

## SYNTHESIS OF A SULFURIZED BICYCLIC SQUALENE DERIVATIVE: GEOCHEMICAL IMPLICATIONS

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In the last decade, a number of biomarkers formed by sulfuration of functionalized biolipids have been identified either by synthesis of reference compounds (e.g., Poinot et al., 1997), or by NMR structural identification of isolated compounds (e.g., Schaeffer et al., 2006). Alternatively, in some cases, identification has been carried out on indirect evidence based on the identification of the corresponding desulfurized hydrocarbon skeleton (e.g., Schouten et al., 1995). Such is the case, for instance, of 1,10-*bis*-(2,2',6'-trimethylcyclohexyl)-3,8-dimethyldodecane **1** (Fig. 1a) which is thought to be related to an organo-sulfur compound bearing two thiacyclohexane rings (**2**; Fig. 1a) and which represents the predominant compound from the alkylsulfide fraction of Shell Beach sample (Monterey Formation, Miocene, USA; Schouten et al., 1995). More recently, Behrens et al. (2000) identified *bis*-(6,11-cyclofarnesa-2-7(14)-diene **3** (Fig. 1a) in recent sediments from a sulfur-rich lacustrine setting (Lake Cadagno, Switzerland), a compound corresponding to a bicyclic squalene derivative that bears functionalities (i.e., double bonds) at adequate positions to undergo sulfuration and to potentially lead to the formation of the organo-sulfur compound detected in the samples from the Monterey Formation. In order to further characterize the structure of the latter biomarker, which has a rather uncommon and rare hydrocarbon skeleton, we have undertaken its precise structural characterization by synthesis of a reference compound following the synthetic scheme shown in Fig. 1b. The targeted reference compound was obtained as a diastereomeric mixture of 4 compounds resolved in GC in a ca. 1:2:2:2 ratio, all of them showing an almost identical mass spectrum with a molecular ion at  $m/z$  478 and a fragmentation pattern in agreement with the structure **2** (fragment at  $m/z$  211, notably; Fig. 1a). However, the intensity of the fragment at  $m/z$  211 is very low in the mass spectrum of the geologically-occurring sulfide (Schouten et al., 1995), whereas this fragment is predominant in the mass spectra of the reference compounds. Moreover, the synthetic and naturally-occurring compound do not have the same retention time in GC, indicating unambiguously that the structure proposed in the literature for the naturally occurring compound is incorrect. We therefore propose that the sulfide present in the samples from the Monterey Formation could have a "spiro-type" structure (cf. structure **4**; Fig. 1a) as is the case

for some organo-sulfur compounds such as C<sub>20</sub> regular polyprenoid sulfides (Poinsot et al., 1997) or hopanoid sulfides (Schaeffer et al., 2006). Synthesis of a reference compound is currently underway in order to confirm our tentative structural hypothesis.

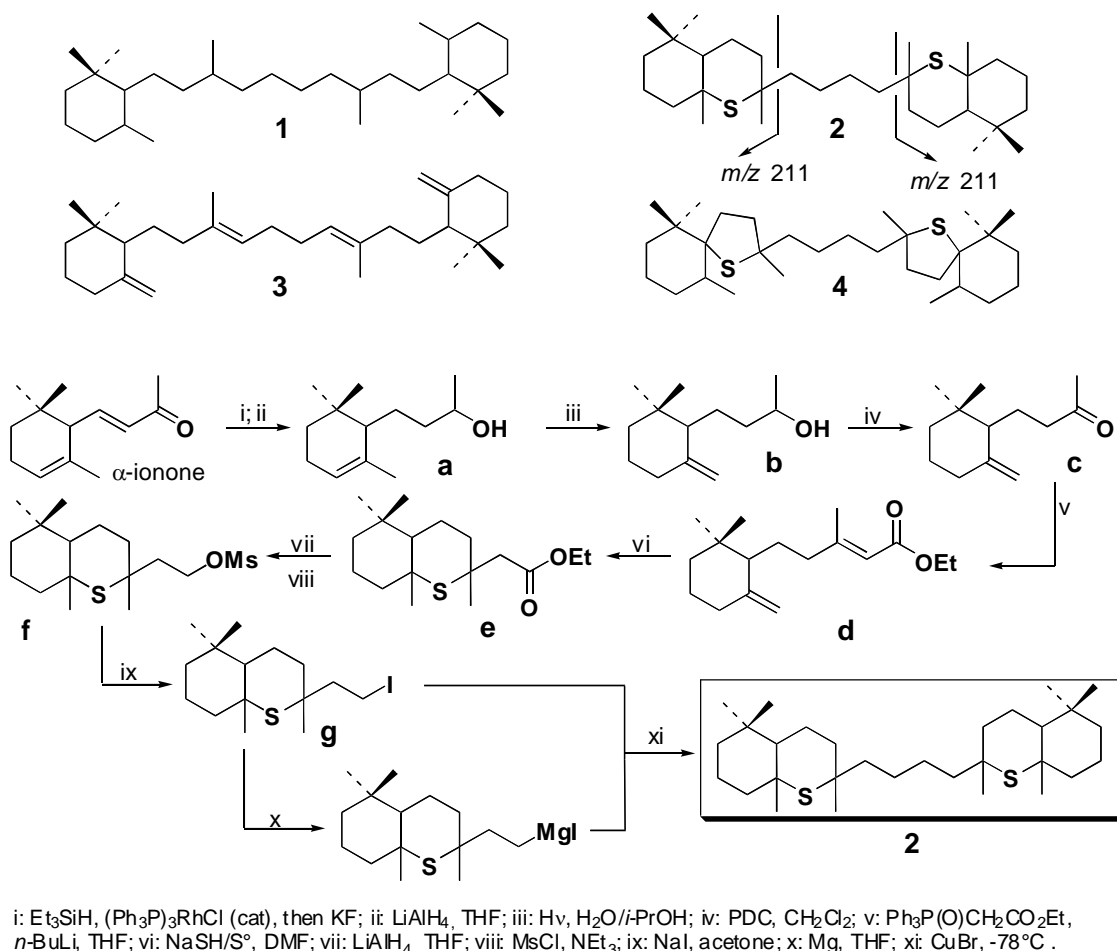


Figure 1. (a) Structures discussed in the text; (b) Synthetic scheme used for the preparation of **1** (obtained as a diastereomeric mixture). The synthetic intermediates **a-g** were characterized by GC-MS and <sup>1</sup>H-NMR spectroscopy.

## REFERENCES

- Behrens, A., Schaeffer, P., Bernasconi, S., Albrecht, P., 2000. Mono- and bicyclic squalene derivatives as potential proxies for anaerobic photosynthesis in lacustrine sulfur-rich sediments. *Geochimica et Cosmochimica Acta* 64, 3327-3336.
- Poinsot, J., Schneckenburger, P., Adam, P., Schaeffer, P., Trendel, J., Albrecht, P., 1997. Novel polycyclic polyprenoid sulfides in sediments. *Journal of Chemical Society, Chemical Communications*, 2191-2192.
- Schaeffer, P., Adam, P., Philippe, E., Trendel, J.M., Schmid, J-C, Behrens, A., Connan, J., Albrecht, P., 2006. The wide diversity of hopanoid sulfides evidenced by the structural identification of several novel hopanoid series. *Organic Geochemistry* 37, 1590-1616.
- Schouten, S., Sinninghe Damsté, J.S., de Leeuw, J.W., 1995. A novel triterpenoid carbon skeleton in immature sulphur-rich sediments. *Geochimica et Cosmochimica Acta* 59, 953-958.