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Non-Conventional Antioxidant Systems: The Intriguing Antioxidant Chemistry of Superoxide Radical and its Possible Implication in Ferroptosis

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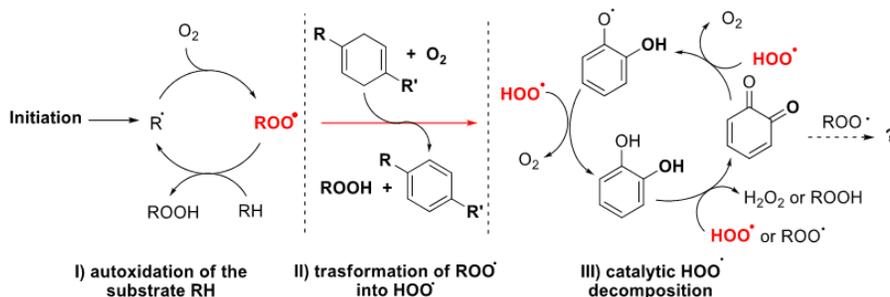
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Superoxide radical or its conjugated acid, the hydroperoxyl radical ($\text{HOO}\cdot$), is the main radical species produced metabolically in living organisms and it is also released during the oxidation of some organic materials like aliphatic alcohols and amines, representing a chain-transfer process which propagates their oxidative degradation. In biological systems, it is considered a detrimental oxidizing species and is implicated in the on-setting of Ferroptosis [1]. We will show that it can also have opposite valence and it can work as potent co-antioxidant, acting as a sacrificial reducing agent that recycles chain-breaking antioxidants like phenols and particularly polyphenols, or it enables the chain-breaking behavior of persistent nitroxides [2-5]. Indeed, its generation by suitable precursors, such as gamma-terpinene or other compounds bearing the 1,4-cyclohexadiene core, in the presence of persistent nitroxides like 2,2,6,6-tetramethylpiperidine-N-oxide (TEMPO) was shown to boost unprecedented antioxidant performance, pairing the most potent natural or man-made chain-breaking antioxidants, while working in a catalytic fashion where TEMPO is continuously recycled [2]. Similarly, gamma-terpinene boosts the antioxidant performance of polyphenols, particularly catechols like synthetic 3,5-di-*tert*-butylcatechol or natural caffeic acid derivatives, or hydroxytyrosol (from olive) in the protection of vegetable lipids of interest in food science [4].



Based on the above chemistry lipophilic antioxidants bearing the catechol or TEMPO active core have been designed and tested under biomimetic settings, in combination with a source of hydroperoxyl/superoxide radical, seeking for a tool to modulate ferroptosis in biological systems [5]. The spontaneous release of hydroperoxyl/superoxide radical during the autoxidation of polyunsaturated lipids under mimetic settings has also been preliminarily investigated and its role will be discussed in the context of antioxidant strategies aimed at modulating Ferroptosis.

References

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