

GLYCOSYL AZIDES – NOVEL SUBSTRATES FOR ENZYMATIC TRANSGLYCOSYLATIONS

Pavla Fialová, Ana T. Carmona¹, Inmaculada Robina¹, Petr Sedmera,
Lucie Hušáková, Vladimír Křen*

*Institute of Microbiology, Academy of Sciences of the Czech Republic, Vídeňská 1083,
CZ-142 20 Prague 4, Czech Republic*

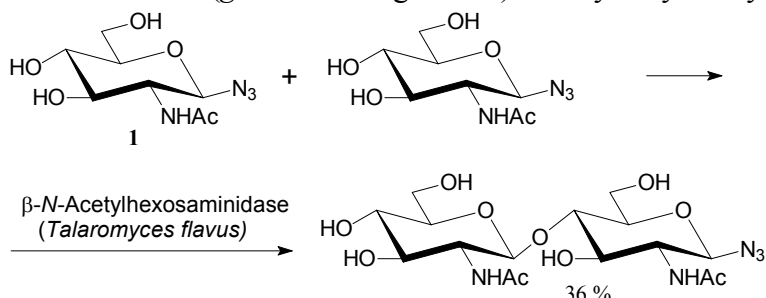
¹*Department of Organic Chemistry, Faculty of Chemistry, University of Seville, E-
41071 Seville, Spain*

kren@biomed.cas.cz, fialovap@biomed.cas.cz

Enzymatic transglycosylation catalyzed by glycosidases is a respected method in carbohydrate synthesis. The spectrum of acceptors is practically infinite, contrary to the limited selection of glycosyl donors, which are usually nitrophenyl glycosides. However, they have a number of disadvantages such as a rather low water solubility. Glycosyl azides can be prepared easily and in a high yield, they are well water soluble and, primarily, they are readily cleaved by glycosidases. Moreover, the azide ion is easily removable, which strongly facilitates the purification of transglycosylation reaction mixtures.

We present a new methodology using 2-acetamido-2-deoxy- β -D-glucopyranosyl azide (**1**) and 2-acetamido-2-deoxy- β -D-galactopyranosyl azide (**2**) as efficient glycosyl donors for a wide range of fungal β -N-acetylhexosaminidases from our enzymatic library. Substrate **1** (*gluco*-configuration) was accepted by all tested β -N-acetylhexosaminidases whereas substrate **2** (*galacto*-configuration) was hydrolyzed by neither of the enzymes.

This unexpected result can be explained by molecular modeling using the active site of the β -N-acetylhexosaminidase from *A. oryzae*.



The transglycosylation reaction using **1** with β -N-acetylhexosaminidase from *Talaromyces flavus* that proved to be the best from the screening (reaction rate, yields) was demonstrated in the preparation respective chitobiose derivative and some other disaccharides. This is probably the first example of the use C-N glycosides as substrates for glycosidase-catalysed synthesis.

Acknowledgement

This work was supported by grants Czech National Science Foundation No. 203/05/0172, Research Concept No. AV0Z50200510 and by COST Chemistry D25/0001/01 (MŠMT OC D25.002).