

NOVEL "ISOHOPANES" AND THEIR USE AS SOURCE MARKERS

Hans Peter NYTOFT

Geological Survey of Denmark and Greenland (GEUS)

Several early eluting hopanes having 33 or more carbon atoms have been detected in coal extracts. Their mass spectra are virtually indistinguishable from those of isomeric regular $17\alpha,21\beta$ -hopanes. 17α -diahopanes which also elute earlier than the regular hopanes have slightly different mass spectra. Furthermore, these compounds are abundant in low maturity coals almost devoid of C_{29} - C_{32} diahopanes. Such hopanes were previously observed in coals (Monthieux and Landais, 1989), but they were not identified.

The mass spectral data suggest a non-rearranged structure and their short retention times indicate a multiple branched side chain. A number of such hopanes were synthesized from isoadiantone, and it was shown that the major unidentified C_{33} - C_{35} compounds coeluted with synthetic hopanes (22S + 22R) having a terminal methyl branch in the side chain (31-methyl-bishomohopanes, 32-methyl-trishomohopanes and 33-methyl-tetrakishomohopanes). Such hopanes could be named "isohopanes". Two minor C_{34} hopanes were tentatively identified as 31-methyl-trishomohopanes and it could be shown that C_{33} - C_{35} 29-methylhopanes are absent in geological samples. In addition to 33-methyl-tetrakishomohopanes, several minor, early eluting C_{35} hopanes were detected (482 → 191) but none of these were identified due to the lack of standards. C_{33} isohopanes isomerize slightly slower at C-22 than regular C_{33} hopanes. The equilibrium 22S/(22S + 22R) ratio for isohopanes is around 0.60.

Like regular hopanes, the the isohopanes extend beyond C_{35} . In addition, hexacyclic hopanes having 35 or more carbon atoms have been noted (480 → 191, 494 → 191 etc.). Their mass spectra (from HPLC-purified fractions) show that the extra ring is not fused to the rest of the hopane skeleton. The hexacyclic C_{35} hopanes were tentatively identified as 29-cyclopentylhopanes. Hopanoids having a multiple branched or cyclic side-chain are probably formed from hopanoids bonded to the kerogen matrix by carbon-carbon bonds.

The ratio between C_{33} and C_{34} isohopanes and regular hopanes with the same number of carbon atoms (isohopane ratios) has been measured for a large number of crude oils, source rocks and coals from all parts of the world (immature samples with $\beta\beta$ -hopanes were not included). The C_{33} and C_{34} isohopane ratios of marine crude oils and source rocks are low (0.02-0.09, 0.10-0.22), higher in lacustrine oils (0.07-0.11, 0.19-0.36) and especially high in

most coals (0.04-0.83, 0.19-1.71). Because coals generally have high isohopane ratios, this should also be the case for oils from coaly sources. North Sea crude oils generated from Middle Jurassic coals (Petersen et al., 2000) have higher isohopane ratios than marine oils and source rocks from the same area. An oil from a coaly source (Taranaki, NZ) had the highest isohopane ratios (0.31 and 0.39) of all the oils investigated so far. These observations suggest, that the isohopanes could be useful as source markers and petroleum correlation tools.

