The competition of charge remote and charge directed fragmentation mechanisms in quaternary ammonium salt derivatized peptides - an isotopic exchange study.

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Derivatization of peptides as quaternary ammonium salts (QAS) is a promising method for sensitive detection by electrospray ionization tandem mass spectrometry (Cydzik et al. J. Pept. Sci. 2011, 17, 445-453). The peptides derivatized by QAS at their N-termini undergo fragmentation according to the two competing mechanisms - charge remote (ChR) and charge directed (ChD). The absence of mobile proton in the quaternary salt ion results in ChR dissociation of a peptide bond. However, Hofmann elimination of quaternary salt creates an ion with one mobile proton leading to the ChD fragmentation. The experiments on the quaternary ammonium salts with deuterated N-alkyl groups or amide NH bonds revealed that QAS derivatized peptides dissociate according to the mixed ChR-ChD mechanism. The isotopic labeling allows differentiation of fragments formed according to ChR and ChD mechanisms.

Słowa kluczowe

Quaternary ammonium salts, Derivatization of peptides, Peptide sequencing

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