

New ionization tags based on the structure of the 5-azoniaspiro[4.4]nonyl tag for a sensitive peptide sequencing by mass spectrometry.

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Streszczenie

Quaternary ammonium salts (QAS), both linear and bicyclic, are often utilized to improve the mass spectrometry (MS) analysis of peptides by fixing a permanent positive charge on the analyzed molecule. However, during collision-induced dissociation (CID) experiments, QAS undergo unwanted side reactions—Hofmann elimination as well as a tertiary amine loss—rendering the data interpretation complicated. In this work, we present 2-thia- and 2-oxa-5-azoniaspiro[4.4]nonyl groups as heterocyclic derivatives of the highly stable ionization group, 5-azoniaspiro[4.4]nonyl, for a sensitive peptide analysis by MS. Due to the permanent positive charge, labeled peptides are characterized by enhanced ionization efficiency during electrospray mass spectrometry (ESI-MS) conditions. Moreover, interpretation of the CID fragmentation of labeled peptides is facilitated since a series of generated fragmentation ions enable a complete sequence coverage. Introduction of a heteroatom into the 5-azoniaspiro[4.4]nonyl scaffold allows for liberation of a stable reporter ion which could be used in selected reaction monitoring (SRM)-targeted quantification experiments. Additionally, we synthesized a deuterated analog of the tag for LC-SRM-targeted quantitative analysis. The obtained results indicate the general usefulness of the proposed heterocyclic quaternary ammonium ionization tag for sequencing and quantification of peptides.

Słowa kluczowe

Derivatization of peptides, Peptide sequencing, Ionization tag, Tandem mass spectrometry

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