



From ether to acid: A plausible degradation pathway of glycerol dialkyl glycerol tetraethers

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Abstract

Glycerol dialkyl glycerol tetraethers (GDGTs) are ubiquitous microbial lipids with extensive demonstrated and potential roles as paleoenvironmental proxies. Despite the great attention they receive, comparatively little is known regarding their diagenetic fate. Putative degradation products of GDGTs, identified as hydroxyl and carboxyl derivatives, were detected in lipid extracts of marine sediment, seep carbonate, hot spring sediment and cells of the marine thaumarchaeon *Nitrosopumilus maritimus*. The distribution of GDGT degradation products in environmental samples suggests that both biotic and abiotic processes act as sinks for GDGTs. More than a hundred newly recognized degradation products afford a view of the stepwise degradation of GDGT via (1) ether bond hydrolysis yielding hydroxyl isoprenoids, namely, GDGTol (glycerol dialkyl glycerol triether alcohol), GMGD (glycerol monobiphytanyl glycerol diether), GDD (glycerol dibiphytanol diether), GMM (glycerol monobiphytanol monoether) and bpdol (biphytanic diol); (2) oxidation of isoprenoidal alcohols into corresponding carboxyl derivatives and (3) chain shortening to yield C₃₉ and smaller isoprenoids. This plausible GDGT degradation pathway from glycerol ethers to isoprenoidal fatty acids provides the link to commonly detected head-to-head linked long chain isoprenoidal hydrocarbons in petroleum and sediment samples. The problematic C₈₀ to C₈₂ tetraacids that cause naphthenate deposits in some oil production facilities can be generated from H-shaped glycerol monoalkyl glycerol tetraethers (GMGTs) following the same process, as indicated by the distribution of related derivatives in hydrothermally influenced sediments.

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1. INTRODUCTION

Lipid biomarkers have the potential of providing valuable information regarding the composition of ancient ecosystems and paleoenvironmental conditions throughout most of the sedimentary record (e.g., Peters et al., 2004). For most of the frequently used biomarkers, such as steroids, hopanoids, pigments and their derivatives, the post-depositional structural transformations are rather well constrained (e.g., Mackenzie et al., 1982; Innes et al., 1997; Peters et al., 2004; Brocks and Schaeffer, 2008) and contribute to the foundation of the geological biomarker concept that links geomolecules to their biological precursors. An exception is the intensively studied group of isoprenoidal glycerol dialkyl glycerol tetraether (GDGT) lipids produced by Archaea. Despite their prominent use as molecular proxies for the reconstruction of paleoenvironmental conditions (e.g., Pearson and Ingalls, 2013; Schouten et al., 2013) and, in their intact polar form, for the ecology of extant archaeal communities (e.g., Lipp and Hinrichs, 2009; Liu et al., 2011; Meador et al., 2015; Yoshinaga et al., 2015), our understanding of their post-depositional behavior is fragmentary.

Three principal archaeal lipid categories are observed in environmental and geological samples: (i) intact polar lipids (IPL) as building blocks of the cellular membrane, consisting of a glycerolalkylether backbone and a polar headgroup which, in most instances, is glycosidic (Sturt et al., 2004; Lipp and Hinrichs, 2009), (ii) the corresponding core glycerol alkyl ethers derived from hydrolytic cleavage of the polar headgroups on timescales of days to several tens of millennia, depending on depositional conditions and enzymatic activity (Harvey et al., 1986; Xie et al., 2013), and (iii) degradation products of core glycerol alkyl ethers that occur as hydrocarbons (Moldowan and Seifert, 1979), alcohols (Schouten et al., 1998; Saito and Suzuki, 2010) and carboxylic acids (Meunier-Christman, 1988; Schouten et al., 2003; Birgel et al., 2008a).

