22nd Iranian Inorganic Chemistry Conference,
23-25 August, 2023
University of Kurdistan

The Reaction Mechanism of Aphid Myrosinase, A Theoretical Study

Sonia Jafari,[a] **Ulf Ryde**[b] **and Mehdi Irani**[a,*]

[a]*Department of Chemistry, Faculty of Science, University of Kurdistan, Sanandaj, Iran*

[b]*Department of Theoretical Chemistry, Lund University, Lund, Sweden*

[*]*E-mail: m.irani@uok.ac.ir*

The aphid *Brevicoryne brassicae* is a specialist feeding on *Brassicaceae* plants. The insect has an intricate defense system involving the myrosinase enzyme that hydrolysis glucosinolates sequestered from the host plant into volatile isothiocyanates [1]. In this study, we investigated the reaction mechanism of aphid myrosinase using a quantum mechanics/molecular mechanics (QM/MM) method [2]. A model of the active site of this enzyme was constructed based on the crystal structure of aphid myrosinase from *Brevicoryne brassicae* (1WCG PDB ID) [1]. The active site can be divided into two parts, the glucose and aglycon binding sites (cf. Figure 1). Our result showed that in the first step of the mechanism (glycosylation), the catalytic residue (Glu-374) performs a nucleophilic attack on the anomeric carbon of the substrate, and then the other carboxyl residue (Glu-167), acting as a general acid, protonates the glycosidic sulfur. This leads to forming of a glycosyl–enzyme intermediate and the aglycon moiety leaves the reaction medium. In the next step (deglycosylation), Glu-167, acting as a general base, activates a water molecule to attack the anomeric center of the intermediate, and the covalent bond between the enzyme and the glycosyl is broken, and the β-glucose molecule is released.

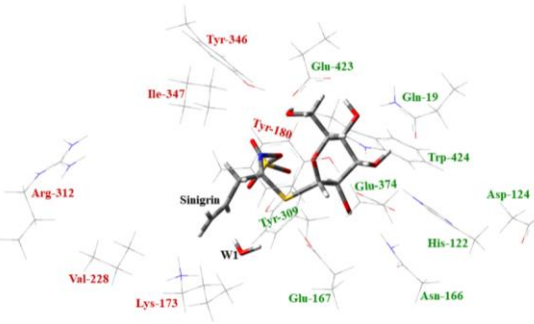


Figure 1. The QM system we used in the calculations. Residues of the glucose binding site are labeled in green and those of the aglycon binding site in red. Sinigrin is the substrate.

Keywords: Aphid myrosinase, Reaction mechanism, QM/MM

References

[1] H. Husebye, S. Arzt, J. W. P. Burmeister, F. V. Hartel, A. Brandt, J. T. Rossiter, and A. M. Bones, *Insect Biochem. Mol. Biol.*, **2005**, 35, 1311.
[2] U. Ryde, *Methods Enzymol.* **2016**, 577, 119.