Substrate Specificity of Three New Intradiol Dioxygenases: an X-ray Characterization

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The crystal structures of Hydroxyquinol 1,2-dioxygenase (1,2-HQD) from Nocardioides simplex 3E [1] and of 3- [2] and 4-chlorocatechol 1,2-dioxygenases [3,4] from the Gram-positive bacterium Rhodococcus opacus 1CP, three Fe(III) ion containing enzymes involved in the aerobic biodegradation of different chloroaromatic compounds, have been recently solved.

The analysis of the structures and their comparison with the catechol 1,2-dioxygenase from Acinetobacter calcoaceticus ADP1 (1,2-CTD), highlights significant differences between these enzymes. The active site cavities present several dissimilarities, with respect to the known catechol cleaving enzyme, suggesting the key-role of specific amino-acidic residues in substrate selection. A co-crystallized benzoate- or hydroxamate-like ions, were found bound to the metal center of the three enzymes and revealed details on novel modes of inhibitors binding. The 1,2-HQD structure show one of the most distinctive characteristics among all intradiol dioxygenases; two extensive openings and the consequent exposure to solvent of the upper part of the catalytic cavity are arranged to favor the binding of hydroxyquinols but not catechols. Among the amino acid residues expected to interact with substrates that are different from the corresponding analogues of 1,2-CTD, a few were selected as responsible for the observed substrate selectivity differences in the three distinctive enzymes.

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