The structure determination of unsaturated archaeol derivatives characteristic for the halophilic archaea lipid-core

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Archaea has a characteristic lipid-core, archaeol. Further, a characteristic diether lipid-core (C_{20}-C_{25} diether (**1**)) which is constructed from one C_{25} and one C_{20} isoprenoid is produced by halophilic archaea[1]. Recently, Dawson et al. showed the existence of several unsaturated isoprenoid diethers (such as tentative structure **2**) in the lipid-core of several halophilic archaea which was incubated with very high salt concentration[2].
Then, **2** were chemically synthesized according to the reported method[3] and the comparison of the mass spectrum of trimethylsilyl (TMS) ether were presented previously at this meeting[4]. **2** is apparently different from those of Dawson’s unsaturated diether.
About these unsymmetrical diether, 1) the “real” structure of Dawson’s unsaturated archaeol derivative were assumed to the structure **3** or **4** from the intermediate of biosynthesis of tetraether lipid in thermophilic archaea[5], 2) **5**, the resioisomer of **2** about the unsaturated ther bond linked at the glycerol 5 has the possibility of Dawson’s unsaturated diether because of the relation of hydroxyarchaeol in the methanogenic archaea. Then, the chemical synthesis and mass fragmentation analysis of the 4 isomer (**2** to **5)** was completed.
The comparison and analysis of the mass spectrum of TMS ether was conducterd for the 4 compound. The structure **2** and **5** is different from the “Dawson’s unsaturated diether”. The srtucture **3** and **4** are relatively similar compared with the structure **2** and **5**, however, difference of the Dawson’s diether were observed. So, the all of the supoposed four structure were not the real structure. Dawson's unsaturated diether does not have a double bond at the methyl group branching position resulting from the usual isoprenoid biosynthesis (e.g. phytol), probably unsaturation is formed after the saturated isoprenoid formation. Or, it is a a mixture of **3** and **4** (including further double bond isomers).

[1] De Rosa *et al., J. Gen. Microbiol.*, **128**, 343 (1982). [2] Dawson *et al. Org. Geochem.*, **48**, 1 (2012). [3] Yamauchi *Res. Org. Geochem.*, **29**, 71 (2013). [4] Yamauchi (2016) *JpGU meeting 2016* BA001-P05. [5] Nemoto et al. (2003) *Extremophiles,* **7**, 235.

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