Structual Evidence of pH-induced Changes of the Reduction Potential of Mavicyanin from Zucchini

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Mavicyanin, a glycosylated protein isolated from *Cucurbita pepo medullosa* (zucchini) is a member of the phytocyanin subfamily containing one polypeptide chain of 109 amino residues and an unusual type-I Cu site in which the copper ligands are His^{45}, Cys^{86}, His^{91}, and Gln^{96}. The crystal structures of oxidized and reduced mavicyanin were determined at 1.6 and 1.9 Å resolution, respectively. Mavicyanin has a core structure of seven polypeptide β-strands arranged as a β-sandwich organized from two β-sheets, and the structure considerably resembles that with stellacyanin from cucumber (CST) or cucumber basic protein (CBP). A flexible region was not observed from superimposition of the oxidized and reduced mavicyanin structures. However, the residue of Thr^{15} rotated 60.0 degrees and O-γ1-Thr^{15} moved from a distance of 4.78 to 2.58 Å toward the ligand Gln^{96} forming a new hydrogen bond between O-γ1-Thr^{15} and ε-O-Gln^{96} upon reduction and changing, significantly altered the coordination structure containing Gln^{96}. It has been proposed that the reorganization of copper coordination geometry above pH 8 aroused reduction potential decreased [Battistuzzi *et al.* (2001) *J. Inorg. Biochem.*83, 223-227]. The rotation of Thr^{15} and the hydrogen bonding with the ligand Gln^{96} may provide structural evidence for the decrease of the reduction potential at high pH.

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