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Mass spectrometric investigation of isobaric peptides of biological interest: ESI-MS versus ToF-SIMS

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A small peptide (TAT1; sequence: GRKKRRQRRRPS) derived from the transcriptional activator TAR (TAT) protein has recently drawn some attention due to its capability to stimulate proteasome activity [1]. ESI MS/MS experiments revealed a great stability of this peptide against fragmentation, mainly related to the high content of arginine residues. Consequently, peptide fragmentation leads to a predominant loss of neutral molecules from the side-chain of arginine rather than the cleavage of peptide bonds. So we have chosen the TAT1 amino-acidic sequence as a base to construct three model isobaric peptides TAT1-Car, Car-TAT1 and T-Car-T, simply adding carnosine (Car) to the C- and N-terminus as well as in the middle of the peptide sequence, respectively. The addition of the Car moiety to the TAT-1 sequence was dictated by the interest that our group has towards Car [2,3]. Due to the peptides high stability, differentiation of the investigated isobaric peptides, in particular Car-TAT1 and T-Car-T, by MS/MS experiments is not easy. On the contrary, ToF-SIMS analysis, combined with multivariate data treatment of spectra, can discriminate among these oligopeptides. Results are discussed and a mechanism of fragmentation is proposed.

References

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