

Mechanism of the Mn(III)-Catalyzed Oxidation of Vanillyl Derivatives : A Biomimetic Reaction for Manganese Peroxidase

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The Mn(III)-catalyzed oxidation of vanillyl derivatives, vanillylacetone and guaiacol, was proposed as a model for the action of manganese peroxidase. Four products of vanillylacetone oxidation, 4-(4-hydroxy-3-methoxy-phenyl)-but-3-en-2-one, 4-[6,2'-dihydroxy-5,3'-dimethoxy-5'-(3-oxo-butyl)-biphenyl-3-yl]-butan-2-one, 4-[6,2'-dihydroxy-5,3'-dimethoxy-5'-(3-oxo-butyl)-biphenyl-3-yl]-but-3-en-2-one and an aromatic ring cleavage product, were identified. Six products formed in the oxidation of guaiacol, 3,3'-dimethoxy-biphenyl-4,4'-diol, 5-(4-hydroxy-3-methoxy-phenyl)-3-methoxy-[1,2] benzoquinone, 3,5,3''-trimethoxy-[1,1',3',1''] terphenyl-4,4',4''-triol, 3-(4-hydroxy-3-methoxy-phenyl)-5,3'-dimethoxy-bicyclohexylidene-2,5,2',5'-tetraene-4,4'-dione, 2-methoxy-[1,4] benzoquinone, 2-methoxy-benaene-1,2-diol were identified. Based on the product structures, Mn(III) generated by manganese peroxidase catalyzed both formation of the substrate phenoxy radical and oxidation of carbon-centered radical intermediates. This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2005-042-D00070).