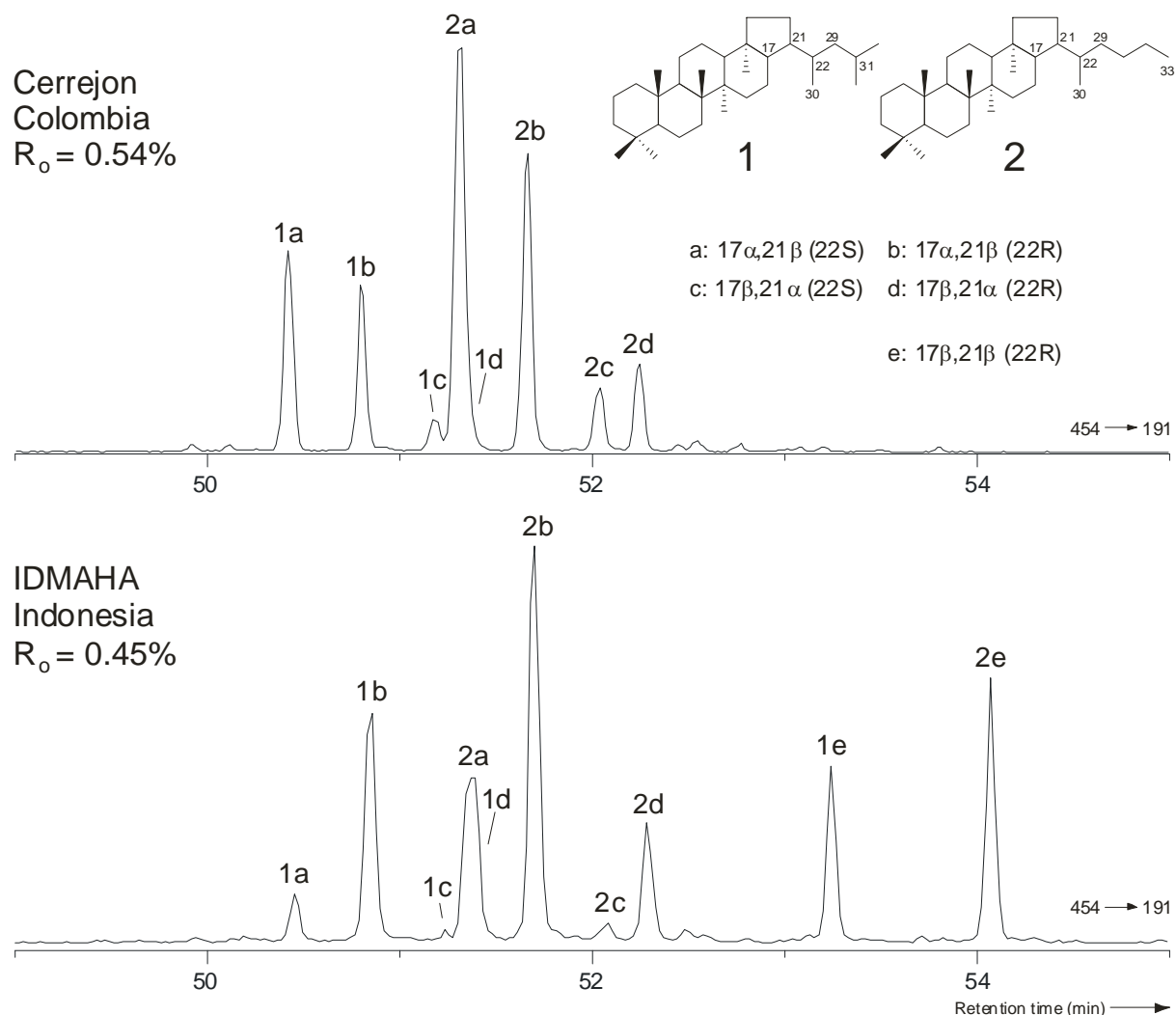


Figure 1. 454 → 191 transition showing C_{33} hopanes in two low rank coals. Note that 31-methyl-bishomohopanes (C_{33} isohopanes) and regular C_{33} hopanes have a similar distribution of stereoisomers. C_{33} isohopane ratio: $(1a + 1b)/(2a + 2b)$. The peak area of 2a is corrected for coeluting 1d assuming identical 1c/1d and 2c/2d ratios.

REFERENCES

- Monthieux, M., Landais, P. (1989) Natural and artificial maturation of coal: Hopanoid stereochemistry. *Chemical Geology*, **75**, 209-226.
- Petersen, H.I., Andsbjerg, J., Bojesen-Koefoed, J.A., Nytoft, H.P., 2000. Coal-generated oil: source rock evaluation and petroleum geochemistry of the Lulita oilfield, Danish North Sea. *Journal of Petroleum Geology* **23**, 55-90.