Examining Potential Super-Photooxidation of a *Bis*(geranyl)phenol: Close Geranyl Proximity Enables Intramolecular Photo-Epoxidation

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Abstract

Strategies to understand sequential singlet oxygen ($^1O_2$) reactions in organic and plant compounds such as plastoquinones (polyprenyls) are needed.[1] This led us to an NMR study for insight to the tandem addition of $^1O_2$ into geranyl phenol with selectivity for the inner geranyl C=C bond, and then later the outer geranyl C=C bond to reach dihydrofurans and allylic hydroperoxides, respectively (Figure 1).[2] In this poster, we describe inroads to understanding of super-oxidation patterns in systems similar to the retinal pigment of the eye, A2E (also called: *N*-retinylidene-*N*-retinylethanolamine). Sensitized photooxidation of 2,6- and 2,4-*bis*(geranyl)phenols seem to produce intramolecular photo-epoxidation in the former but not the latter comound (Figure 2). *Iso*-hydroperoxide or perepoxide-like species are proposed which preferably epoxidize a nearby alkene group and also can cleave H_2O_2. Future work will also extend the photolysis to assess a possible third and fourth additions of $^1O_2$, where downstream conjugated dienes could undergo a [4 + 2] cycloaddition to reach endoperoxides.

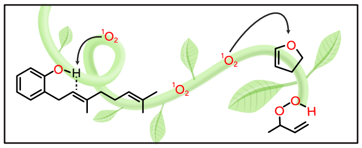

Figure 1. Geranyl phenol photooxidation.

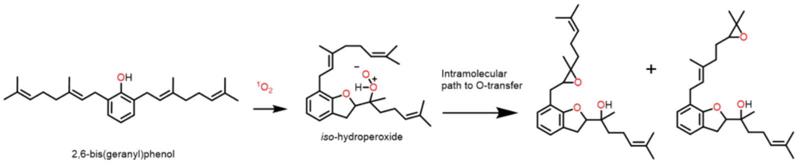

Figure 2. Apparent facile intramolecular photo-epoxidation in the 2,6-compound.

References

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2. Nahar, K.; Essang, S.; Lapoot, L.; Greer, A. Tandem Singlet Oxygenation: Regioselective Reaction of Two $^1O_2$ Molecules by a Non-conjugated Diprenyl Phenol. *Photochem. Photobiol.,* in press, DOI: 10.1111/php.70005

Acknowledgements. Support from the National Science Foundation (CHE-2154133) is acknowledged. We thank Leda Lee for assistance with the graphic arts.