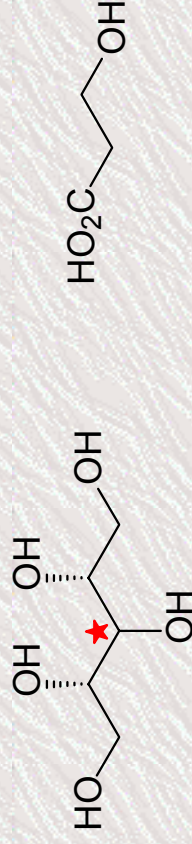


Sorbitol

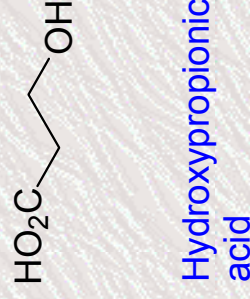


Xylitol

pseudo-
★ chiral
center



Arabinitol



Hydroxypropionic acid

These compounds divide fairly well into two groups:

- Those with the same carbon number and carbon skeleton as the sugars
- Those with fewer carbons or altered carbon skeletons

All of the first group are typically produced by simple chemical methodology. For example:

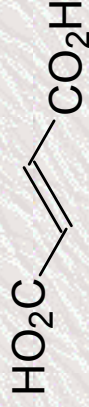
- Sorbitol by catalytic hydrogenation of glucose
- Levulinic acid by acid catalyzed dehydration of sugars
- Glucaric acid by oxidation of starch with nitric acid or hypochlorite
- Xylitol by catalytic hydrogenation of xylose

With one exception, all of the second group are produced biologically. For example:

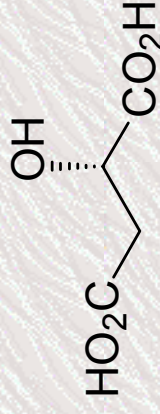
- Glycerol by yeast fermentation of sugars, (and by hydrolysis of fats and oils)
- Glutamic acid by fermentation of glucose or xylose with *B. subtilis* or genetically modified *E. coli*
- Hydroxypropionic acid by anaerobic fermentation of glucose



