Addition/Correction

Biliverdin Reduction by Cyanobacterial Phycocyanobilin:Ferredoxin Oxidoreductase (PcyA) Proceeds via Linear Tetrapyrrole Radical Intermediates [*J. Am. Chem. Soc.* 2004, *126*, 8682–8693].

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J. Am. Chem. Soc., **2005**, 127 (9), 3230-3231• DOI: 10.1021/ja059902w • Publication Date (Web): 15 February 2005

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ADDITIONS AND CORRECTIONS

Biliverdin Reduction by Cyanobacterial Phycocyanobilin:Ferredoxin Oxidoreductase (PcyA) Proceeds via Linear Tetrapyrrole Radical Intermediates [*J. Am. Chem. Soc.* **2004**, *126*, 8682−8693]. Shih-Long Tu, Alexander Gunn, Michael D. Toney, R. David Britt, and J. Clark Lagarias*

Page 8683. In Figure 1, the stereochemistries of the asymmetric carbon atoms in the structures of 3Z/3E-PCB, 3Z/3E-iso-PΦB, 3Z-PΦB, and 3Z-PCB should all be changed to the *R* configuration.

Page 8689. In Figure 7, the stereochemistries of the asymmetric carbon atom in species **6**, species **8**, and "keto" 3Z/3E-isoPΦB should be changed to the *R* configuration.

The corrected figures are shown here.

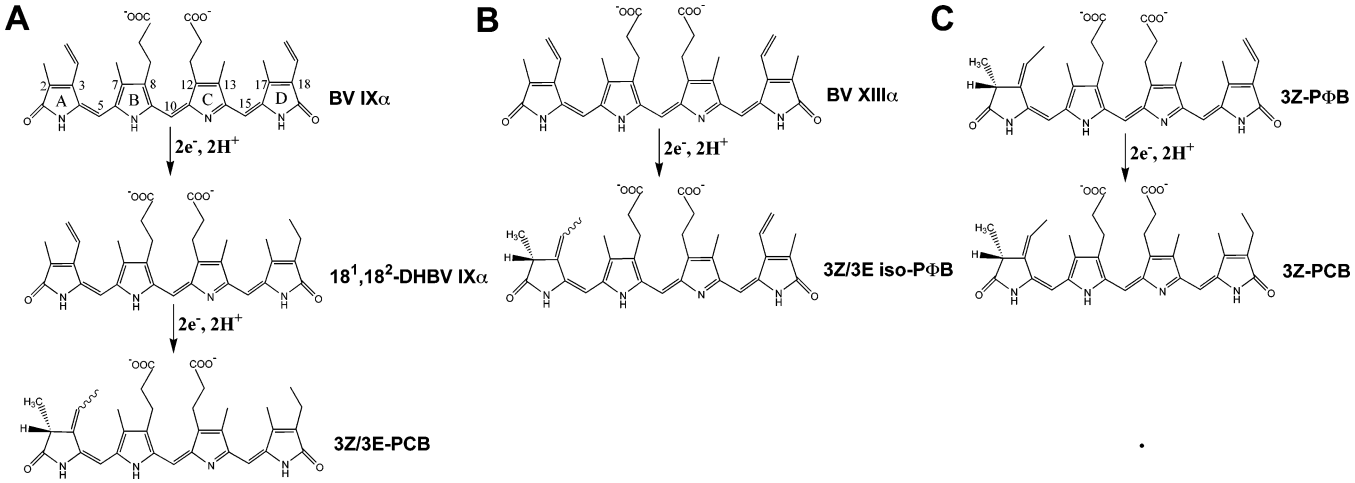

Figure 1. Bilin substrates, intermediates and products of phycocyanobilin:ferrodoxin oxidoreductase (PcyA). PcyA mediates the four-electron reduction of biliverdin IXα (BV) to 3Z/3E-phycocyanobilin (PCB) (panel A) via the intermediacy of the two-electron reduced stable intermediate 18^1,18^2-dihydrobiliverdin IXα (18^1,18^2-DHBV). PcyA also mediates two electron reductions of biliverdin XIIIα (BV13) to 3Z/3E-isophytochromobilin (3Z/3E-isoPΦB) (panel B) and of 3Z-PΦB to 3Z-PCB (panel C).

