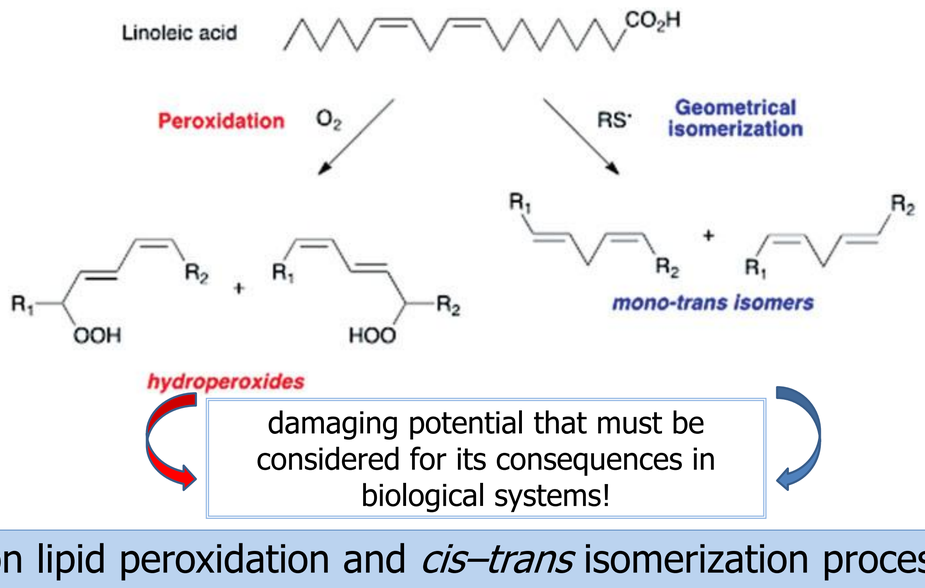
THE EFFECT OF NATURAL ANTIOXIDANTS IN THIYL RADICAL-INDUCED LIPID MODIFICATION PROCESSES

IVANA TARTARO BUJAK and BRANKA MIHALJEVIĆ
Ruđer Bošković Institute, Radiation Chemistry and Dosimetry Laboratory, Zagreb, Croatia

International Conference on Applications of Radiation Science and Technology (ICARST 2017)
24 to 28 April 2017, Vienna, Austria

INTRODUCTION

The reactions of polyunsaturated fatty acids (PUFA) with free radicals are known to occur via two main processes: **lipid peroxidation** and ***cis–trans* isomerization**. Free radical reactivity of thiol compounds is the common link between two processes, since lipid peroxidation is inhibited by thiols whereas geometrical isomerization is catalysed by S-centered radical (RS•). Both processes produce profound changes of lipid structures which can be linked with damaging effects on cell membranes in living organisms. Therefore, the protection against lipid degradation under oxidative and free radical conditions is of special interest.[1]



THE AIM: to elucidate the influence of different naturally occurring antioxidants on lipid peroxidation and *cis–trans* isomerization processes in biomimetic lipid model system in the presence of thiol.

Methodology

Lipid model systems (non-ionic mixed micelles):
0.50 mM , linoleic acid, 9*c*,12*c*-C18:2 (LiH),
0.28 mM Tween®-20,
2.80 mM β-mercaptoethanol (2-ME),
5.00 mM $NaH_2PO_4 \times H_2O$, pH 5

Antioxidants:
60 μM ascorbic acid (AscH)
50 μM α-tocopherol (α-TOH)
87 μM resveratrol (ResOH)

Gamma irradiation: panoramic ^{60}Co source under air-equilibration (P = 274.8 Gy min^{-1}), t = 19°C.
Lipid peroxidation level: via determination of hydroperoxides concentrations of linoleic acid (LiOOH): spectrophotometric ferric thiocyanate method.[2]
Geometrical isomers distribution: capillary gas chromatography.

