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Products of Cu(II)-catalyzed oxidation of α-synuclein fragments containing M^1-D^2 and H^{50} residues in the presence of hydrogen peroxide.

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Streszczenie

Metal-catalyzed oxidation (MCO) of proteins is mainly a site-specific process in which one or a few amino acids at metal-binding sites on the protein are preferentially oxidized. The oxidation of proteins by MCO can lead to oxidation of amino acid residue side chains, cleavage of the peptide bonds and formation of covalent protein-protein cross-linked derivatives. In an attempt to elucidate the products of the copper(II)-catalyzed oxidation of the 29-56, M29-D30-56 and Ac-M29-D30-56 fragments of alpha-synuclein, high performance liquid chromatography (HPLC) and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) methods and Cu(II)/hydrogen peroxide as a model oxidizing system were employed. The peptide solution (0.50 mM) was incubated at 37 degrees C for 24 h with metal : peptide : hydrogen peroxide 1 : 1 : 4 molar ratio in phosphate buffer, pH 7.4. Oxidation targets for all studied peptides are the histidine residues coordinated to the metal ions. For the M29-D30-56 and Ac-M29-D30-56 peptides the oxidation of the methionine residue to methionine sulfoxide and sulfone is observed. The cleavage of the peptide bond M29-D30 for the M29-D30-56 peptide was detected as metal binding residues. The fragmentations of the M29-D30-56 peptide near the Lys residues were observed supporting the participation of this (Lys) residue in the coordination of the copper(II) ions.

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