10.1021/ja059902w CCC: $30.25

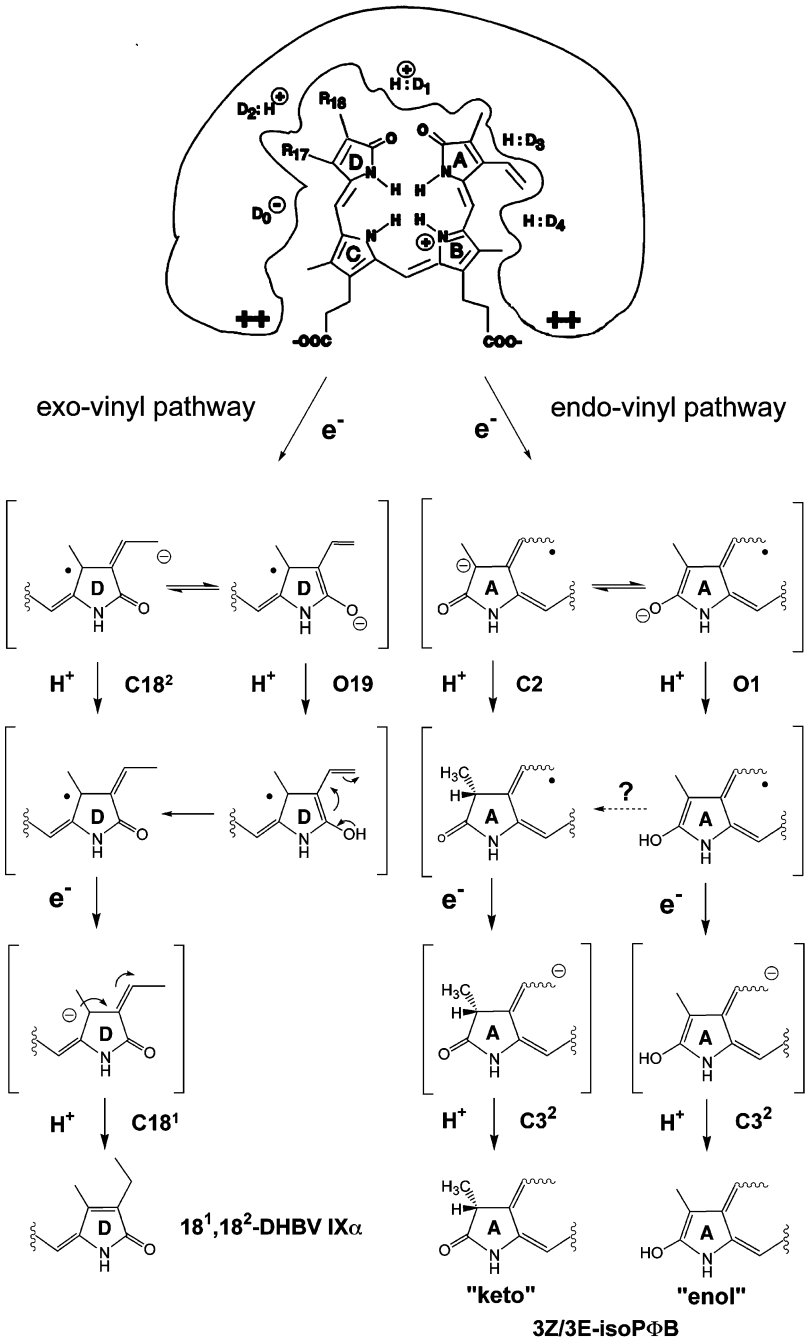

Figure 7. Proposed mechanisms for PcyA-catalyzed exo-vinyl and endo-vinyl group reductions. Substrates BV and BV13 bind to PcyA in a cyclic, porphyrin-like conformation. Protonation of the bilin substrate by proton-donating residue D_0 facilitates electron transfer from reduced ferredoxin. For the exo-vinyl pathway, the one-electron reduced neutral BV radical **1** (shown in two resonance structures) becomes protonated by residue D_1 on either carbon atom $C18^2$ or oxygen atom O19 to generate the cation radicals **2** or **3**. Through intramolecular tautomerization, species **3** should readily convert to species **2**. The second electron transfer produces the most long-lived intermediate **4**, which upon protonation on the C181 position by residue D_2 yields $18^1,18^2$-DHBV. For the endo-vinyl pathway, the one-electron reduced neutral BV13 radical **5a** (R_{18} = methyl and R_{17} = vinyl) or the neutral $18^1,18^2$-DHBV radical **5b** (R_{18} = vinyl and R_{17} = methyl) becomes protonated by residue D_3 on either carbon atom C2 or oxygen atom O1 to generate the cation radicals **6** and/or **7**. The second electron transfer produces the long-lived intermediate **8** and/or **9**, which upon protonation on the $C3^2$ position by residue D_4 yields keto and enol forms of 3*Z*/3*E*-isoPΦB or 3*Z*/3*E*-PCB products.

JA059902W

10.1021/ja059902w
Published on Web 02/15/2005