Determination of the absolute stereochemistry of the hydroxyl group in 2-hydroxyarchaeol, the main lipid core of methanogenic and methanotrophic archaea

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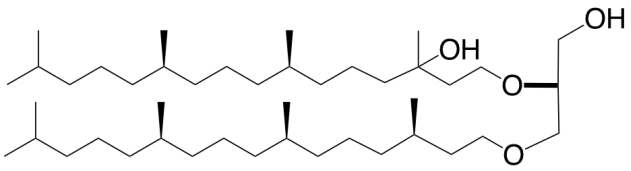
One of the major characteristics of archaea is the lipid core which consist of saturated isoprenoid chain and glycerol with ether bond formation. Furthermore, main lipid core of methanogenic and methanotrophic archaea is hydroxyarchaeol. The saturated isoprenoid is altered to the isoprenoid which has one hydroxyl group in the C-3 of the isoprenoid. Two regioisomeric structures, *sn*-2- and *sn* -3-hydroxyarchaeol (**1**and **2**), are existed depending on the position of the hydroxylated isoprenoid bonding to glycerol.. The distribution of the two isomer is species-dependent [1].
2-Hydroxyarchaeol (**1**) is an important biomarker indicating accumulation of methane hydrate under the seafloor, anoxic oxidation of methane, methane formation at the lake, marsh, and digestive tract of ruminant. Structure determination [1] and analysis of hydroxyarchaeol from the field samples were performed by many researchers [2][3][4], however, the absolute stereochemistry of the hydroxyl group in the ether chain, the most characteristic feature of the molecule had not been determined so far.
The previous study of the author (NY), the synthetic preparation of 2-hydroxyarchaeol equivalent by “racemic” hydroxyl groups revealed that the “racemic” 2-hydroxyarchaeols behave as two equal amounts of the compounds because of the stereochemistry of the hydroxyl group. The result was different from several analysis of field samples which descrived the 2-hydroxylarchaeol as a single compound [5].
For the determination of the stereochemistry of the hydroxyl group of 2-hydroxyarchaeol, asymmetric synthesis of the hydroxyl-group containing ether chain part was conducted and the two stereoisomers of 2-hydroxyarchaol were synthesized.
The stereochemistry of this hydroxyl group was derived from the Katsuki-Shapless epoxidation of phytol. The two isomers were regioselectivity converted to the 2-hydroxyarchaol. The analyses of “racemic” 2-hydroxylarchaeol, two isomers of synthetic 2-hydroxyarchaeol stereoisomer (**3** and **4**), and 2-hydroxyarchaeol from the lipid of *Methanosarcina barkeri* revealed the absolute stereochemistry of the aforementioned hydroxy group is 3*R* (compound **3**). The comparison of the ^{13}C NMR of synthetic 2-hydroxyarchaeol stereoisomer (**3** and **4**), and 2-hydroxyarchaeol from the methanogen culture showed slight difference because of the stereochemistry of methyl group of saturated hydrocarbon of the synthetic isomers. This result may suggest the stereochemistry of methyl group is influenced at the nature of hydroxyarchaeol-containing lipid.

[1] Sprott et al.,J Biol Chem(1990) 265: 13735.
[2] Hinrichs et al., Nature (1999) 398:802.
[3] Blumenberg et al., Science (2004) 101, 11111.
[4] Stadnitskaia et al., Org Geochem (2008) 39:1007.
[5] Yamauchi Res Org Geochem (2014) 30:33.

Keywords: methanogenic archaea, methanotrophic archaea, archaeol, structural determination



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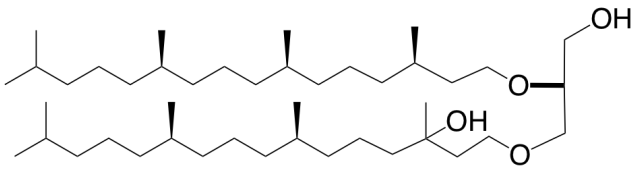

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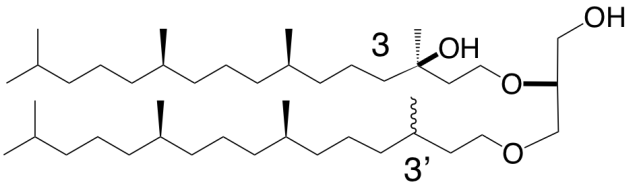

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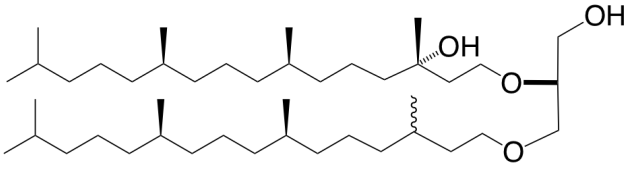

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