



Note

Autoxidation of chlorophyll phytyl side chain in senescent phototrophic organisms: A potential source of isophytol in the environment



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ABSTRACT

In this short paper, it is demonstrated that autoxidation (free radical induced oxidation) of the chlorophyll phytyl side chain in senescent phytoplanktonic cells and higher plants constitutes a potential source of isophytol (3,7,11,15-tetramethylhexadec-1-en-3-ol) in the environment. To explain the formation of this isoprenoid alcohol, mechanisms involving the formation of the precursor 3-peroxy-3,7,11,15-tetramethylhexadec-1-ene are proposed.

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1. Introduction

3,7,11,15-Tetramethylhexadec-1-en-3-ol (isophytol; **1**) is generally considered as a relatively short lived intermediate in the biotic and abiotic degradation of the chlorophyll phytyl side chain in the biosphere (Rontani and Volkman, 2003). Probably due to the very easy dehydration of its tertiary OH group in the presence of clays (de Leeuw et al., 1974), isophytol (**1**) was rarely detected in sediments (Fang et al., 2006). In contrast, it was reported in the essential oil of several terrestrial plants (Rasool et al., 1991; Li et al., 2008; Wang et al., 2010; Tao et al., 2013; Srinivasan and Kumaravel, 2016). It was also detected in red (*Polysiphonia denudata*; De Rosa et al., 2001) and green (*Ulva pertusa*; Xu et al., 2007) algae and in macrophytes (*Hydrilla verticillata*, Byju et al., 2012). Brooks and Maxwell (1974) observed its formation during incubation of uniformly labeled ¹⁴C-phytol with sediment from Esthwaite Water (eutrophic lake in Cumbria) and attributed its formation to rearrangement of phytol by an unknown mechanism. The enzyme-catalyzed allylic rearrangement observed during bacterial degradation of phytol under denitrifying conditions (Rontani et al., 1999), or the involvement of carbenium ions during clay-catalyzed dehydration of phytol (de Leeuw et al., 1974) could account for the isomerization (Rontani and Volkman, 2003) and

could be at the origin of the presence of isophytol in sediments (Fang et al., 2006). However, these two processes cannot explain the formation of this isoprenoid alcohol in plants or algae.

We propose here another potential source of this compound, i.e. autoxidation of chlorophyll phytyl side chain in senescent autotrophic organisms.

2. Experimental

2.1. Sampling

Phytoplankton cells were collected from Commonwealth Bay (East Antarctica, 66°56S; 142°27E) during the IPEV-COCA2012 cruise in January 2012. Surface water was sampled using a 25 µm ring net deployed from the R/V Astrolabe. Concentrated phytoplankton cell suspensions were stored frozen (−20 °C) prior to analysis.

Senescent leaves of *Posidonia oceanica* were collected from the Catalan beach at Marseille (France), freeze dried, placed in a mortar and intensively ground.

2.2. Induction of autoxidation

Phytoplankton cells (23 mg dry weight) and *P. oceanica* debris (100 mg dry weight) were suspended in seawater (20 ml) and transferred to 50 ml screw cap glass flasks. After addition of FeSO₄

