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The indium mediated acyloxyallylation of aldoses – a revisiting worthwhile

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The indium-mediated acyloxyallylation of aldoses, introduced a decade ago, is an elegant way for the two-carbon elongation of reducing sugars (upon ozonolysis). In the original prove-of-concept study, the use of D-pentoses and standard D-hexoses delivered heptoses and octoses, respectively; it was shown that out of the four possible diastereomers, the product with *lyxo*-configuration (*syn*, *anti* - addition) is dominantly formed in all cases with reasonable selectivity. [1]

Recently, we have developed this methodology into the first short, large-scale synthesis of the bacterial sugar L-glycero-D-manno heptose. *En route*, we have elucidated the two further formed diastereomers (*gluco*>*allo*), now allowing to make hypotheses on the type of selectivity observed in such acyloxyallylations of aldoses. [2]

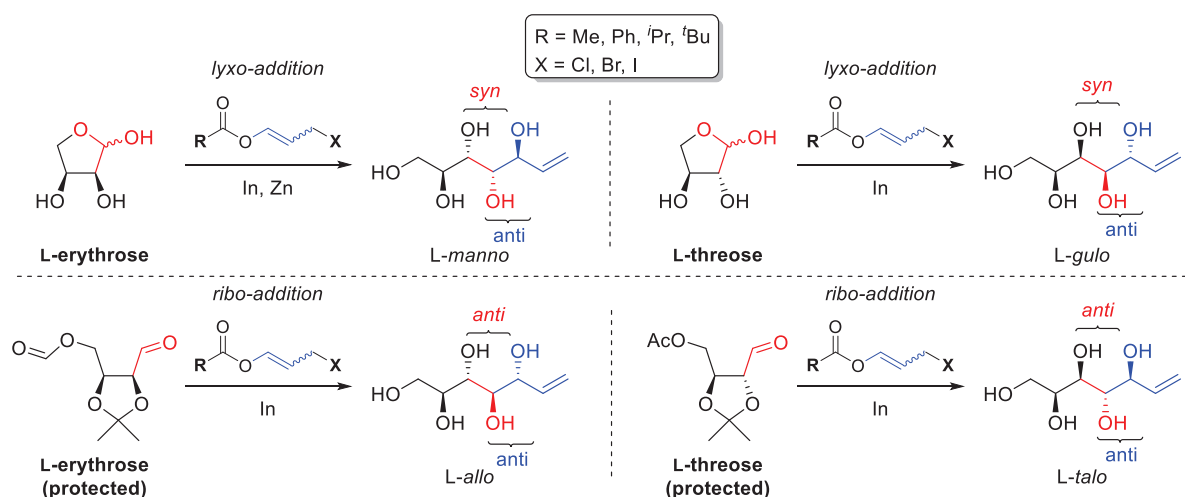


Figure 1. Diastereodivergence in the acyloxyallylation of protected and unprotected tetroses

We next engaged in an in-depth methodological investigation, choosing to study the protected and unprotected tetroses (L-shown) as starting materials. Consequently, all expectable products are hexoses, thus allowing unambiguous identification *via* comparison with authentic samples (Fig. 1). The effect of steric bulk ($R = \text{Me}, i\text{Pr}, t\text{Bu}$) in the reagent on the diastereoselectivity was investigated and we could achieve the first analogous transformation mediated by cheap zinc instead of indium.

Thorough analysis confirmed the product distribution observed in our case study (*lyxo*>*xylo*>*ribo* addition) for erythrose and threose, thus to be of a general nature. Most interestingly, a complete diastereodivergence was found with the corresponding 2*O*, 3*O*-protected derivatives as starting material, giving *ribo*-addition (*anti*, *anti*) in a very pronounced fashion. This allowed us to establish a short scalable synthesis of L-allose from L-arabinose (upon ozonolysis; Fig. 1, bottom left), as a second example of an exotic sugar made readily available *via* acyloxyallylation.

[1] Palmelund A.; Madsen R.; Chain Elongation of Aldoses by Indium-Mediated Coupling with 3-Bromopropenyl Esters. *J. Org. Chem.* **2005**, *70*, 8248-8251.

[2] Stanetty C.; Baxendale I. R.; Large-Scale Synthesis of Crystalline 1,2,3,4,6,7-Hexa-*O*-acetyl-L-glycero- α -D-manno-heptopyranose. *Eur. J. Org. Chem.* **2015**, *2015*, 2718-2726.