

IDENTIFICATION OF A NEW SERIES OF SPIROTRITERPANES AND THEIR POSSIBLE USE FOR MATURITY ASSESSMENT AT HIGH MATURITIES

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A series of pentacyclic triterpanes having unusual mass spectra has previously been observed (Nytoft and Bojesen-Koefoed 2001). It was suspected, that they were the saturated counterparts of the spiro-triterpenes described by Hauke *et al.* (1994). The C₃₀ member of the series (30Sp) has now been synthesized and the structure (Fig.1) has been confirmed by NMR.

Small amounts of synthetic C₂₇, C₂₉, C₃₀ and C₃₁ hop-17(21)-enes were subjected to acid-catalyzed isomerisation yielding neohop-13(18)-enes, fernenes and spirotriterpenes (Δ 7, Δ 10 and Δ 9-11) and several minor compounds. Pure spirotriterpenes were isolated from the mixtures using reverse phase HPLC and again subjected to acid catalyzed isomerisation. It could be shown that the formation of spirotriterpenes from hop-17(21)-enes and neohop-13(18)-enes was irreversible in the case of the C₃₀ and C₃₁ whereas neohop-13(18)-enes were formed again by isomerisation of the C₂₇ and C₂₉ spirotriterpanes. Hydrogenation of C₂₇ spirotriterpenes was possible using very mild conditions (PtO₂, hexane, room temperature). The C₃₀ spirotriterpane was obtained by hydrogenation of a mixture of spirotriterpenes and neohop-13(18)-ene (PtO₂, 0.1N perchloric acid in acetic acid, 70° C). The almost pure C₃₀ spirotriterpane for NMR investigation was isolated using HPLC. A C₃₀ 18 α -neohopane was obtained in another fraction and also characterized by NMR (Fig. 1). This compound coeluted with a compound which was tentatively identified as C₃₀ 18 α -neohopane (30Ts) by Farrimond and Telnæs (1996) and had an identical mass spectrum.

The mass spectra of spirotriterpanes (Nytoft and Bojesen-Koefoed, 2001) contain a very small m/z 191 fragment but a very intense m/z 221 fragment (~60%), which is absent in the mass spectra of most other triterpanes. The spirotriterpanes can be quantified using the m/z 221 mass chromatogram, whereas the M⁺ \rightarrow 221 transition is less useful.

The stability (DMM-force field) of the C₃₀ spirotriterpane (30Sp) is very similar to that of the C₃₀-17 α -diahopane and it is considerably more stable than the non-rearranged 17 α ,21 β -hopane (A.C.T Van Duin, personal communication 2001). This probably means that 27Sp is more stable than Tm and possibly also more stable than Ts. The concentration of spirotriterpanes is low in normal crude oils, but the content increases relative to that of regular

hopanes and 18 α -neohopanes with increasing maturity. Maturity parameters based on spirotriterpanes such as 27Sp/(27Sp + 27Ts) could thus be useful at very high maturities (e.g. condensates).

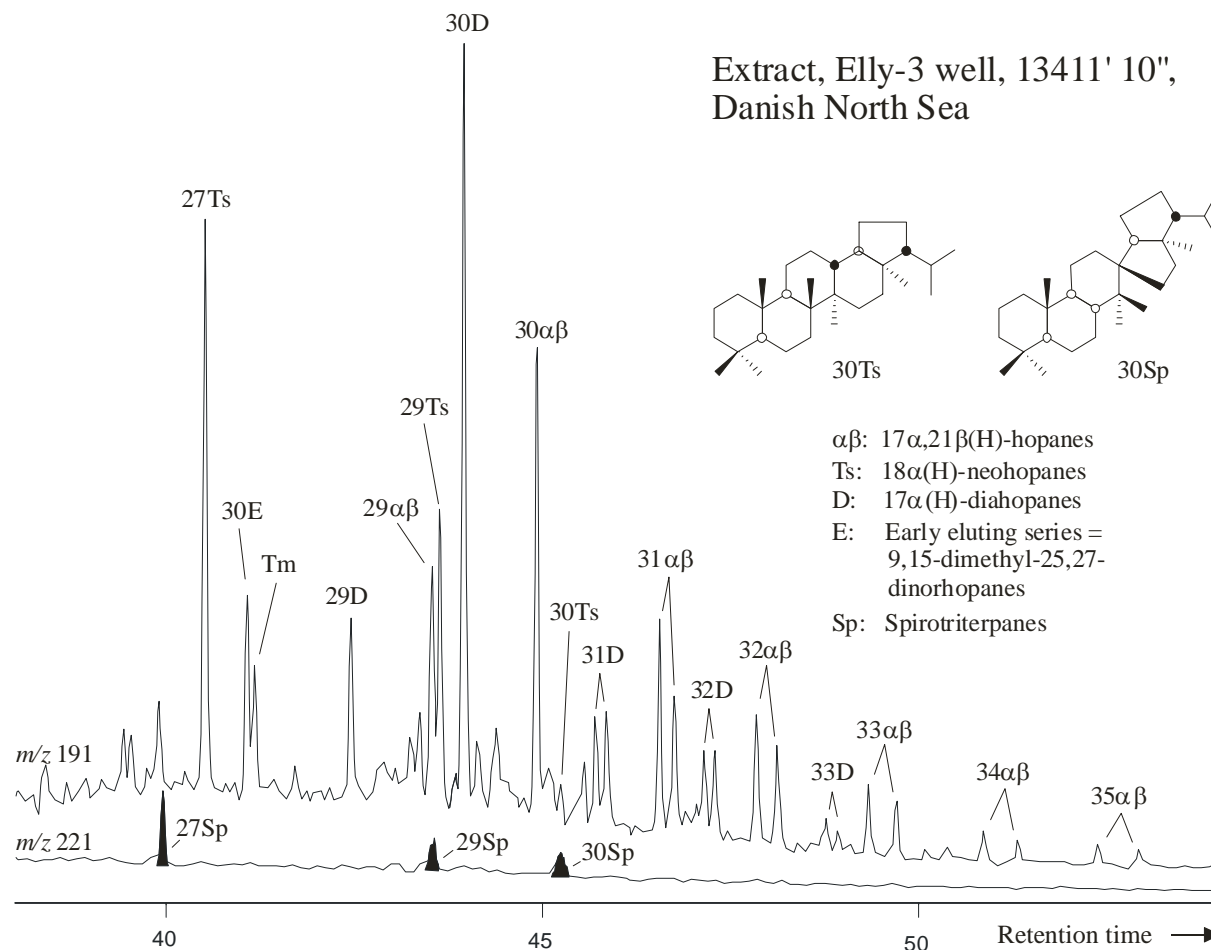


Figure 1. Mass chromatograms (m/z 191 and m/z 221) showing regular hopanes and four series of rearranged hopanes extracted from an overmature source rock.

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