Structural investigation of gamma irradiation process upon different classes of peptide sequences


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The reaction products and mechanisms involved in the radiolysis of macromolecules of biological relevance are object of several studies. Aiming at unravel the potential of strong electromagnetic irradiation strategy for peptide structure modifications, some biologically relevant peptides were submitted to controlled gamma irradiation. The products generated were examined by electrospray triple-quadrupole tandem mass spectrometry applying the daughter ion scanning by collision induced dissociation method in association with amino acid analysis. Regardless of the peptide sequence, a non-linear and progressive degradation of peptides assayed was detected. Furthermore, these peptides could be separated in different classes accordingly to their half-life dose. For instance, angiotensin II (AII) and bradykinin (BK) and analogs such as Pro4-BK or Ang (1-7) were more stable than the melanocyte-stimulating hormone (α-MSH) or substance P. Usually, derivatives generated from this experiment revealed that they are produced by oxidation process, yielding a variation of +16 Da in their molecular weight. The Phe oxidation affecting its aromatic side chain produced Tyr but also its o- and m-isomers. The same effect was also detected with the Met residue. Of relevance, it was possible to verify that even in small peptide structures, this experimental protocol applying strong electromagnetic radiation depicted the occurrence of a clear residue- and sequence-dependent effect. The herein applied innovative approach relies indeed in the hope of also isolating unusual peptides derivatives, not easily achieved by the use of conventional solid phase peptide synthesis methodology.

Keywords: gamma radiation, peptides, mass spectrometry, structural modification
Supported by: FAPESP and CNPq