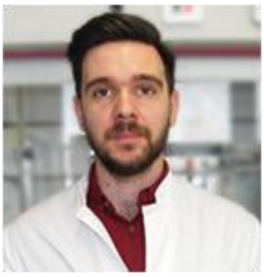
ENZYMATICALLY INDUCED LOSSEN REARRANGEMENT AS A BIOCONJUGATION AND LABELING TOOL



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Glucosinolates are sulfur-containing secondary metabolites whose structure is based on a β-D-glucopyranose unit linked through an *O*-sulfated (*Z*)-thiohydroximate function to a variable aglycon. They are found in the cruciferous vegetables, such as broccoli, mustard, arugula, wasabi and play an important role in the defence mechanism of these plants against potential predators.(1) Hydrolysis of the anomeric C-S bond by myrosinase, a specific β-thioglucohydrolase, leads to the formation of isothiocyanate species (ITC). The result is a shift from stable, non-toxic, and water-soluble precursors to a toxic, highly reactive, difficult to prepare and store and, in most cases, water-insoluble function.(2) This unique enzyme-substrate system in Nature can be explored as a novel bioconjugation tool for various applications such as synthesis of neoglycoproteins, selective protein labeling or nanoparticle functionalization.(3)

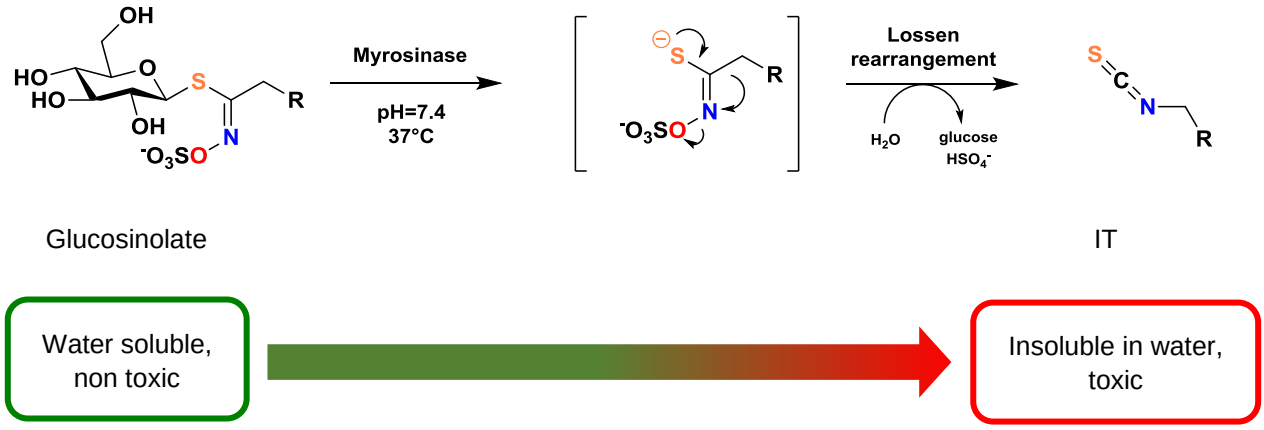

Figure 1. Myrosinase-Glucosinolate system to generate isothiocyanates

Herein, we describe our recent results on the design, synthesis, and reactivity of various artificial glucosinolates. We also showed that those compounds are substrates of myrosinase and can be hydrolysed into the corresponding ITCs. In addition, we will describe the synthesis of glucosinolates specifically designed as tools to study and detect myrosinase's activity *in vitro,* and the synthesis of « pseudo » glucosinolates from which we are able to generate ITCs using enzymes different from myrosinase.

References

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(3) (a) Fredy, J. W.; Cutolo, G.; Poret, B.; Nehmé, R.; Hubert-Roux, M.; Gandolfo, P.; Castel, H.; Schuler, M.; Tatibouët, A.; Sabot, C.; Renard, P.-Y. *Bioconjugate Chemistry* **2019**, *30*, 1385–1394. (b) G. Cutolo, B. Didak, J. Tomas, B. Roubinet, M.Schuler, P. Lafite, R. Nehmé, L. Landemarre, A.Tatibouët *Glyconjugate*, **2021**, *submitted*