RESULTS

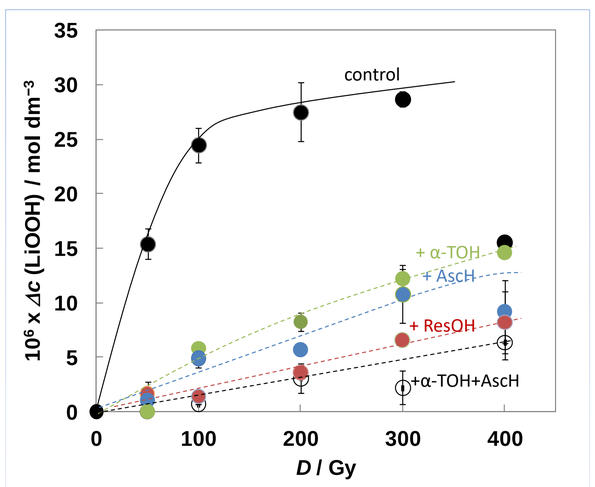
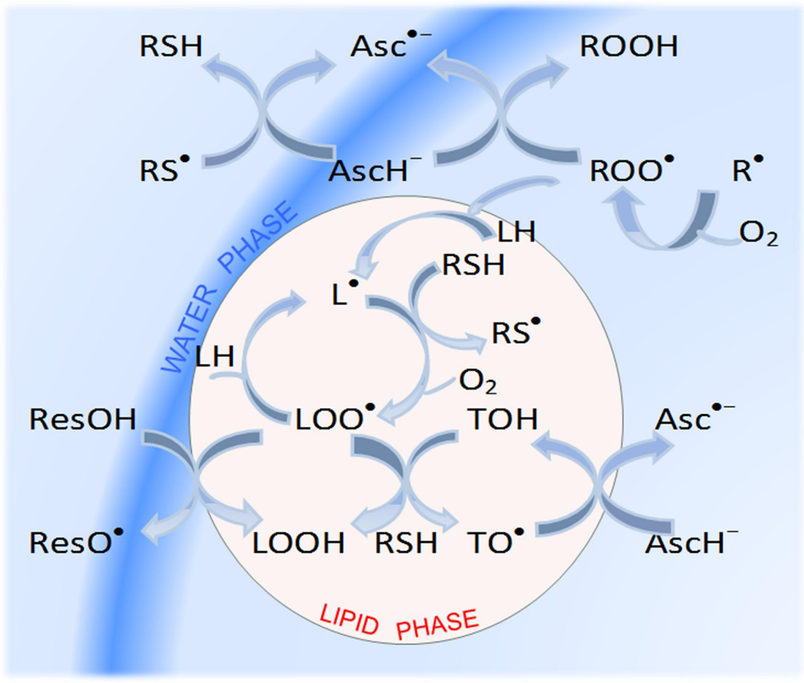


Figure 1. The formation of LiOOH as a function of irradiation dose in the presence of different antioxidants.



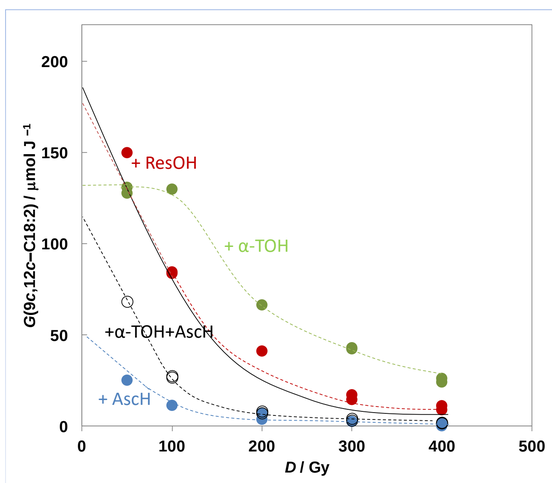
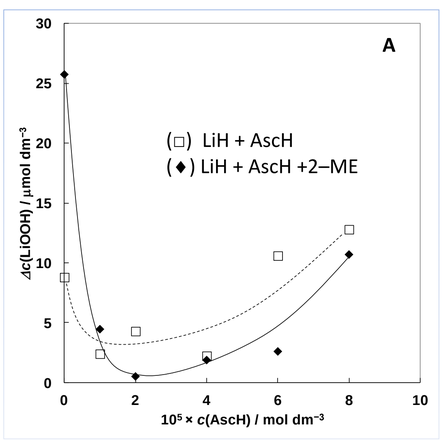


Figure 2. The radiation chemical yields (G-value) of disappearance of the natural lipid geometry of LiH as a function of irradiation dose.



