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Free radicals and sulfur-containing proteins: Assessment of structural modifications and damages in lipid domains

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Effects of radical stress in the biological environment is a very active field of research connecting varies discipline in life science. Exposure of proteins to free radicals may cause structural and functional changes. In particular, a single radical event that leads to an initial damage involving sulfur-containing amino acid residues could produce a reactive species able to damage another cell compartment such as lipid domains. In this contest, damages to some sulfur-containing proteins (i.e. ribonuclease A, metallothioneines, human serum albumin, substance P) were considered to elucidate the effects of radical stress exposure on the overall protein structure. Experiments were carried out in both aqueous solutions and vesicle suspensions. Free radical generation, mimicking an endogenous radical stress, was obtained by gamma-irradiation of aqueous solutions. By changing the appropriate conditions of irradiation, a selection of the reacting radical species was carried out.

The protein degradation due to radical exposure was evaluated by Raman spectroscopy [1-3]. In fact, Raman spectrum can provide valuable information on both amino acid side chains (i.e. S-S, Tyr, Trp, Cys-Metal) and conformational changes in the protein secondary structure. Protein structure and amino acid content resulted to play an important role in blocking the ready access of free radicals both to the sulfur-containing residues and the active site, so strongly affect both the radio-sensitivity of proteins.

By using a biomimetic model based on unsaturated lipid vesicle suspensions the occurrence of tandem protein/lipid damage was shown [1-2]. In fact, protein degradation is accompanied by structural alteration of unsaturated lipids forming liposome vesicles, which changed the naturally occurring cis geometry to the trans configuration. In fact, the reactions of reductive reactive species with methionine residues and/or sulfur-containing ligands afford diffusible sulfur-centered radicals, which migrate from the aqueous phase to the lipid bilayer and act as isomerising species of the double bonds.

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