

High-Temperature, Solid-Phase Reaction of α -Amino Groups in Peptides with Lactose and Glucose: An Alternative Mechanism Leading to an α -Ketoacyl Derivative

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Streszczenie

The reaction of proteins with reducing sugars results in the formation of Amadori products, which involves the Nterminal group and/or ϵ -amino group of the lysine side chain. However, less attention has been given to the reactivity of the Nterminus of a peptide chain under similar conditions. In our work, we focused on the reaction of the α -amino group of peptides in the presence of a reducing sugar, specifically lactose. We optimized the reaction conditions of model peptides with lactose in the solid phase and showed that temperatures above 120 °C lead to the deamination of the N-terminal amino acid moiety, ultimately resulting in α -ketoacids. We carried out detailed studies to confirm the structure of the deaminated product using analytical methods such as ESI-MS and LC-MS/MS, as well as chemical methods that involved the reduction of the carbonyl group combined with isotopic exchange and the reactivity of the carbonyl group with the hydroxylamine derivative. The structure of the reaction product was also confirmed by chemical synthesis. We suggested plausible mechanisms for the formation of the deaminated product and considered the probable path of its formation. Our aim was to determine whether the reaction proceeds according to the Streckerbased mechanism and direct imine isomerization by carrying out reactions of model peptides in the presence of lactose under aerobic and anaerobic conditions and comparing the results obtained.

Słowa kluczowe

LC-MS/MS analysis, lactosylated peptides, α -ketoacid derivatives, deamination catalyzed by a reducing sugar

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