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Radiation-induced destruction of hydroxyl-containing amino acids and dipeptides

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HIGHLIGHTS

- Ser and Thr undergo several types of C–C destruction under radiolysis.
- Free-radical mechanisms for destruction of Ser and Thr have been proposed.
- Ser- and Thr-containing dipeptides can eliminate aldehydes via C–C bond cleavage.
- Photo-induced decomposition of dipeptides can lead to side chain elimination.

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ABSTRACT

The yields of molecular products resulting from radiolysis of hydroxyl-containing amino acids and dipeptides under various conditions were determined. The possibility of a new radiation-induced destruction pathway has been shown for serine and threonine, as well as for the dipeptides having residues of these amino acids at the N-terminal part of the respective molecule. This process includes formation of N-centered radicals from the starting molecules followed by their decomposition with elimination of side substituents. On radiolysis, serine and threonine were also shown to undergo free-radical destruction to form acetaldehyde and acetone, respectively. A mechanism has been proposed including consecutive stages of fragmentation of α-hydroxyl-containing carbon-centered radicals with elimination of ammonia and decomposition of the secondary radicals with elimination of CO_2. The yields of CO_2 obtained on radiolysis of serine and threonine were significantly higher (except for solutions at pH 12) than those for alanine and valine, which have no hydroxyl groups in their structures. The obtained data indicate that the hydroxyl-containing amino acids occupy a special place among other amino acids as regards the variety of radiation-induced reactions which they may undergo due to their structural features.

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1. Introduction

Hydroxyl-containing amino acids (AAs) serine (Ser) and threonine (Thr) play an important role in biosystem functioning. Thr belongs to the AAs that are essential for humans and animals. In a living organism, Ser serves as a precursor of such biomolecules as sphingolipids, glycine and cysteine, as well as the purine and pyrimidine bases; also, being a structural part of phosphatidylserine, it is an important component of phospholipids (Hernandes and Troncone, 2009; Lehninger et al., 2000). The residues of Ser and Thr are found in all organisms as components of peptide and protein molecules. Due to their hydrophilic nature, these residues are generally located on the outer side of the macromolecules. The activity of a number of enzymes (trypsin, chemotrypsin, choline esterase, elastase, etc.) is associated with the specific reactivity of the hydroxyl groups present in the Ser moieties, which are structural components of the enzyme's active sites (Lehninger et al., 2000; Rawlings and Barrett, 1994). Generally, phosphorylation of the hydroxyl-containing AAs residues with protein kinases entails changes or modifications of the protein's functions. These changes may affect enzymatic activity, location of the protein in a cell, or interaction of the protein with other proteins (Cohen, 2002; Lehninger et al., 2000).

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Biological significance of hydroxyl-containing AAs stimulates the interest towards studying their radiation stability and the pathways of their radiolytic transformations. To date, it has been reliably established that the major processes occurring under the action of radiation on aqueous solutions of the most of AAs are deamination and decarboxylation of the starting compounds (Bonifacic et al., 1998; Garrison, 1987; Monig et al., 1985; Von Sonntag, 1987). A characteristic feature of the processes occurring on radiolysis of the AAs containing sulfhydryl groups, aromatic or heterocyclic moieties in their structures is radiation-induced modification of the side substituents (Garrison, 1987; Von Sonntag, 1987). The irreversible radiation-induced processes leading to destruction of the carbon skeleton and elimination of side substituents taking place in aliphatic AAs and peptides were insufficiently explored. This study has been undertaken with a view for assessment of possibility and probability for these processes to be realized and investigation of features accompanying the destruction processes occurring on radiolysis of aqueous solutions of Ser, Thr and their derivatives.

2. Experimental section

2.1. Chemical compounds

D,L-Ser, D,L-Ser phosphate, L-Thr, O-methyl-L-Thr, D,L-Thr phosphate, D,L-alanine, (D,L-Ala), D,L-valine (D,L-Val) and Ser–Ala were purchased of highest purity grade available (Sigma-Aldrich, Fluka) and used as supplied. L-Thr-L-Val, L-Val-L-Thr and L-Val-L-Val were synthesized as described in (Cherevin et al., 2008). Structures of the synthesized compounds were confirmed using ^{1}H NMR, IR spectroscopy and mass spectrometry. Structures of the compounds under study are presented in Fig. 1.

