

**DEMETHYLATED HIGHLY CYCLIZED REGULAR POLYPRENOIDS:
FORMATION AND GEOCHEMICAL SIGNIFICANCE**

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GC-MS analysis of a series of severely altered bitumen from a Spanish quarry revealed the presence of a complex mixture of regular polycyclic polyprenoid hydrocarbons comprising non demethylated and demethylated components. The latter occur mainly as hydrocarbons demethylated at junction of rings A/B, compounds demethylated at rings E/F/G and compounds both demethylated at rings A/B and rings E/F/G, as evidenced by NMR structural identification of three isolated homologues (**1** and structures cited in Grosjean et al. 2001, cf. Fig. 1), the identification of **1** being reported here for the first time. The presence, throughout the World, of non demethylated polycyclic polyprenoid hydrocarbons together with the hydrocarbon series demethylated at rings E/F/G in sediment extracts and crude oils comprising both biodegraded and unaltered samples gives clues to the biological precursor lipids of highly cyclized polyprenoids. Indeed, our results suggest that the demethylation process involved in the formation of the latter is unlikely to be related to a late biodegradation process, but rather results from the early transformation of precursor molecules bearing functionalised methyl groups on rings E/F/G. In contrast, polyprenoids demethylated at junction of rings A/B have only been detected in the most biodegraded samples from the Spanish quarry, their relative abundance increasing with the increase of alteration. Consequently, it can be proposed that this demethylated series was originally present in the non altered samples in trace amounts, and subsequently enriched due to a higher resistance towards biodegradation as compared to the non demethylated series and that demethylated at rings E/F/G junction. Alternatively, and perhaps more likely, it can also be envisaged that the hydrocarbons demethylated at junction of rings A/B are formed by extensive alteration of the non demethylated structures. Whatever the demethylation process involved, it appears that this demethylated series shares the same ring A/B partial structure as that of 25-norhopanes which may confer to these biomarkers a particularly high resistance towards further biodegradation. In addition to these polyprenoid hydrocarbon series, a novel series of carboxylic acids related to the polycyclic polyprenoids has been tentatively identified in the

samples from the Spanish quarry and comprises both non demethylated polyprenoids and structures exclusively demethylated at rings E/F/G. It is proposed that the acids represent alteration products of polyprenoids bound to aromatic subunits from macromolecular material that have been released upon severe oxidation reactions during exposure to weathering. From our results, we propose a general diagenetic pathway leading from functionalized polyprenoid precursors to the various sedimentary polyprenoid hydrocarbons and acids identified in recent years.

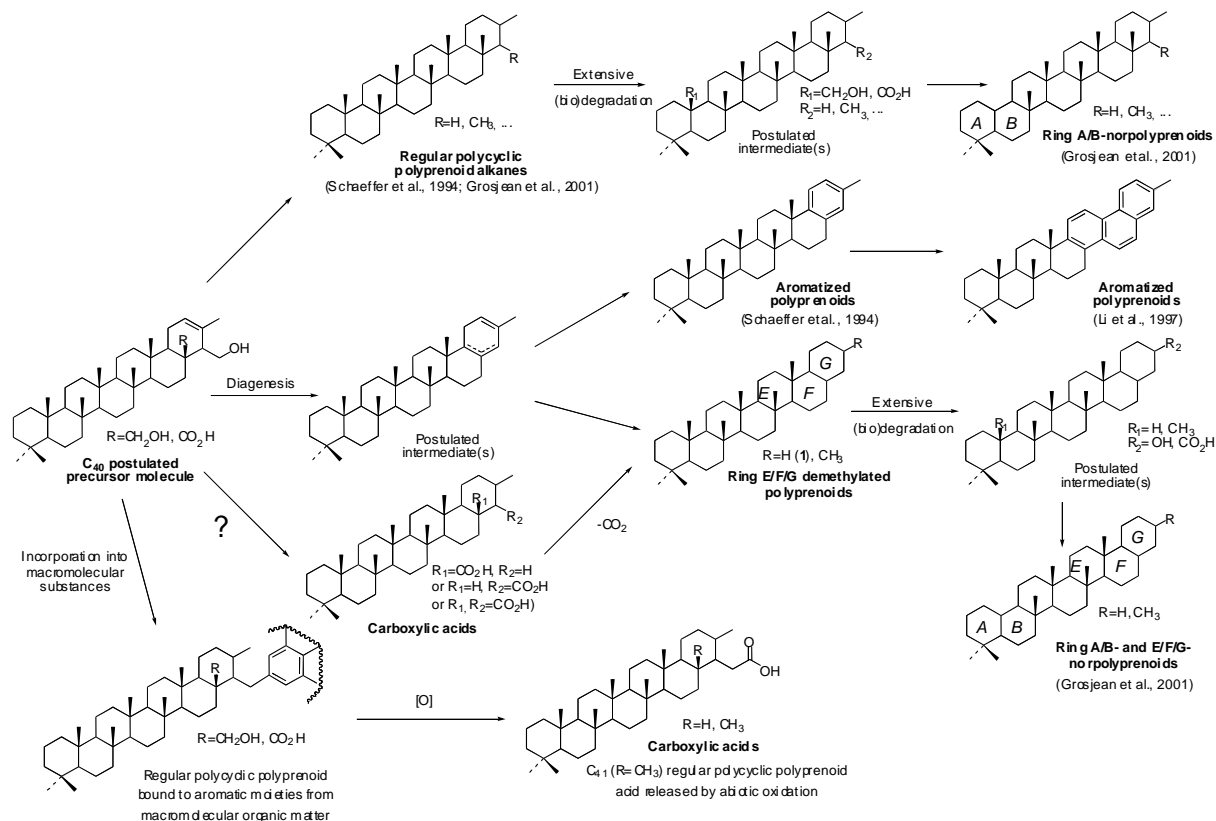


Figure 1. Hypothetical diagenetic pathway leading to the formation of demethylated polycyclic regular polyprenoids in the sub-surface.

REFERENCES

- Grosjean, E., Poinot, J., Charrié-Duhaut, A., Tabuteau, S., Adam, P., Trendel, J., Schaeffer, P., Connan, J., Dessort, D., Albrecht, P., 2001. Synthesis and NMR characterization of novel highly cyclized polyprenoid hydrocarbons from sediments. *Journal of the Chemical Society, Perkin Trans I*, 711-719.
- Li, M., Riediger, C.L., Fowler, M.G., Snowdon, L.R., 1997. Unusual polycyclic aromatic hydrocarbons in Lower Cretaceous Ostracode Zone sediments and related oils of the Western Canada sedimentary basin. *Organic Geochemistry* 27, 439-448.
- Schaeffer, P., Poinot, J., Hauke, V., Adam, P., Wehrung, P., Trendel, J.M., Albrecht, P., Dessort, D., Connan, J., Albrecht, P., 1994. Novel optically active hydrocarbons in sediments: Evidence for an extensive biological cyclization of higher regular polyprenols. *Angewandte Chemie, International Edition in English* 33, 1166-1169.