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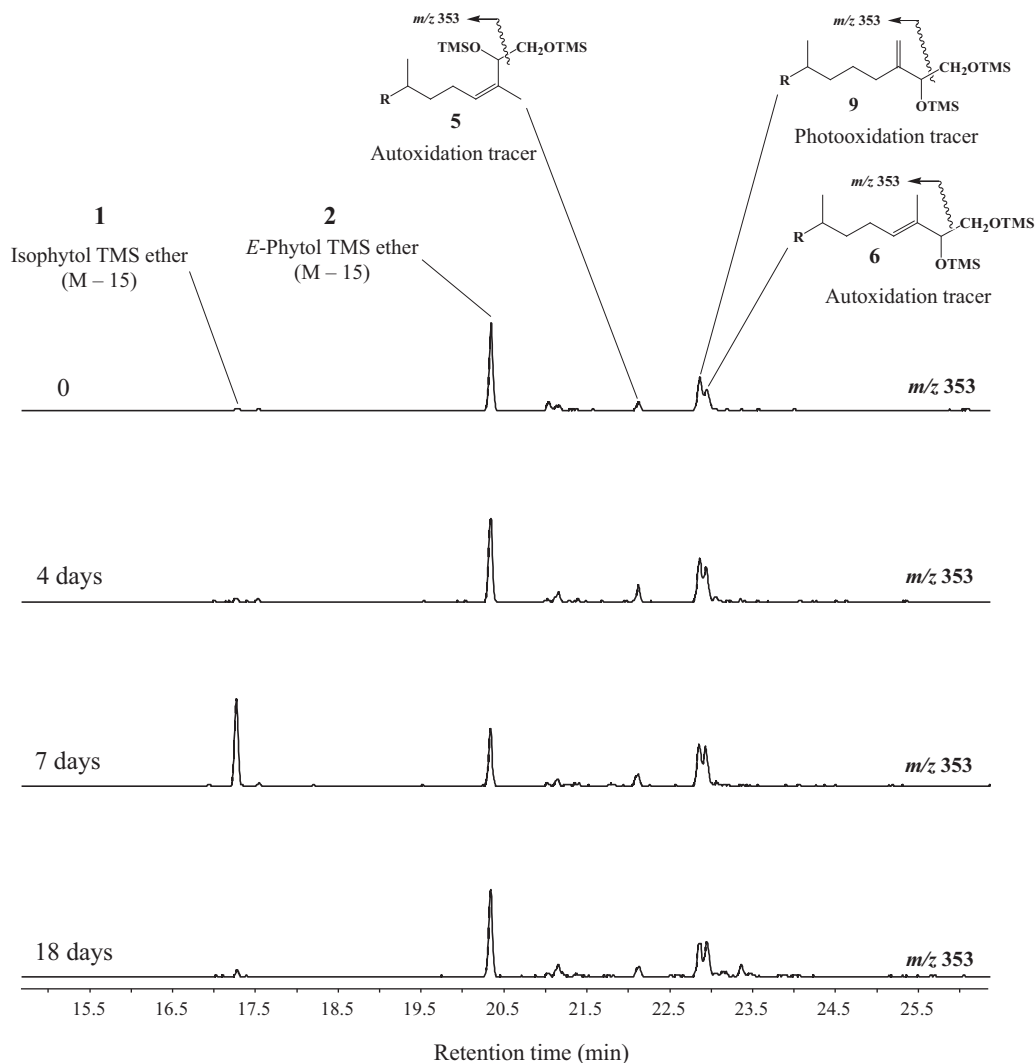


Fig. 1. Ion chromatograms (at m/z 353) showing the autoxidation of chlorophyll phytyl side chain and production of isophytol (**1**) during incubation of Antarctic phytoplanktonic cells under darkness in the presence of Fe^{2+} . [*E*-phytol (**2**) = 3,7,11,15-tetramethylhexadec-2(*E*)-en-1-ol, (**5**) = 3,7,11,15-tetramethylhexadec-3(*Z*)-en-1,2-diol, (**6**) = 3,7,11,15-tetramethylhexadec-3(*E*)-en-1,2-diol, (**9**) = 3-methylidene-7,11,15-trimethylhexadecan-1,2-diol].

(1 ml; 0.1 M), the flasks were stirred in the dark at 4 °C (temperature close to that of Antarctic water) in the case of phytoplankton and at room temperature (temperature close to that of coastal Mediterranean Sea water in summer) in the case of *P. oceanica*. Autoxidation was stopped after different incubation times by filtering samples on pre-combusted (450 °C; 6 h) glass fiber filters (Whatman GF/F, 0.7 μm) under low vacuum.

2.3. Treatment of autoxidized material

Filters containing autoxidized phytoplankton cells and *P. oceanica* debris were treated with excess NaBH_4 or NaBD_4 in MeOH (10 mg/ml; 25 ml, 30 min) to reduce labile hydroperoxides (resulting from photo- or autoxidation) to alcohols that were more amenable to analysis using gas chromatography–electron ionization mass spectrometry (GC–EIMS). After reduction, water (25 ml) and KOH

(2.8 g) were added and the resulting mixtures saponified under reflux (2 h). After cooling, the resulting solutions were acidified (HCl, 2 N; 20 ml) to pH 1 and extracted with dichloromethane (DCM; 3 \times 20 ml). The combined DCM extracts were dried over anhydrous Na_2SO_4 , filtered and concentrated using rotary evaporation (40 °C).

2.4. Derivatization

After solvent evaporation, residues were taken up in 300 μl of a mixture of pyridine and *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA; Supelco; 2:1, v:v) and silylated for 1 h at 50 °C to convert OH-containing compounds to the trimethylsilyl (TMS) ether derivatives. After evaporation to dryness under a stream of N_2 , the derivatized residues were taken up in a mixture of EtOAc and

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