

THE OCCURRENCE OF UNUSUAL HOPENES IN HYDROPYROLYSATES GENERATED FROM SEVERELY BIODEGRADED OIL SEEP ASPHALTENES

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Hydropyrolysis (pyrolysis assisted by high hydrogen gas pressures) is an emerging technique that possesses the unique ability to produce high yields of biomarkers from coals, petroleum source rocks and heavy oil fractions whilst minimising alteration to their isomeric distributions (stereochemistries) (Love et al., 1995). The reliable bound biomarker profiles generated offer powerful solutions to key exploration problem areas where the conventional free biomarker approach fails such as for very heavily biodegraded oils (Russell et al., 2004).

In this study we show how hydropyrolysis can be used to generate reliable biomarker profiles from a West African oil seep which had been subjected to such severe biodegradation that it contained no recognisable biomarkers. Asphaltenes isolated from the seep oil were pyrolysed under slow heating conditions (250°C to 520°C at 8°C min.⁻¹), a hydrogen pressure of 15 Mpa in the presence of a sulphided molybdenum catalyst. The *m/z* 191 mass chromatogram of the product oil is presented in Fig. 1, and shows a full suite of hopanes including excellent preservation of the longer chained homologues. The higher abundance of C29 $\alpha\beta$ norhopane relative to the C30 $\alpha\beta$ hopane is typical of hydropyrolysis products, as is the absence of Ts, which as a rearrangement product should always be absent from the bound phase. Hydropyrolysis enables a more complete characterisation of this oil seep in terms of both its maturity and important source information, such as the occurrence of gammacerane, than would be possible with traditional pyrolysis techniques.

In addition to the expected suite of hopanes the hydropyrolysates also contained a number of abundant hopenes. Peak X on Fig. 1 was identified as 22,29,30-trisnorhop-17(21)-ene and is very common in hydropyrolysis oils. Peaks Y and Z are more unusual, and after fractionation by HPLC the hopene rich fractions were subjected to mild hydrogenation (PtO₂ and pentane at room temperature for 30 min.) and acid catalysed isomerisation (0.1M perchloric acid in glacial acetic acid at room temperature for 30 min.). The hydrogenation products and very rapid isomerisation to hop-17(21)-ene together with the spectra and relative retention positions of these two compounds (Fig. 1) allowed them to be identified as: Y - C30

17 α (H)-hop-20(21)-ene, and Z - C30 17 β (H)-hop-20(21)-ene. Such compounds are very rare in nature although the 17 α (H) compound has been previously reported by Bisseret and Rohmer (1993), and was obtained from the heating of hop-17(21)-ene in molten sulphur. Whether these compounds were original constituents of the bound asphaltene structure, and were simply released by hydrolysis, or generated from other hopenes during the hydrolysis procedure is not currently understood. However, they have been found in very few other hydrolysis products and their occurrence appears to be related to the presence of sulphur, as demonstrated by the experiments of Bisseret and Rohmer (1993), and the high sulphur content (2.6%) of this asphaltene.

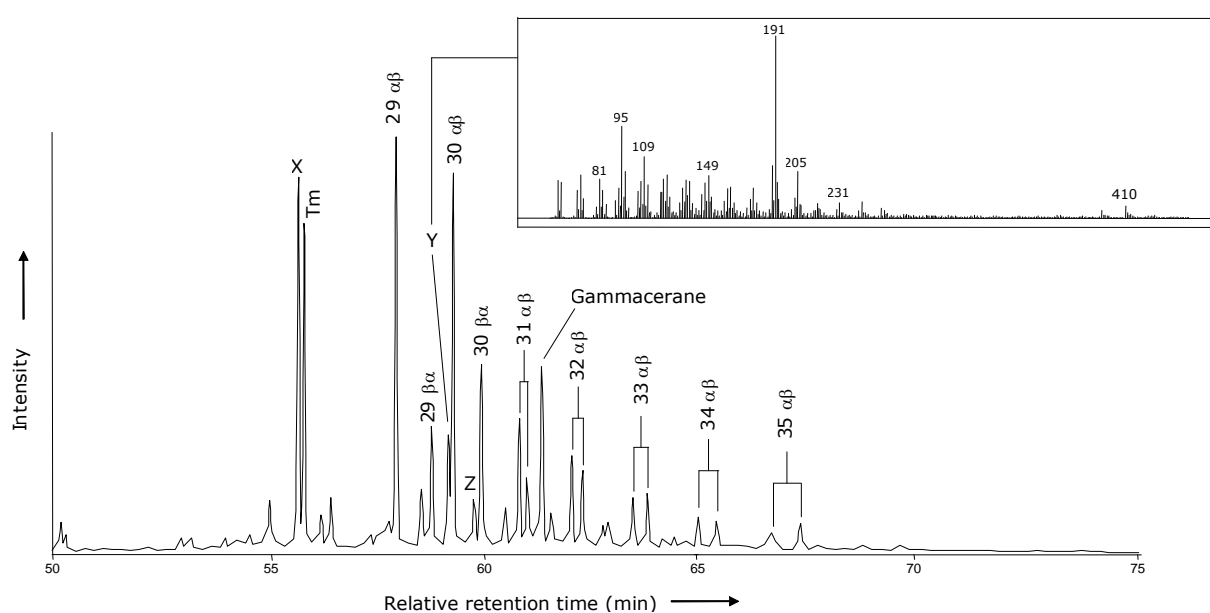


Figure 1. m/z 191 mass chromatogram of the aliphatic fraction of the oil generated from the hydrolysis of asphaltenes isolated from a heavily biodegraded West African oil seep. The inset shows the spectra for peak Y, identified as C30 17 α (H)-hop-20(21)-ene.

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