Crystal Structure of PcyA-biliverdin IXa Complex

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In higher plants, algae, and cyanobacteria, phytobilins which are produced from heme, are utilized as light harvesting and photoreceptor pigments. PcyA (phycocyanobilin:ferredoxin oxidoreductase), one of ferredoxin-dependant bilin reductases, catalyzes two-step site-specific reduction of biliverdin IX α (BV) to produce phycocyanobilin, one of the phytobilins. The reduction of the vinyl group of BV D-ring precedes the reduction of BV A-ring. Thus the vinyl group should be distinguished from the methyl group by PcyA.

PcyA from *Synechocystis* sp. PCC 6803 was co-crystallized with BV. The structure of PcyA-BV complex was determined by MIRAS using gold and mercury derivatives and refined using 1.25 Å resolution data to an *R*-factor of 0.175 and a free *R*-factor of 0.198. PcyA is folded in three-layer $\alpha/\beta/\alpha$ sandwich structure. Electron density of BV was clearly visible and its orientation and conformation were explicitly determined. Basic patch nearby BV is suitable to interact with acidic protein, ferredoxin. BV positions between β-sheet and α -helices of C-terminal side. His is hydrogen-bonded to lactam oxygen atoms of BV. Asp is very close to the center of BV. These two residues discriminate between BV and closed tetra-pyrrole compounds containing metal such as heme and chlorophyll. Most interestingly, Glu covalently bonds with the vinyl group of BV D-ring. This allows strict recognition of correct orientation of BV.

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