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## The effect of aromatic amines and phenols in the thiyl-induced reactions of polyunsaturated fatty acids

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## H I G H L I G H T S

- LH micelles were used for the parallel study of peroxidation/*cis*–*trans* isomerization.
- Both 2-mercaptoethanol and diphenylamine alone protect LH from oxidation.
- Aminyl radicals promote thiyl-radical-induced *cis*–*trans* isomerization of LH in air.

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## A B S T R A C T

Thiols are well known for their role in cellular redox homeostasis, while aromatic amines and phenols are the best known classes of chain-breaking antioxidants. On the other hand, thiyl radicals are known to catalyse the double bond isomerization in PUFA. We investigated the role and interplay of 2-mercaptoethanol and diphenylamine in the parallel processes of peroxidation and *cis*–*trans* isomerization of linoleic acid (LA) during gamma radiolysis, both in solution and micelles. Both compounds, used alone were able to protect LA from oxidation; however pro-oxidant activity and enhanced isomerization was observed when they were used together, depending on the experimental settings. Instead,  $\alpha$ -tocopherol protected LA from both oxidation and isomerization in the presence of thiols under any tested settings. The mechanistic scenario is discussed highlighting the role of diphenylaminyl radicals in promoting thiyl-radical-induced *cis*–*trans* isomerization in the presence of oxygen.

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## 1. Introduction

Due to the crucial roles of lipids in structural and signaling activities, the control of lipid reactivity and transformations is an interdisciplinary research field extending over chemistry to biology and medicine (Chatgililoglu et al., 2014; Halliwell and Gutteridge, 2007). In this context, the protection against their degradation under oxidative and free radical conditions is of special interest. The reactions of polyunsaturated fatty acids (PUFA) with free radicals are known to occur via two main processes: (i) lipid

peroxidation (Niki, 2012) and (ii) *cis*–*trans* isomerization (Lykakis et al., 2015; Ferreri and Chatgililoglu, 2012). The mechanism and products of each process have been studied extensively and are now fairly well documented and understood. Scheme 1 shows the interplay of the two processes in the case of linoleic acid moiety and the corresponding main products. The initial step of peroxidation is hydrogen abstraction from the bisallylic position, which can be performed by a variety of radicals, followed by the reaction with oxygen. Conjugated diene hydroperoxides having the *trans,cis* double bond geometry are the initial stable products (Yin et al., 2011). In free radical isomerization, the addition–elimination of a thiyl radical is enough to produce mono-*trans* geometrical isomers (Chatgililoglu and Ferreri, 2005). An overall damaging potential is produced, that must be carefully considered for its consequences in a biological scenario, since peroxidation is a chain reaction (Yin et al., 2011) and isomerization is a catalytic process (Ferreri et al.,

Abbreviations: ArOH,  $\alpha$ -tocopherol; LH, Linoleic acid; PUFA, Polyunsaturated Fatty Acids; Ph<sub>2</sub>NO<sup>\*</sup>, diphenylnitroxyl radicals; LOOH, Lipid hydroperoxide; PB, phosphate buffer; RS<sup>\*</sup>, thiyl radicals;  $\Psi$ , volume part of the solvent in a solvent mixture

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