Complexation abilities of neuropeptide gamma toward copper(II) ions and products of metal-catalyzed oxidation.

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Streszczenie

The stability constants, stoichiometry, and solution structures of copper(II) complexes of neuropeptide gamma (NPG) (D^{1}-A-G-H^{4}-G-Q-I-S-H^{9}-K-R-H^{12}-K-T-D-S–F-V-G-L-M^{21}-NH_2) and acethyl–neuropeptide gamma (Ac–D^{1}-A-G-H^{4}-G-Q-I-S-H^{9}-K-R-H^{12}-K-T-D-S-F-V-G-L-M^{21}-NH_2) were determined in aqueous solution. For both peptides the additional deprotonations were observed; therefore, the potentiometric data calculations for NPG were only made in 2.5–7.4 pH range. For Ac–NPG one additional deprotonation was observed, likely hydroxy group of Ser residue, and the potentiometric data calculations in the 2.5–10.5 pH range may be performed. The potentiometric and spectroscopic data (UV–vis, CD, EPR) for the neuropeptide gamma show that a D^{1} residue stabilizes significantly the copper(II) complexes with 1N {NH_2,β-COO^{-}}, 2N {NH_2,β-COO^{-},N_{Im}}, and 3N {NH_2,β-COO^{-},$2N_{Im}$} coordination modes as the result of coordination through the β-carboxylate group. The Ac–NPG forms with the copper(II) ions the 3N {$3N_{Im}$} complex in a wide 4.5–7.5 pH range. At higher pH deprotonation and coordination of the sequential amide nitrogens occur. Metal-catalyzed oxidation of proteins is mainly a site-specific process in which amino acids at metal-binding sites to the protein are preferentially oxidized. To elucidate the products of the copper(II)-catalyzed oxidation of NPG and Ac–NPG the liquid chromatography–mass spectrometry method (LC-MS) and the Cu(II)/H_2O_2 as a model oxidizing system were employed. For solutions containing a 1:4 peptide–hydrogen peroxide molar ratio oxidation of the methionine residue to methionine sulphone was observed. For the 1:1:4 Cu(II)–NPG–H_2O_2 system oxidation of two His residues and cleavage of the G^{3}-H^{4} and R^{11}-H^{12} peptide bonds were detected, supporting involvement of His^{4} and His^{12} in binding of the copper(II) ions. Oxidations of three histidine residues to 2-oxohistidines and fragmentations of Ac–NPG near the His (H^{4}, H^{9},H^{12}) residues support participation of the histidyl–imidazole nitrogen atoms in coordination of the metal ions.

Adres publiczny

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