

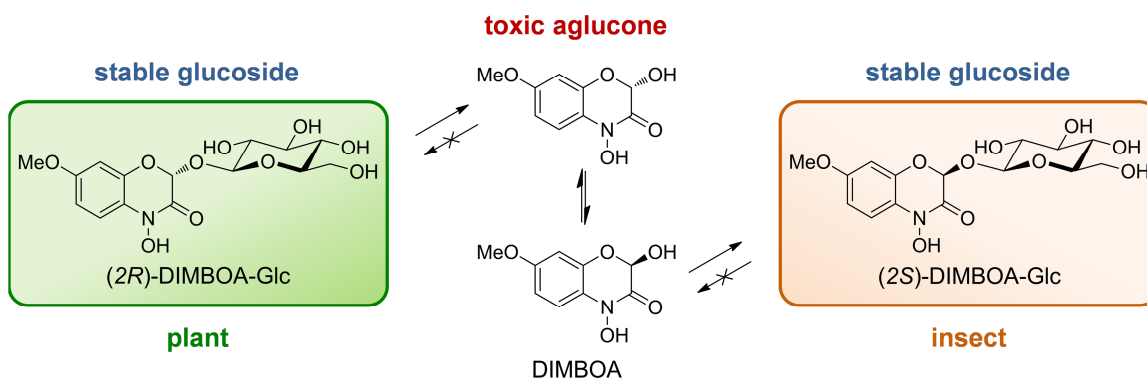
DETOXIFICATION OF MAIZE CHEMICAL DEFENSES BY LEPIDOPTERAN HERBIVORES

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In order to avoid or overcome damage by herbivores, grasses (Poaceae) such as rye, wheat, and maize rely on a family of indole-derived chemical defenses called benzoxazinoids (BXDs). [1] These compounds are stored in plant cells as stable glucosides and, upon herbivory, are converted into toxic aglucones by the action of plant glucosidases. However, some herbivores evolved adaptations that enable them to feed on well-defended plants, leading to the emergence of some species as serious agricultural pests. Although BXDs biosynthesis in plants is well studied, [2] little is known about their metabolism in insects. In this context, we aim to better understand the strategies used by lepidopteran herbivores to avoid toxicity by BXDs.

Comparing lepidopteran herbivores feeding on maize, we observed that *Spodoptera frugiperda*, *S. littoralis* and *S. exigua* excrete the non-toxic DIMBOA-Glc (the most abundant BXD in maize) in the frass. We performed *in vitro* assays with gut tissue preparations and confirmed that this compound is result of enzymatic reglucosylation of DIMBOA by the insect. Surprisingly, the compound produced by the insect is (2*S*)-DIMBOA-Glc, an epimer of the plant-derived (2*R*)-DIMBOA-Glc. We demonstrate that plant glucosidases are not able to hydrolyze the insect metabolite, thus preventing it from exerting its toxicity after it is transformed by the insect. Therefore, we identified the reglucosylation of DIMBOA involving overall inversion of stereochemical configuration as a detoxification mechanism employed by *Spodoptera* species. [3] Moreover, we present our ongoing work on identifying the UGT enzymes relevant for BXD detoxification in *S. frugiperda*, based on a transcriptomic approach, and how we plan to further explore BXD metabolism through feeding assays using radiolabeled BXDs. Collectively, the elucidation of BXD metabolism in insects clarifies their coevolution with plants and provides targets for innovative approaches in ecological and agricultural research.



[1] Niemeyer, H.M. 2009. Hydroxamic Acids Derived from 2-Hydroxy-2*H*-1,4-Benzoxazin-3(4*H*)-one: Key Defense Chemicals of Cereals. *J. Agric. Food Chem.* 57: 1677-1696.

[2] Frey, M., Schullehner, K., Dick, R., Fiesselmann, A. and Gierl, A. 2009. Benzoxazinoid biosynthesis, a model for evolution of secondary metabolic pathways in plants. *Phytochem.* 70: 1645-1651.

[3] Wouters, F.C., Reichelt, M., Glauser, G., Bauer, E., Erb, M., Gershenzon, J. and Vassão, D.G. 2014. Reglucosylation of the Benzoxazinoid DIMBOA with Inversion of Stereochemical Configuration is a Detoxification Strategy in Lepidopteran Herbivores. *Angew. Chem. Int. Ed.* 53: 11320-11324.