2.2. Preparation of solutions for irradiation

Twice-distilled water was used for preparation of aqueous solutions of the compounds being studied. The required pH value was adjusted using $HClO_4$ or NaOH. The solutions were placed in glass ampoules and bubbled through with argon (99.9%) for 45 min to remove oxygen. Quartz ampoules were used in photochemical experiments.

2.3. Irradiation conditions

The prepared samples were irradiated in a γ-unit with a ^{60}Co source. The dose rate was (0.39 ± 0.01) Gy/s. The absorbed dose range was 0.47–1.87 kGy, which was determined by Fricke dosimetry using a radiation chemical yield $G(Fe^{3+}) = 16.2 \times 10^{-7}$ mol/J (Fricke and Hart, 1966).

UV irradiation was performed using continuous spectrum of a high pressure mercury arc tube lamp (DRT-100). The dose rate of absorbed radiation amounting to $(5.0 \pm 0.3) \times 10^{15}$ quantum/s was measured in the wavelength range of 230–320 nm using a standard ferrioxalate actinometer (Calvert and Pitts, 1966). The sample distance from the source was 20 cm, and the irradiation time varied in the range of 10 to 80 min.

2.4. Product analysis

HPLC-UV measurement: Analysis of the carbonyl-containing products of radiolysis and photolysis was performed using the high-performance liquid chromatography (HPLC) technique on a Shimadzu LC-10AD$_{VP}$ instrument after derivatization with 2,4-dinitrophenylhydrazine. Chromatographic conditions: Nucleosil 120-5 C_{18} column of 250 mm length, 4 mm ID; a mobile phase methanol/water (60/40, v/v); flow rate 0.7 ml/min; temperature 37 °C; injected volume 4 μl, UV–vis detector ($\lambda = 366$ nm).

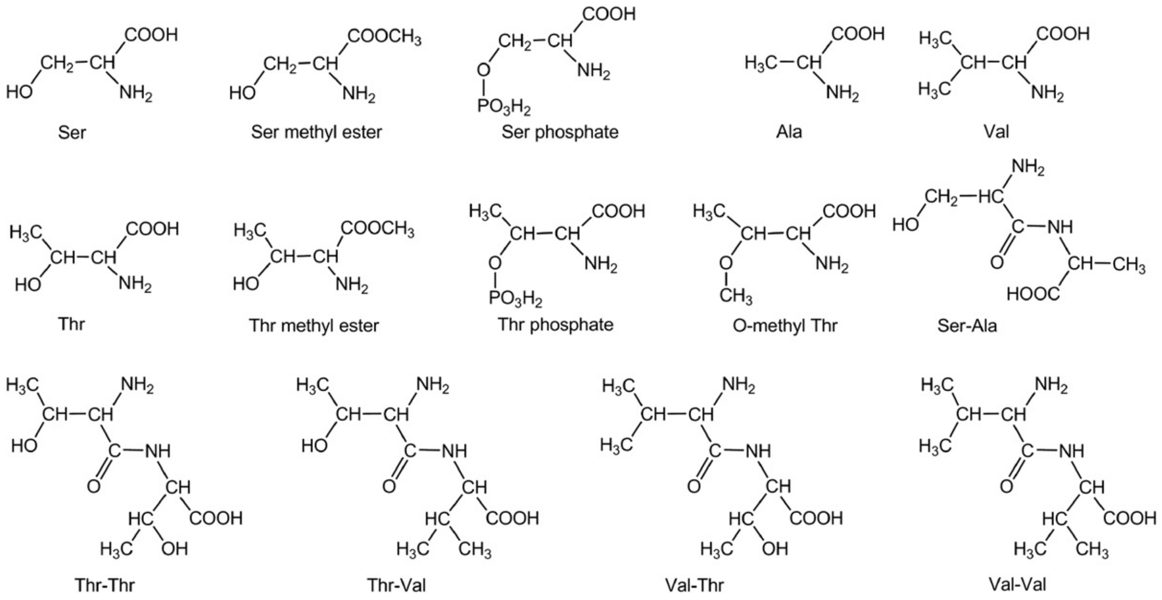

Fig. 1. Structures of the compounds under study.

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