## The Structure of Protocyanin, a Complex Pigment from Blue Cornflower

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Protocyanin is a complex pigment extracted from flower petals of blue cornflower, *Centaurea cyanus*. The components of protocyanin were recently demonstrated to be anthocyanin (AN), flavone glycoside (FL), Fe<sup>3+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> ions<sup>[1]</sup>. For X-ray structure determination, protocyanin was reconstructed from the components and crystallized in space group  $P2_12_12_1$  with unit cell dimensions of a = 29.7, b = 49.2 and c = 78.3Å. Two protocyanin molecules are contained in an asymmetric unit. Data were collected on the beam line 6A at Photon Factory KEK to1.05 Å resolution.

The refined molecule has pseudo three-fold symmetry and four metals align along the pseudo three-fold axis in order of  $Ca^{2+}$ ,  $Fe^{3+}$ ,  $Mg^{2+}$  and  $Ca^{2+}$ . The four metals are coordinated to six AN and six FL molecules. The inner Fe<sup>3+</sup> and  $Mg^{2+}$  ions are each coordinated to three AN's, respectively, while the outer two  $Ca^{2+}$  ions are each coordinated to three fL's. Both AN and FL molecules are self-associated with each other as AN-AN and FL-FL in pair and this hydrophobic association also exists between AN and FL molecules, building copigmentation stacks. Protocyanin is a tetra-metal (Fe<sup>3+</sup>, Mg<sup>2+</sup>, 2Ca<sup>2+</sup>) nuclear complex, a new type of supramolecular pigment.

[1] Takeda K., Osakabe A., Saito S., Furuyama D., Tomita A., Kojima Y., Yamadera M., Sakuta M., *Phytochemistry*, *submitted*.

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