

## Copper(II) complexes of neurokinin A with point mutation (S5A) and products of copper-catalyzed oxidation : role of serine residue in peptides containing neurokinin A sequence.

### Autorzy

Elżbieta Jankowska

Marta M. Błaszak

Teresa Kowalik-Jankowska

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### Streszczenie

A potentiometric, spectroscopic (UV-visible, CD and EPR) and electrospray ionization mass spectrometric (ESI-MS) study of Cu(II) binding to the neurokinin A with point mutation (S5A) (ANKA), His-Lys-Thr-Asp-Ala(5)-Phe-Val-Gly-Leu-Met-NH<sub>2</sub> and its N-acetyl derivative (Ac-ANKA), Ac-His-Lys-Thr-Asp-Ala(5)-Phe-Val-Gly-Leu-Met-NH<sub>2</sub> were carried out. For the ANKA and Ac-ANKA the additional deprotonation was not observed. It suggests that for the tachykinin peptides with C-terminal sequence of neurokinin A for the additional deprotonation the presence of the serine residue is necessary. For the Cu(II)-ANKA 1:2 system at physiological pH 7.4 the CuH<sub>2</sub>L<sub>2</sub> species is present with histamine-like 4N, 2×{NH<sub>2</sub>,NIm} coordination mode. With increasing pH the deprotonation and coordination of amide nitrogen atoms occur and the CuH-2L, CuH-3L complexes are formed. In pH range 4.5 - 9.5 the dimeric Cu<sub>2</sub>HL<sub>2</sub>, Cu<sub>2</sub>L<sub>2</sub> and Cu<sub>2</sub>H-1L<sub>2</sub> species in solution are also present. To elucidate the products of the copper(II)-catalyzed oxidation of the ANKA and Ac-ANKA, the liquid chromatography-mass spectrometry (LC-MS) method and Cu(II)/hydrogen peroxide as a model oxidizing system were employed. In the presence of hydrogen peroxide with 1:1 peptide-H<sub>2</sub>O<sub>2</sub> molar ratio for both peptides the oxidation of the methionine residue to methionine sulfoxide was observed. For the Cu(II)-peptide-hydrogen peroxide in 1:2:2 molar ratio systems oxidations of the histidine residues to 2-oxo-histidines and methionine sulfoxide to methionine sulfone were detected.

### Słowa kluczowe

Neurokinin A, stability constants, Copper (II) complexes, metal-catalyzed oxidation

### Adres publiczny

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