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Photochemical reactions of carotenoids and related terpenoids with hydroxyl radicals produce highly oxidized compounds that resemble refractory marine DOM

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Refractory marine dissolved organic matter (rDOM) persists in the ocean for thousands of years, forming a long-lasting carbon reservoir that plays an important role in marine carbon sequestration. Recent studies established carotenoid degradation products (CDPs) as a relevant model for rDOM and proposed the radical-assisted photochemical degradation of terpenoids as a potential pathway of rDOM generation. The chemical characteristics of rDOM suggest that biochemical precursors like terpenoids, which include carotenoids, undergo high extents of hydroxylation. However, few CDP-related, water-soluble products have been identified and described following photo-degradation. In this study, citral, an acyclic monoterpene aldehyde that resembles the linear isoprenoid portion of carotenoids, and beta-ionone, a cyclic isoprenoid that serves as a smaller model carotenoid compound were examined under simulated solar irradiation assisted by hydrogen peroxide to determine whether stable hydroxylated products could be generated. Through nuclear magnetic resonance spectroscopy and 1D and 2D-gas chromatography coupled to high-resolution mass spectrometry(GC-MS), we showed that major photo-degradation products were highly oxygenated. Citral photo-products included epoxy-glycol-aldehydes and alditol- and monosaccharide-like structures, whereas beta-ionone products included dihydroactinidiolide (DHA), loliolide, menthofuran-like structures, and polymers containing diterpene- (C20) and sesterterpene- (C25) structures. The progressive photo-degradation of citral and beta-ionone through hydroxylation led to an increase in O/C and a decrease in H/C in the photo-degradation products. Several of these products shared the elemental characteristics of rDOM. To determine whether the similarity in elemental composition translates to similarities in chemical structures between our experimental system and marine rDOM, we are currently applying a variety of alcohol derivatization methods to selectively extract hydroxylated compounds from marine DOM. By identifying the range of structures present with marine DOM and comparing them to our CDP model structures, we hope to develop model compounds that accurately mimic rDOM and enable better mechanistic studies of DOM sources, transformation processes, and fates in marine systems.