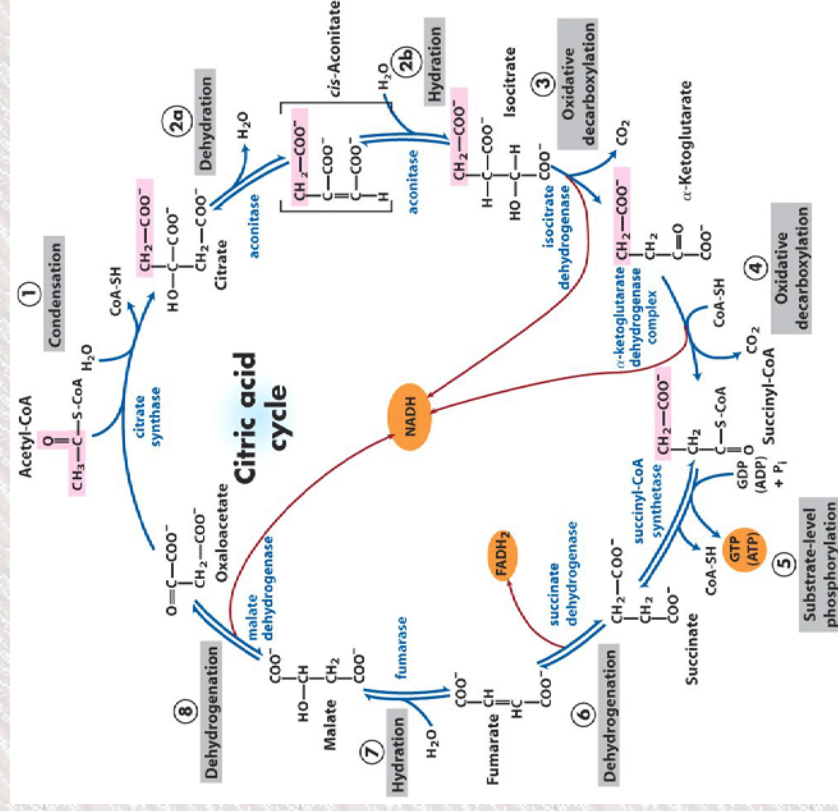
Succinic acid



Fumaric acid

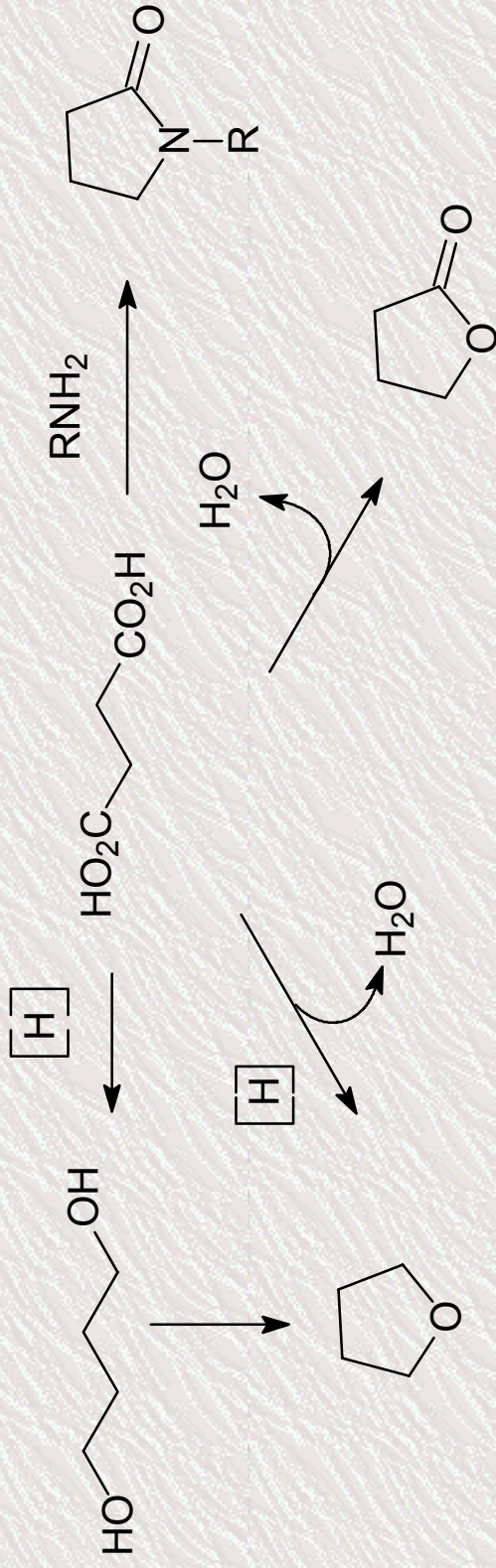


(S)-Malic acid

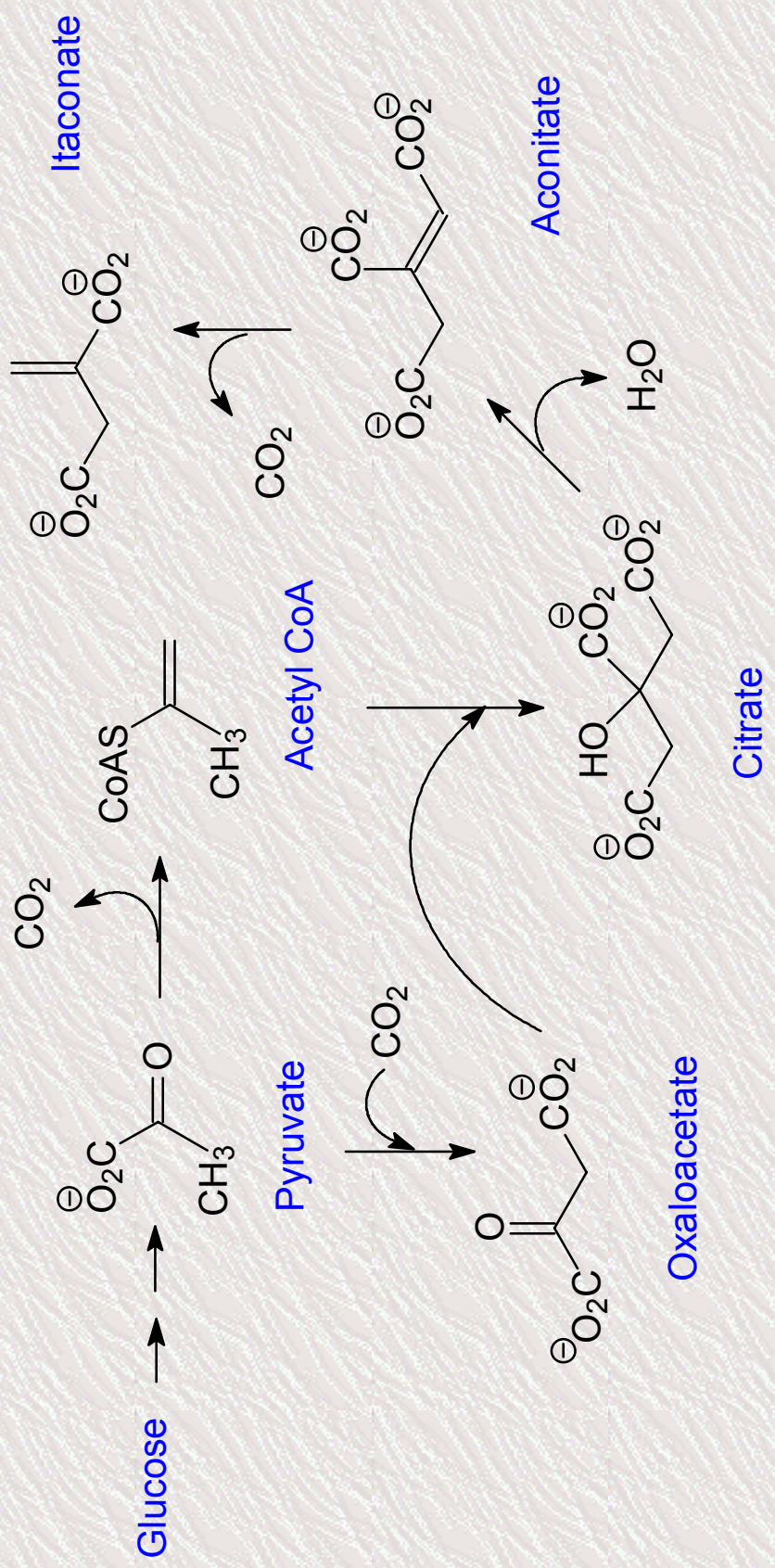


- Overexpression of succinate has been engineered in numerous strains of *E. coli*
- Knocking out other NADH consuming pathways increases yield, up to 130%
- Some strains will utilize xylose as well as glucose
- Purity of feedstock an issue when using biomass: phenolics from lignin inactivate bugs
- Flow systems with immobilized bacteria have been tested

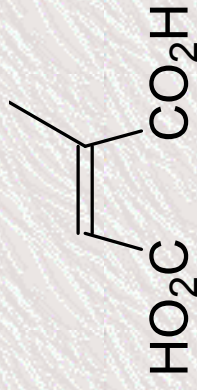
Primary Transformations of Succinic Acid



