Phytochelatins Bind Zn(II) with Micro- to Picomolar Affinities without the Formation of Binuclear Complexes, Exhibiting Zinc Buffering and Muffling Rather than Storing Functions

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Streszczenie

Phytochelatins (PCs) are poly-Cys peptides containing a repeating γ-Glu-Cys motif synthesized in plants, algae, certain fungi, and worms by PC synthase from reduced glutathione. It has been shown that an excess of toxic metal ions induces their biosynthesis and that they are responsible for the detoxification process. Little is known about their participation in essential metal binding under nontoxic, basal conditions under which PC synthase is active. This study presents spectroscopic and thermodynamic interactions with the PC2−PC5 series, mainly focusing on the relations between Zn(II) complex stability and cellular Zn(II) availability. The investigations employed mass spectrometry, UV−vis spectroscopy, potentiometry, competition assays with zinc probes, and isothermal titration calorimetry (ITC). All peptides form ZnL complexes, while ZnL2 was found only for PC2, containing two to four sulfur donors in the coordination sphere. Binuclear species typical of Cd(II)-PC complexes are not formed in the case of Zn(II). Results demonstrate that the affinity for Zn(II) increases linearly from PC2 to PC4, ranging from micro- to low-picomolar. Further elongation does not significantly increase the stability. Stability elevation is driven mainly by entropic factors related to the chelate effect and conformational restriction rather than enthalpic factors related to the increasing number of sulfur donors. The affinity of the investigated PCs falls within the range of exchangeable Zn(II) concentrations (hundreds of pM) observed in plants, supporting for the first time a role of PCs both in buffering and in muffling cytosolic Zn(II) concentrations under normal conditions, not exposed to zinc excess, where short PCs have been identified in numerous studies. Furthermore, we found that Cd(II)-PC complexes demonstrate significantly higher metal capacities due to the formation of polynuclear species, which are lacking for Zn(II), supporting the role of PCs in Cd(II) storage (detoxification) and Zn(II) buffering and muffling. Our results on phytochelatins' coordination chemistry and thermodynamics are important for zinc biology and understanding the molecular basis of cadmium toxicity, leaving room for future studies.

Słowa kluczowe

Ions, Metals, Peptides and proteins, Spectroscopy, Stability

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