UV Resonance Raman Spectroscopic Studies of Metal Ion Assisted Activation Mechanism of Human Hematopoietic Prostaglandin D₂ Synthase

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Prostaglandin (PG) D₂ is known to be a mediator of allergy, inflammation response, and sleep regulation in the variety of Human tissues. Hematopoietic PGD₂ synthase (H-PGDS) catalyzes the isomerization of PGH₂ to PGD₂. Very recently, the activation of human H-PGDS by Ca²⁺ and Mg²⁺ was reported [1].

Recent development of stable UV lasers and sensitive detectors has made it possible to utilize UV resonance Raman (UVRR) spectroscopy for the structural analysis of protein molecules. With those points in mind, we have studied the metal ion assisted activation mechanism of human H-PGDS by UVRR spectroscopy.

A new Raman band at 1600 cm⁻¹ (characteristic for tyrosine phenolate) was detected for the Ca²⁺-bound H-PGDS. The 1600 cm⁻¹ Raman band is shifted to 1612 cm⁻¹ by the addition of glutathione to the solution of Ca²⁺-bound H-PGDS. The Raman bands at 1600 and 1612 cm⁻¹ was assigned to Tyr8 from the comparison of the UVRR spectra of Y8F mutant. The higher frequency shift of the 1600 cm⁻¹ Raman band to 1612 cm⁻¹ suggests the re-protonation of the phenolate moiety of Tyr8.

Reference.