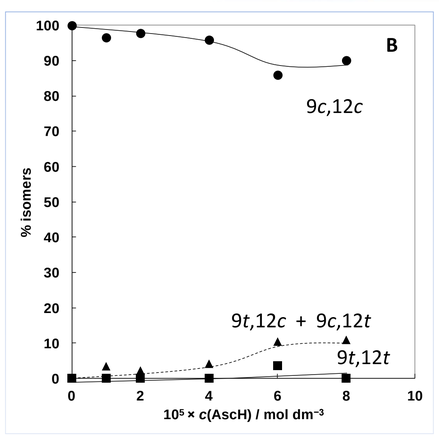
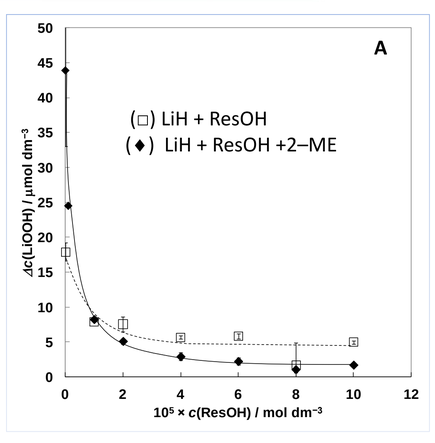


Figure 3. Effect of various concentrations of ascorbic acid on the formation of: A) LiOOH and B) geometrical isomers; D =100 Gy.



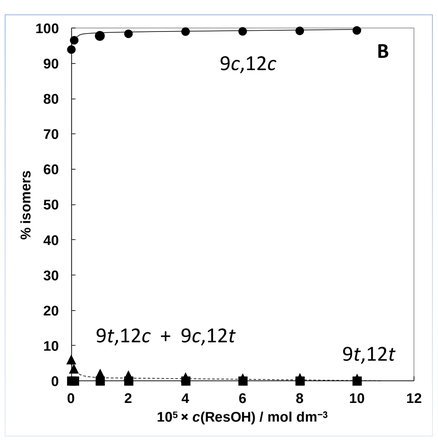


Figure 4. Effect of various concentrations of resveratrol on the formation of: A) LiOOH and B) geometrical isomers; D =100 Gy.

The antioxidative effect of AscH was evident in the range of concentrations from 1 μM to 30 μM, whereas at higher concentrations the prooxidative efect occured (Fig. 3A). This effect of AscH was enhanced in the presence of thiol (Fig. 3A). At higher concentrations of AscH trans isomerization of LiH was induced by higher concentrations of AscH simultaneously initiating peroxidation process indicating the additional generation of thiyl radicals with an increase of the AscH concentration.

The lipid peroxidation process in lipid model system was inhibited by addition of ResOH (above 5 μM ResOH) and geometrical isomerization was simultaneously inhibited through the entire range of ResOH concentrations (Fig. 4A and 4B) demonstrating that ResOH is more efficient for the thiyl radicals trap than AscH.

CONCLUSION

- The addition of different natural occuring antioxidants at the biomimetic concentrations retarded the process of lipid peroxidation (Fig. 1), with efficiancy as follows:

  α-TOH < AscH < ResOH < α-TOH/AscH mixture.

  At the same time, less effective isomerization of LiH at the initial phase was observed when different antioxidants were present in comparison to control LiH (Fig. 2). The antioxidant ability of scavenging RS• leads to the inhibition of isomerization which follows the order:

  ResOH < α-TOH < α-TOH/AscH mixture < AscH.

- Results indicate that lipid isomerization and peroxidation inhibition by natural antioxidants is correlated to the compartment where radical initiation occurs and to the double bond location in organized systems, that is in the lipophilic interior. In this heterogenous environment antioxidants co-localize in order to get an anti-isomerizing activity and protection of the natural lipid geometry.

References
1. I. Tartaro Bujak et al., *Free Radical Res.* **50** (2016) 518.
2. B. Mihaljević et al., *Free Radical Biol. Med.* **21** (1996) 53.