

Solid-phase synthesis of peptides containing aminoadipic semialdehyde moiety and their cyclisations.

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Rok wydania

2018

Czasopismo

Scientific Reports

Numer woluminu

8

Strony

10462/1-10462/11

DOI

10.1038/s41598-018-28798-9

Kolekcja

Naukowa

Język

Angielski

Streszczenie

Pathological levels of oxidative stress (OS) have been implicated in many diseases including diabetes mellitus, neurodegenerative diseases, inflammatory diseases, atherosclerosis, and cancer. Studies of oxidative stress are however complicated by the low concentration of oxidation products. To resolve this problem, we tested a new derivative of aminoadipic semialdehyde (Fmoc-Aea-OH) in the solid-phase synthesis of carbonylated peptides. We prepared a series of peptides with free and acetylated N-terminal amino groups using the Fmoc-Aea-OH reagent. LC-MS, ESI-MS, and MS/MS spectra confirmed the sequences of the modified peptides, although the LC-MS and ESI-MS spectra were dominated by signals corresponding to dehydration products. NMR studies of acetylated products revealed that the dominant product formed in this reaction contains a 1,2,3,4-tetrahydropyridine-2-carboxylic acid residue. Another side reaction in this system was the cleavage of the amide bond between the Aea residue and the amino acid moiety preceding it resulting in the formation of a side product with a six-membered ring at the N-terminus (2,3,4,5-tetrahydropyridine-2-carboxylic acid residue). We found that, depending on the peptide sequence, one of those side products is predominant. Our work suggests new methods for the solid-state synthesis of peptides containing unnatural amino acids.

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<http://dx.doi.org/10.1038/s41598-018-28798-9>