Understanding the Origin of Suicide Inactivation in the Extradiol Dioxygenases

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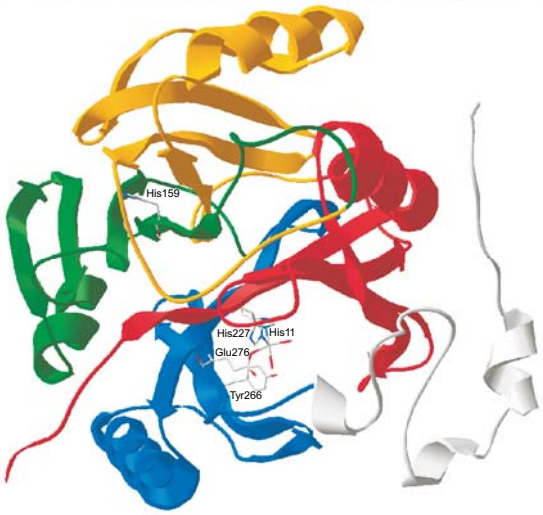
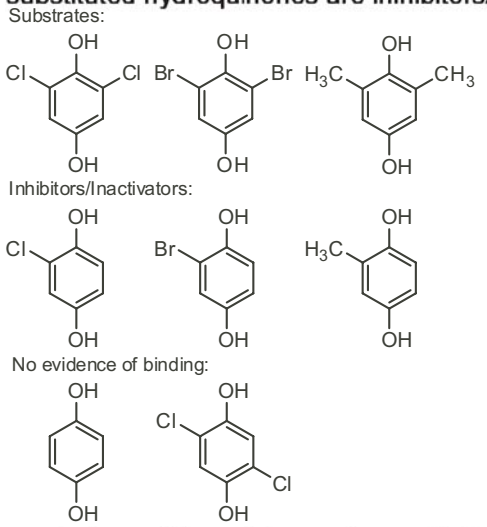
We have re-focussed our efforts to study poorly characterized non-catechol ring-cleaving dioxygenases, especially the hydroquinone dioxygenases that actually *prefer* chlorinated (and even brominated) substrates, PcpA and LinE. We are using a two-pronged approach of studying both the actual enzymes and synthesis of novel model complexes.

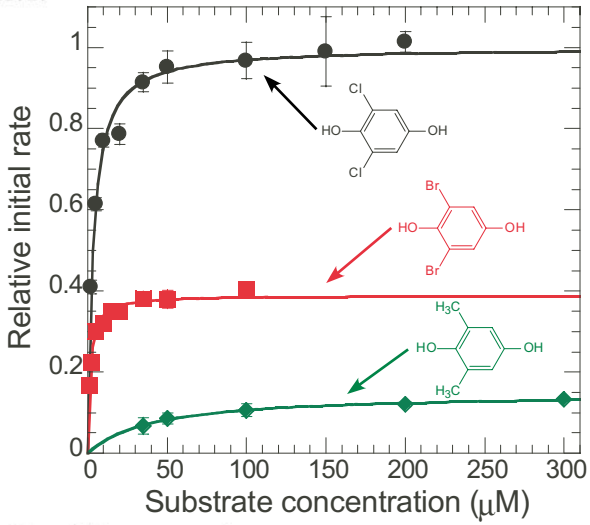
1. Biochemical studies of unusual Fe(II)-containing ring-cleaving dioxygenases that cleave chlorinated substrates.

Structural model of 2,6-dichlorohydroquinone dioxygenase (PcpA) validated by site-directed mutagenesis.



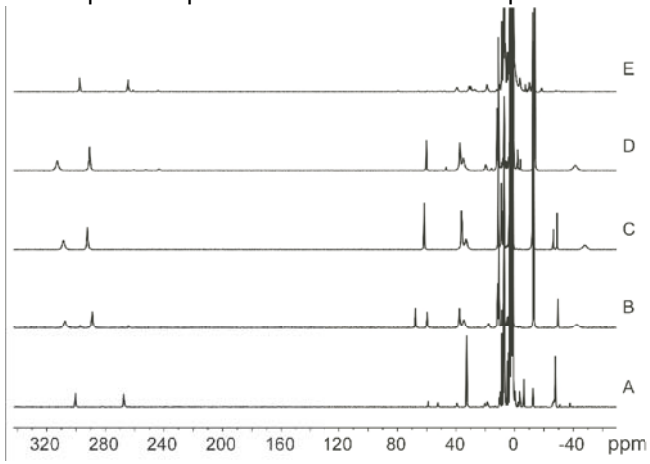
Substrate-specificity of PcpA: only 2,6-disubstituted hydroquinones are substrates, mono-substituted hydroquinones are inihibitors/inactivators.





2. Fe(II)-containing model complexes that contain *ortho*-chlorophenolates with Fe-Cl secondary bonds.

Paramagnetic NMR spectra of (TACH-o-tol) Fe(II) complexes upon addition of substituted phenols.



Crystal structure of [(TACH-o-tol)Fe^{II}(2-dichloro-phenolate)]OTf (left) and [(TACH-o-tol)Fe^{II}(2,6-dichloro-phenolate)]OTf (right).