

Acid-base properties of the (1-4, 18-36) fragments of neuropeptide K and their mono- and polynuclear copper(II) complexes products of metal-catalyzed oxidation.

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Streszczenie

Mononuclear and polynuclear complexes of the (1-4,18-36)NPK, Asp(1)-Ala-Asp-Ser(4)-Gly(18)-His(19)-Gly-Gln-Ile-Ser-His(24)-Lys-Arg-His(27)-Lys-Thr-Asp-Ser-Phe-Val-Gly-Leu-Met(36)-NH₂, and mononuclear complexes of its acetyl derivative Ac-Asp(1)-Ala-Asp-Ser(4)-Gly(18)-His(19)-Gly-Gln-Ile-Ser-His(24)-Lys-Arg-His(27)-Lys-Thr-Asp-Ser-Phe-Val-Gly-Leu-Met(36)-NH₂ have been studied by potentiometric, UV-vis, CD, EPR spectroscopic, and mass spectrometry (MS) methods. As it was observed for other tachykinins (neurokinin A, neuropeptide gamma and its fragments) containing the same C-terminal sequence His-Lys-Thr-Asp-Ser-Phe-Val-Gly-Leu-Met-NH₂, also for the fragments of neuropeptide K the additional deprotonation most likely on the serine OH group was observed. It is likely that tachykinin peptides contain catalytic Ser/His/Asp triad or dyads Ser/Lys and the serine protease activity. The high water solubility of the resulting metal complexes allowed us to obtain complete complex speciation at different metal-to-ligand ratios ranging from 1:1 to 4:1 for (1-4,18-36)NPK, while only the 1:1 molar ratio was studied for Cu(II)-Ac-(1-4,18-36)NPK because of precipitation. For the metal-to-ligand 1:1 molar ratio the (1-4,18-36)NPK forms in a wide 6.5-10.5 pH range the CuHL complex with a 3N {NH₂,2N(-),β-COO(-)-Asp(3)} binding site. For a metal-to-ligand 1:1 molar ratio at higher pH than 9.5 the dimeric species dominate. For the Ac-(1-4,18-36)NPK peptide the imidazole nitrogen atoms are the primary metal-binding sites forming macrochelates in the pH 4-7.5.

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