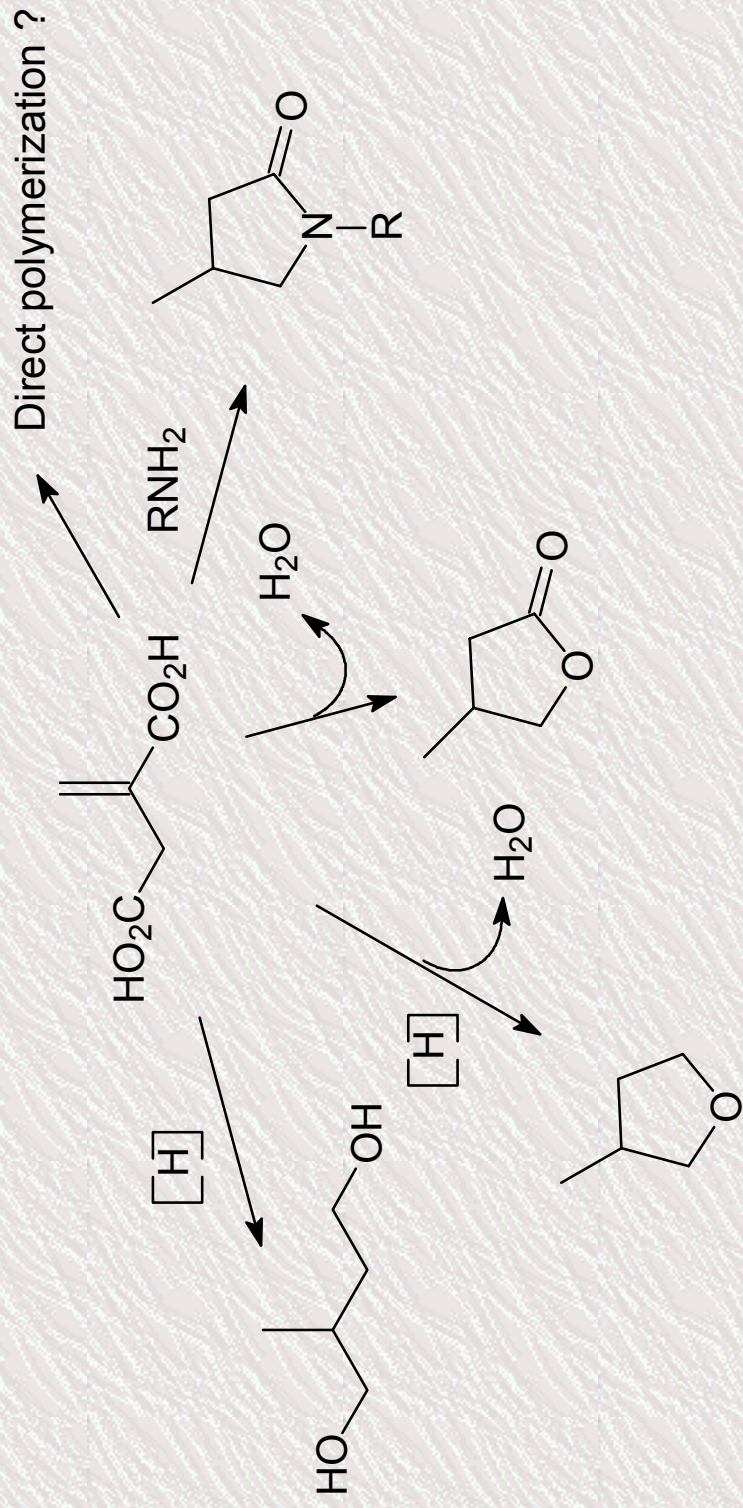
Biochemical Pathway to Itaconic Acid



- Itaconic acid secreted by fungi to acidify their environment
- Chief fungus employed is *Aspergillus terreus*
- With glucose substrate, yields are 40-60%
- Five-carbon sugars give only 15-30%
- Isomerization to the more stable citraconic acid is a problem



Primary Transformations of Itaconic Acid



Major Issues

- Startup requires large capital investment
- Petroleum-based competitors still relatively cheap
- Competition from biomass-to-fuel
- Heterogeneity, purity of feedstocks
- Relative fragility of bacteria, fungi

Thanks to my colleagues Joe Genco and
Barbara Cole for helpful discussions.