

## Hydrogenation of Glutamic Acid to Value Added Products

Johnathan E. Holladay, Todd Werpy

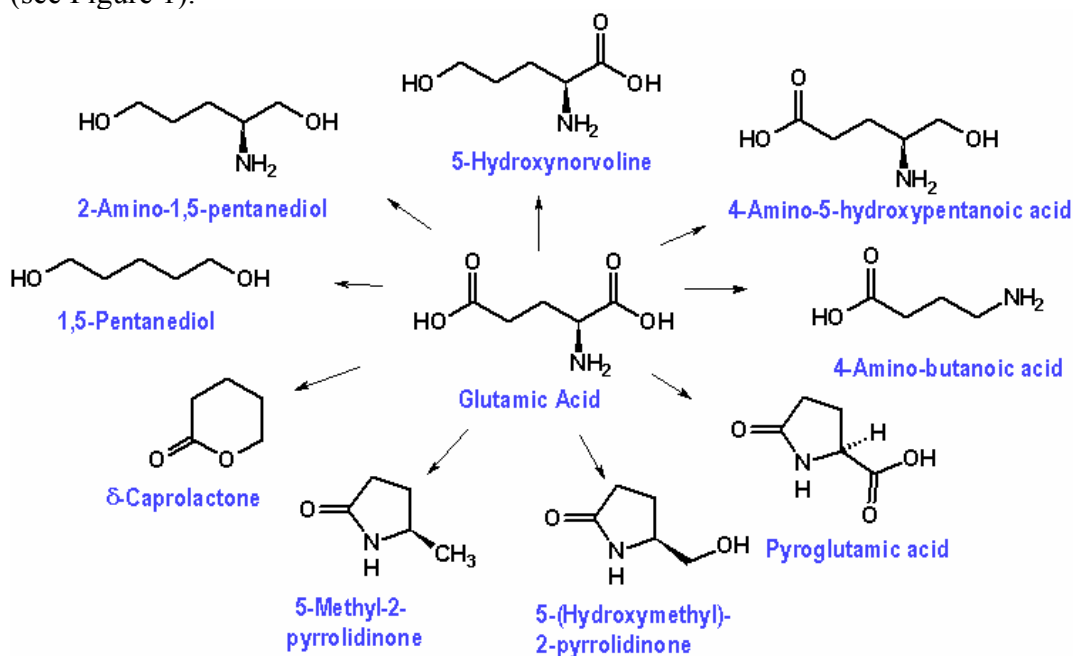
Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99352, USA.

### Introduction

Technology to convert biomass to chemical building blocks provides an opportunity to displace fossil fuels and increase the economic viability of bio-refineries. Particularly, starch/glucose provides a significant opportunity for producing both high value and commodity chemicals without a significant impact on food supply or infrastructure. Coupling fermentation capability with aqueous phase catalysis provides novel routes to monomers and chemicals from glucose, including those not accessible from petrochemical routes. In this presentation we will discuss novel pathways to C-4 and C-5 compounds that utilize aqueous phase catalysis of glutamic acid, a fermentation product of glucose.

### Results and Discussion

Glutamic acid provides a platform to numerous compounds through thermal chemical approaches including, hydrogenation, cyclization, decarboxylation and deamination (see Figure 1).



The difference in  $pK_a$  of the two carboxylic acid groups (2.19 and 4.25) suggests that it may be possible to selectively reduce the carboxylic acid moieties of glutamic acid. Cyclization of glutamic acid<sup>1</sup> is known to occur at elevated temperatures providing

access to 2-pyrrolidinones. Deamination would result in 1,5-pentanediol or caprolactone and selective decarboxylation would result in 4-aminobutanoic acid.

Hydrogenation of amino acids also provides access into chiral compounds with high enantio-purity. Stereospecific hydrogenation of amino acids has been documented in the literature.<sup>2,3</sup> Examples in the literature include hydrogenation of glutamic acid and pyroglutamic acid (2-pyrrolidinone-5-carboxylic acid) published since the inception of our work.<sup>4</sup>

This presentation will detail thermochemical processes that we have developed leading to valuable chemical intermediates from glutamic acid, including compounds not shown in Figure 1. The major emphasis will be on the catalyst systems (various precious metals on supports along with co-catalysts). In addition <sup>13</sup>C NMR and MALDI Mass spec data will be used to provide a mechanistic picture of the reactions. The results show that hydrogenation of glutamic acid has unique characteristics from other amino acids and that the paradigms in the literature do not hold up for this platform reaction.

#### References

1. M. J. Blish, *US Patent* 2,738,353 (1956).
2. a) S. Antons, A. S. Tilling and E. Wolters, *PCT Intl. Appl.* WO 9938838 (1999). b) S. Antons, *U.S. Patent* 5,731,479 (1998). c) S. Antons and B. Beitzke *U.S. Patent* 5,536,879 (1996).
3. F. T. Jere, D. J. Miller and J. E. Jackson *Org. Lett.* in press.
4. S. Antons, A. S. Tilling, and E. Wolters *US Patent* 6,310,254 (2001).