

DEHYDROICETEXANES IN SEDIMENTS AND CRUDE OILS: MARKERS FOR CUPRESSACEAE?

H.P. Nytoft¹, G. Kildahl-Andersen², S. Lindström¹, F. Rise², D. Mitrović³, N. Đoković, D. Životić³, K. Stojanović³

¹Geological Survey of Denmark and Greenland, Denmark, ²University of Oslo, Norway, ³University of Belgrade, Serbia

Introduction

Williford et al. (2014) detected an unknown isomer of dehydroabietane in high concentration at the Triassic-Jurassic boundary in East Greenland but failed to determine the exact structure. It was suggested as a marker of terrestrial ecosystem stress. We have detected two compounds having mass spectra like that in Williford et al. (2014) in coal, mudstone and crude oil. They were isolated from Upper Miocene Serbian lignite and Triassic-Jurassic boundary mudstones from Sweden using preparative HPLC and characterized as *cis*- and *trans*-icetexa-8,11,13-trienes (or dehydroicetexanes) using NMR spectroscopy. This is, to our knowledge, the first occurrence of compounds having the icetexane skeleton in geological samples.

Results

The dehydroicetexanes have a diterpenoid skeleton with a 6-7-6 framework as opposed to 6-6-6 in the more common abietanes. Natural icetexane diterpenoids with varying degrees of oxygenation and oxidation have been isolated from a variety of terrestrial plant sources (Simmons and Sarpong, 2009). They have been known for nearly 40 years.

The simplest subclass of icetexanes are the pisiferins having only OH at C-12. They seem to be especially abundant in the *Chamaecyparis* genus. Only five or six species of *Chamaecyparis* can be found today in East Asia and North America. Fossil data indicate that earlier members of *Chamaecyparis* were widely distributed in the mid to high latitudes, but the distribution of the genus was restricted during climatic coolings in the Neogene (Liu et al., 2009).

We have found dehydroicetexanes in coal and mudstone from Denmark, Ellesmere Island (North Canada), Greenland, Serbia and Sweden ranging in age from the Triassic to Upper Miocene (Pontian ~ 6 Ma). So far, they have only been detected in crude oil from West Greenland and arctic Canada. *Cis*-dehydroicetexane is the dominant dehydroicetexane in Serbian lignite (huminite reflectance ~0.3%) and other very immature sediments. An equilibrium (ca. 15% *cis* and 85% *trans*) is reached at $R_o = 0.5\%$. 16 oil samples from West Greenland contained 14-20% *cis* and 80-86% *trans*.

Dehydroicetexanes appear to be thermally stable. They are relatively minor compounds compared to dehydroabietane in low maturity samples whereas most West Greenland oils are rich in dehydroicetexanes but almost devoid of dehydroabietane. Samples with a low TOC (mudstones) have a much higher dehydroicetexane/dehydroabietane ratio than coal having the same thermal maturity (from 0.1 to 10 within a 25 cm thick seam from West Greenland with TOC from 3.6 to 69.0%).

The mudstones had a relatively higher proportion of other rearranged compounds such as diasteranes and rearranged hopanoids suggesting that dehydroicetexanes could also derive from rearrangement of abietanes such as 20-hydroxymethylferruginol (pisiferol) from other conifers.

Conclusions

Two novel monoaromatic hydrocarbons were isolated and characterized as *cis*- and *trans*-icetexa-8,11,13-trienes (or dehydroicetexanes; Fig. 1) using NMR spectroscopy. They may be markers for Cupressaceae.

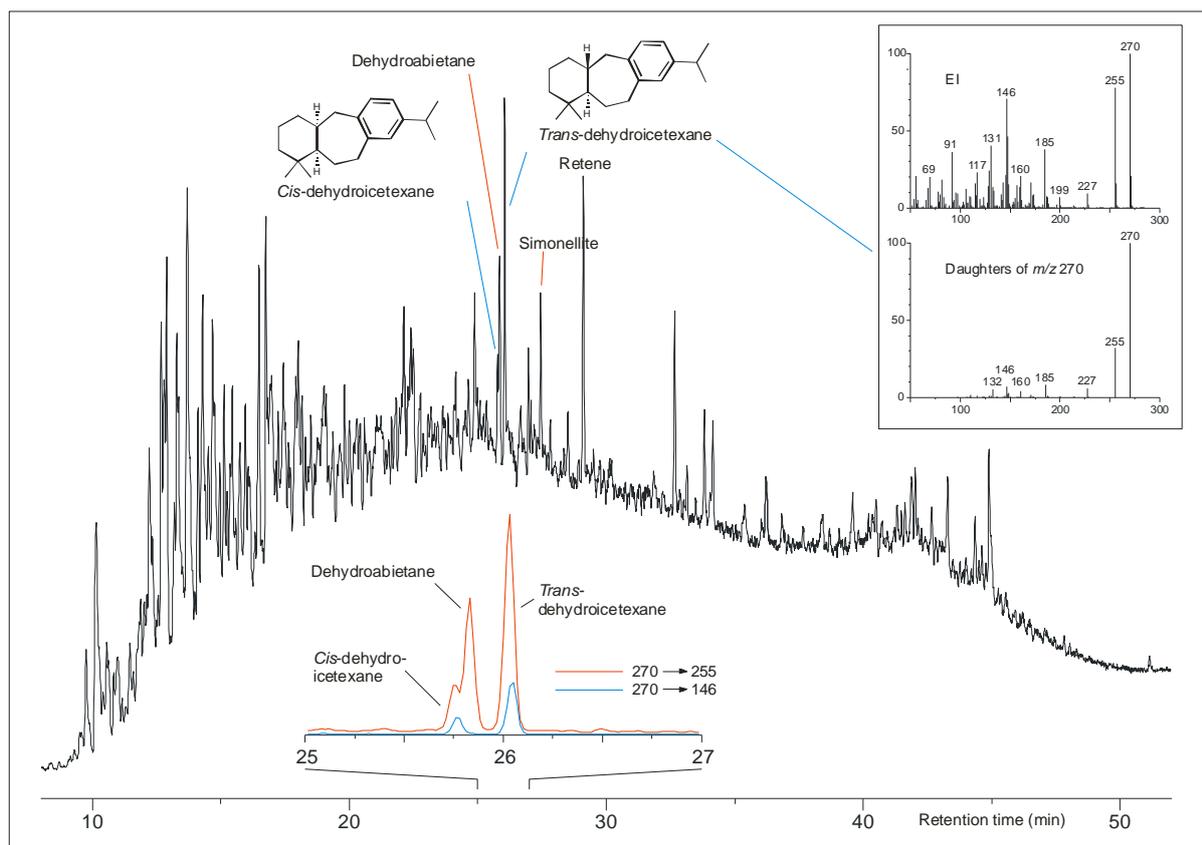


Figure 1 GC-MS analysis (TIC, full scan) and GC-MS-MS (270 \rightarrow 255 and 270 \rightarrow 146) of the aromatic fraction of a Canadian oil (Amauligak, Beaufort-Mackenzie). Inset shows EI and m/z 270 daughter spectra of pure *trans*-dehydroicetexane from Triassic-Jurassic boundary mudstones from Sweden. Spectra of *cis*-dehydroicetexane are almost identical.

References

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