

Photowhittling: A biomimetic polyprenyl chain-shortening in phenolic precursors to plant defense molecules

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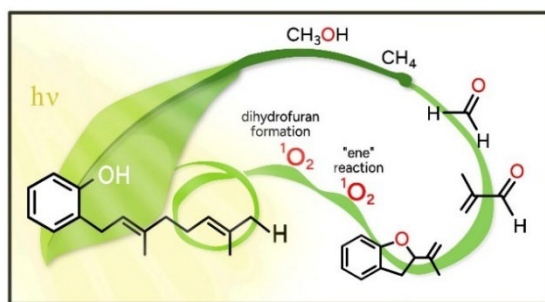
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Abstract

A new area of “photowhittling” is described. Under prolonged sensitized photooxidation we noticed that the $[\text{CH}_2\text{CH}=\text{CH}(\text{CH}_3)\text{CH}_2]_n$ chains in *o*-prenyl phenols ($n = 1-3$) underwent downsizing to reach a common dihydrobenzofuran reminiscent of a plant defense compound known to induce muscle tremors in grazing animals. Surprisingly, total quenching rate constant (k_T) data showed contrasting solvent effects of the prenyl phenols compared to alkyl phenols. On replacing an alcohol solvent with benzene, prenyl phenol rate constants increased by 6-11 fold while alkyl phenol rate constants decreased by 1.5-3 fold. We attribute this contrasting solvent effect to hydrogen bonding of $^1\text{O}_2$ to the phenol OH forming an *iso*-hydroperoxide intermediate, which in the absence of the prenyl group leads to phenol dearomatization. NMR data showed the appearance of small molecules (H_2O_2 , methacrolein, formaldehyde, methanol, and methane) in the downsizing process. The photoproduct mixture was complicated, but the appearance of these five small molecules along with DFT calculations provided a mechanistic framework for the trimming mechanism. The trimming mechanism arose secondary hydroperoxide lability and β -scission reactions, but not carbonization to CO_2 and H_2O . This study establishes a computationally supported, bioinspired framework for photowhittling of a non-conjugated polyene, distinct from photobleaching of conjugated polyenes, such as a cyanine. In our case the photowhittling biomimetically converges on a plant defense-like molecule. Earlier work which served as a stepping stone can be found in refs 1 and 2.



References

1. Nahar, K.; Essang, S.; Lapoot, L.; Greer, A. Tandem Singlet Oxygenation: Regioselective Reaction of Two $^1\text{O}_2$ Molecules by a Non-Conjugated Diprenyl Phenol. *Photochem. Photobiol.* **2026**, *102*, 469–478.
2. Iyer, A.; Lapoot, L.; Greer, A. Mechanistic and Curtin–Hammett Studies of the $^1\text{O}_2$ Oxidation of a Prenyl Phenol and Phenolate Anion. *J. Phys. Org. Chem.* **2025**, *38*, e70014.