The second group, i.e., the core lipids, is among the most extensively studied biomarker class in the last decade (Pearson and Ingalls, 2013; Schouten et al., 2013), in particular the GDGT derivatives. More than thirty years ago Chappe et al. (1982) had reported the widespread presence of glycerol di- and tetraethers in sediments and petroleum. GDGTs accumulate in cold and moderately heated aquatic sediments with seemingly little molecular alteration and remain intact in sediments over tens of millions of years (e.g., Kuypers et al., 2001). GDGTs, including the bacterial non-isoprenoidal types (Weijers et al., 2006; Liu et al., 2012b), are among the most prominent lipids in marine sediments and soils. Their ubiquity and abundance result from both the widespread distribution of their producing, largely uncultured, microbes and their relatively high recalcitrance caused by the ether-linkages. Within the domain Archaea, GDGTs are taxonomically widely distributed and probably produced by members of all phyla (Pearson and Ingalls, 2013; Schouten et al., 2013).

Thermal diagenesis (Rowland, 1990) and hydrous pyrolysis (Pease et al., 1998) experiments have shown the generation of isoprenoidal hydrocarbons from fresh archaeal

cultures. The exact fate of GDGTs is not clear, but they seem to be the most plausible precursors of a wealth of compounds of putative archaeal origin found in thermally mature formations. These compounds include head-to-head linked C₃₂ to C₄₀ isoprenoid hydrocarbons in petroleum samples (Moldowan and Seifert, 1979), biphytanic diols (Schouten et al., 1998; Saito and Suzuki, 2010) and biphytanic diacids (Meunier-Christman, 1988; Birgel et al., 2008a) in recent sediments and rock samples of possibly diagenetic and/or biogenic origin; however these diols or diacids have never been detected in any archaeal cell extracts. Another group of recently discovered, widespread compounds includes a series of glycerol ether derivatives, the glycerol dibiphytanol diethers (GDDs; Knappy and Keely, 2012; Liu et al., 2012a). Although the occurrence of core GDDs and their glycosidic intact polar lipids in archaeal cell extracts suggests that they play a role in archaeal lipid biosynthesis (Liu et al., 2012a; Meador et al., 2014), a diagenetic contribution of these lipids in natural settings cannot be ruled out (e.g., Yang et al., 2014).

Another conspicuous compound series of putative archaeal origin are the so-called ‘H-shaped’ or ‘ARN’ C₈₀–C₈₂ isoprenoidal tetracarboxylic acids found in certain petroleum types (Lutnaes et al., 2006, 2007) and believed to contribute significantly to the problematic naphthenate deposits formed during oil processing (e.g., Baugh et al., 2004, 2005). The archaeal lipids that are structurally related to the C₈₀ tetraacids are ‘H-shaped’ glycerol monoalkyl glycerol tetraethers (H-GMGTs) found in thermophilic archaeal taxa (Morii et al., 1998; Schouten et al., 2008a), although H-GMGT-0 may also have non-thermophilic origins (Schouten et al., 2013). Whether the C₈₀ tetraacids are degradation products of H-GMGTs or actually biosurfactants directly synthesized by Archaea living in the crude oil remains ambiguous (Lutnaes et al., 2006, 2007). To date, isoprenoidal tetracarboxylic acids have not been detected in archaeal cells.

Based on the distribution patterns of newly identified series of GDGT degradation products in sedimentary samples (hydrothermally overprinted sediments from the Guaymas Basin and a hot spring in China, Miocene seep carbonates, and marine subsurface sediments), cell extracts and hydrolysis experiments, here we construct a precursor-product reaction network from GDGTs to alcoholic and carboxylic acid biphytane derivatives. Additionally, through the identification of five types of putative intermediates in the sediment from Guaymas Basin, we provide strong support for the hypothesis that isoprenoidal C₈₀ to C₈₂ tetraacids are derived from step-wise degradation of ‘H-shaped’ GMGTs.

2. MATERIALS AND METHODS

2.1. Sample collection and preparation

Nitrosopumilus maritimus strain SCM1 was grown aerobically at 28 °C and pH 7.5 in 8.5 l HEPES-buffered Synthetic Crenarchaeota Medium (1.5 mM NH₄Cl; Könneke et al., 2005; Martens-Habbena et al., 2009). The medium was inoculated with 5% of a mid-logarithmic phase

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