

PYROLYTIC FORMATION OF ALKYLSTERANES — ASSIGNING GEOLOGICAL ORPHANS TO THEIR BIOLOGICAL PARENTS

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Steranes alkylated at position C-3 occur in significant concentrations in many geological samples (e.g. Fig. 1). However, biological equivalents are not known from any living organisms and the formation pathway remains equally enigmatic, rendering them some of the most prominent orphan biomarkers. In some geological samples, the presence of sulphur functionalities indicated that the 3-alkyl group was originally functionalised, which together with a dominance of pentyl-derivatives pointed towards origins from C₅ sugars. 3-alkylsteranes were therefore inferred to represent an entirely new class of natural products. Classified as putative ‘bacteriosteroids’ they were thought to reflect the bacterial fusion of eukaryotic (dietary) steroids with sugars to yield steroids with hopanepolyol-like side-chains (Dahl et al., 1992; 1995). Other hypotheses encompass the likely bacterially mediated alkylation of sterene-intermediates (Summons and Capon, 1988) or algal sources (Schaeffer et al., 1993). We simulated the geological maturation of regular 3-hydroxylated sterols by laboratory-based thermolysis and pyrolysis in the presence of carbon-catalysts and observed the formation of significant quantities of C-3 alkylated products that exhibit alkyl chain lengths of up to eight carbon units—similar to distributions in many geological extracts. Co-elution with an extract of the Ediacaran Araras group, previously shown to contain a series of 3 β -*n*-alkyl steranes (Sousa Jr. et al., 2016), reveals that the lower members correspond to geological $\alpha\alpha\alpha$ R isomers of steranes that have a straight hydrocarbon chain added to the 3 β -position (Fig. 1). Our results show that 3-alkylsteranes readily form *via* carbon-catalysed geological process acting on regular (3-OH) sterol precursors. Considering that 3-alkylated steroids have never been identified in any living organism, there is thus no reason to assume that any of the geological 3-alkyl steroids have direct biosynthetic origins. Instead, regular sterols or their diagenetic intermediates are likely abiogenically alkylated in proportions that may be related to the diagenetic and catagenetic conditions, as well as the composition of the bitumen, kerogen and mineral matrix.

Formation of alkylsteranes in experiments with pure sterols and carbon catalysts strongly suggest that alkyl-moieties derive from the cracking of hydrocarbons. Similar cracking reactions are also important during natural petroleum formation. Considering the free radical decomposition of 1-phenyldodecane in pyrolysis experiments (Lewan, 1998), we hypothesise that hydrocarbon cracking releases alkyl radicals that preferentially attach to the double bond of ster-2-ene intermediates. In fact, in experiments with just C₂₇ sterols, 3-alkyl patterns seem to reflect progressive side-chain cleavage with alkylation up to C₈, low relative abundances of C₂ and C₇ homologs due to isoprenoid branching of the side-chain, and a similarity in 3-alkyl and nor-sterane patterns. During natural petroleum formation when a diverse range of radical types is released during cracking and subsequent radical propagation reactions, various types of alkyl-moieties, including those with different types of functionalisation, may similarly attach to the C-2 double bond. As (organic) sulphur compounds are particularly prone to radical formation at low thermal stress (Lewan, 1998), organic sulphur radicals would have a higher likelihood to encounter still unreacted ster-2ene intermediates during diagenesis or the early stages of petroleum formation. Such an organosulphur-radical pathway may explain why some

geological 3-alkylsteroids were observed to yield sulphur functionalisations (e.g. Dahl et al., 1992).

The concentration of sulphur radicals was also proposed to be a rate-controlling factor in petroleum formation, with C-S and S-S bonds providing initiating free radicals for cracking of C-C bonds at low thermal stress (Lewan, 1998). Low atmospheric oxygen concentrations may promote formation of pore water euxinia in organic-rich sediments that, due to the ease of homolytic sulphide cleavage, may in turn favour radical initiation at relatively shallow burial. Such early onset of catagenetic radical reactions could potentially explain the high ratios of 3-alkyl/desmethyl steranes in various Neoproterozoic bitumens compared to those in most younger geological formations.

Thirty years after their original discovery in geological samples (Summons and Capon, 1988), 3-alkyl steranes may finally be assigned to their biological parent molecules: regular 3-hydroxy sterols. Accordingly, the source organisms are the same as those of the 3-demethylated steranes in the same samples—largely eukaryotic organisms and predominantly algae in the marine realm.

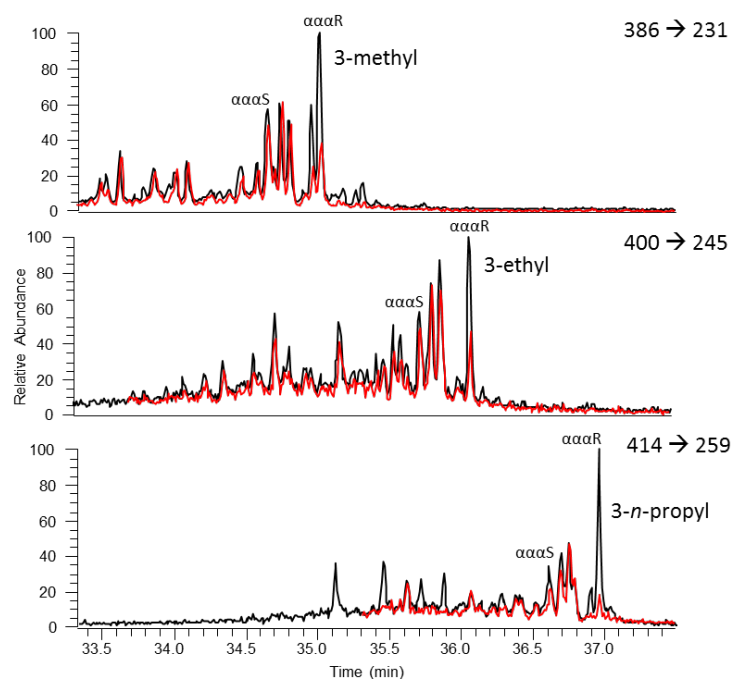


Figure 1 Co-injection (black) of a Neoproterozoic Araras Gp. bitumen (red) and the laboratory maturation product of a C₂₇ sterol.

A pseudohomologous series of alkyl-steranes produced during sterol maturation corresponds to the aaaR isomers of 3 β -n-alkylcholestanes (here shown for the 3-methyl, 3-ethyl and 3-propyl members) previously identified in the Araras group.

References

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