

A dedicated glutathione S-transferase mediates carbon-sulfur bond formation in gliotoxin biosynthesis.

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Abstract

Gliotoxin is a virulence factor of the human pathogen *Aspergillus fumigatus*, the leading cause of invasive aspergillosis. Its toxicity is mediated by the unusual transannular disulfide bridge of the epidithiodiketopiperazine (ETP) scaffold. Here we disclose the critical role of a specialized glutathione S-transferase (GST), GliG, in enzymatic sulfurization. Furthermore, we show that bishydroxylation of the diketopiperazine by the oxygenase GliC is a prerequisite for glutathione adduct formation. This is the first report of the involvement of a GST in enzymatic C-S bond formation in microbial secondary metabolism.

Involved units

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