

**C₈₀₋₈₂ ARCHAEBACTERIAL TETRAPROTIC ACIDS IN CRUDE OILS:
STRUCTURAL IDENTIFICATIONS, DISTRIBUTIONS AND IMPLICATIONS FOR
EXPLORATION AND PRODUCTION**

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Archaeal C₈₀ tetraprotic acids (TPAs; otherwise known as ‘ARN’ acids or high molecular weight naphthenic acids) have been reported in a few heavy immature crude oils (Baugh *et al.*, 2005) and a tentative structure has been reported for one C₈₀ acid based on analysis of mixtures (Lutnaes *et al.*, 2006). We now report the isolation and identification of a series of individual Archaeal C₈₀₋₈₂ TPAs, correction of the previous C₈₀ structure, quantitative analysis of the concentrations and distributions of the acids in a wide variety of crude oils and determination of the ¹³C isotopic signatures of the TPAs. The resulting information is important for oil exploration and for resolution of some oil production problems where deposition of metal salts of the acids causes pipeline blockages and corrosion difficulties.

TPAs were isolated from crude oils of North Sea and West African oilfields by ion exchange and other methods and converted to methyl esters as reported previously (Lutnaes *et al.*, 2006). Examination of the methyl esters by high temperature gas chromatography (HTGC) and High Performance Liquid Chromatography (HPLC) using an evaporative light scattering detector (ELSD), revealed the distributions of resolved 4-8 ring acids for the first time and electrospray ionisation mass spectrometry (ESI-MS) also revealed the presence of previously unreported C₈₁ and C₈₂ acids. Milligram quantities of several of the individual TPAs were isolated by HPLC and the structures (e.g. Figure 1) elucidated by nuclear magnetic resonance (NMR) spectroscopy. In some cases high field (900 MHz) spectroscopy was needed in order to differentiate between regioisomers. A previous tentatively assigned structure was found to be slightly in error but all of the acids contained a unique cross-linked bridge. This feature was previously only tentatively assigned in the tetraether membrane lipids of certain hyperthermophilic Archaea (Lutnaes *et al.*, 2006).

Use of weighed amounts of the individual isolated acids allowed calibration of the HPLC-ELSD response and hence the concentrations of each TPA in the crude oils to be

determined and measured. The distributions of 4-8 ring acids differed in the various oils, possibly reflecting the growth temperatures of the bacteria from which the acids are assumed to have originated. The ^{13}C isotopic signatures of some of the acids were consistent with such a hypothesis. It is possible that an index of palaeotemperature similar to that proposed for bacterial tetraethers, can now be constructed and examples are given. This will have important implications for exploration geochemistry, whilst the detailed knowledge of the TPA structures will be useful for guiding the production of chemicals to act as inhibitors of TPA salt deposition in pipelines.

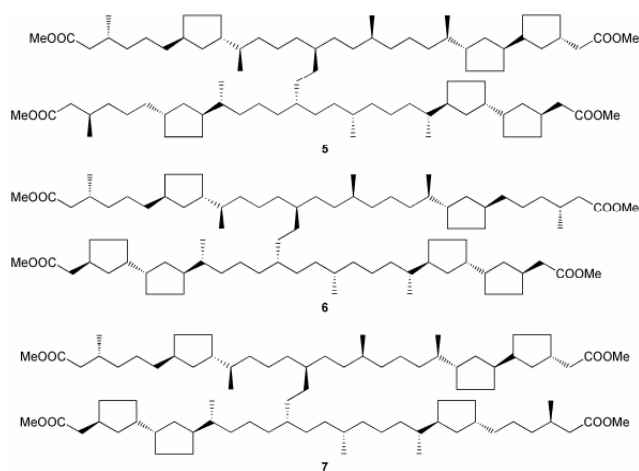


Figure 1. Structures of the regioisomers of some of the C₈₀ 6 ring Archaeal tetra protic acids (TPAs) as methyl esters assigned by NMR spectroscopy after isolation by HPLC. Structure 5 comprises the most abundant TPA in the oils studied to date (cf Lutnaes *et al.*, 2006).

REFERENCES

- Baugh, T.D., Grande, K.V., Mediaas, H., Vindstad, J.E. (2005) *SPE 93011*, SPE International Oilfield Scale Symposium. Aberdeen, U.K.
 Lutnaes, B.F., Brandal, Ø., Sjöblom, J. and Krane, J. (2006) *Organic & Biomolecular Chemistry*, **4**, 616-620