

ORIGIN OF 4-DESMETHYL-DINOSTERANES IN SEDIMENTS AND OILS

Sebastiaan W. RAMPEN, Stefan SCHOUTEN and Jaap S. SINNINGHE DAMSTÉ

Department of Marine Biogeochemistry & Toxicology, Royal Netherlands Institute for Sea Research (NIOZ), PO Box 59, 1790 AB Den Burg, Texel, The Netherlands.

Dinosterol (4 α ,23,24-trimethyl-5 α -cholest-22E-en-3 β -ol) is a well-known sterol synthesized by dinoflagellates. The presence of dinosterol and its diagenetic products, dinosterane and triaromatic dinosteroids, in sediments is generally accepted as a marker for dinoflagellate productivity (e.g. Boon et al., 1979), although a few other sources are known. In addition to dinosterol, other sterols possessing side-chains methylated at positions C-23 and C-24 are assumed to be specific for dinoflagellates, even though 4-desmethyl-23,24-dimethylsterols have been reported in a number of other organisms (e.g. Volkman et al., 1980). Moldowan and Jacobson (2000) showed that their diagenetic products, triaromatic 4-desmethyl-dinosteranes (23,24-dimethylcholestanes), can be useful as age-diagnostic biomarkers as they almost exclusively occur in oils and marine source rocks from the Triassic and younger. Still, there are only a few reports on 4-desmethyldinosterane (e.g. Schouten et al. 1997).

We have analyzed >100 cultures of different diatom species and although dinosterol was not found, we identified relatively abundant 23,24-dimethylsterols in twenty-one diatoms belonging to six different orders, indicating that diatoms may be an important source for these sterols and their diagenetic products. For unambiguous identification, we isolated 23,24-dimethylcholest-22E-en-3 β -ol (4-desmethyldinosterol) from a 300L culture of *Ditylum brightwellii* (sterol composition shown in Fig. 1) and determined its structure using NMR. An aliquot of the purified 23,24-dimethylsterol was used to synthesize a 4-desmethyldinosterane. The mass spectrum of 4-desmethyldinosterane is very similar to that of 24-ethylcholestane, but 4-desmethyldinosterane has an enhanced m/z 98 ion fragment, caused by cleavage in the methylated side chain.

Partial mass chromatograms of m/z 98 from desulphurized samples of the Miocene Monterey Formation (Schouten et al., 1997) revealed four putative 4-desmethyldinosterane isomers, likely with varying C-5 and C-23 configurations. In the desulphurized fractions from the Miocene Monterey Formation, 23S,24R-dimethyl-5 α -cholestane is the most dominant isomer, followed by 23R,24R-dimethyl-5 α -cholestane; the latter co-elutes with 24-ethylcholestane, something also observed for dinosterane and 24-ethyl-4-methylcholestane

(Summons et al., 1987). This co-elution may cause an overestimation of 24-ethylcholestane concentrations, as the presence of 23,24-dimethylcholestane is easily overlooked.

Moldowan and Jacobson (2000) have shown that dinosterane and triaromatic dinosteroid concentrations quickly increased to maximum values in the Triassic, whereas the concentration of triaromatic 4-desmethyl dinosterane started to increase from the Triassic but reached its maximum value only during the Cretaceous. This difference in sterane concentration profiles may be caused by increasing 4-desmethyl dinosterol contributions of diatoms, which do not synthesize dinosterol, as diatoms evolved during this time. Thus, the occurrence of 23,24-dimethylcholestanes in sediments should not automatically be related to dinoflagellate input, but a diatomaceous origin should also be taken into consideration.

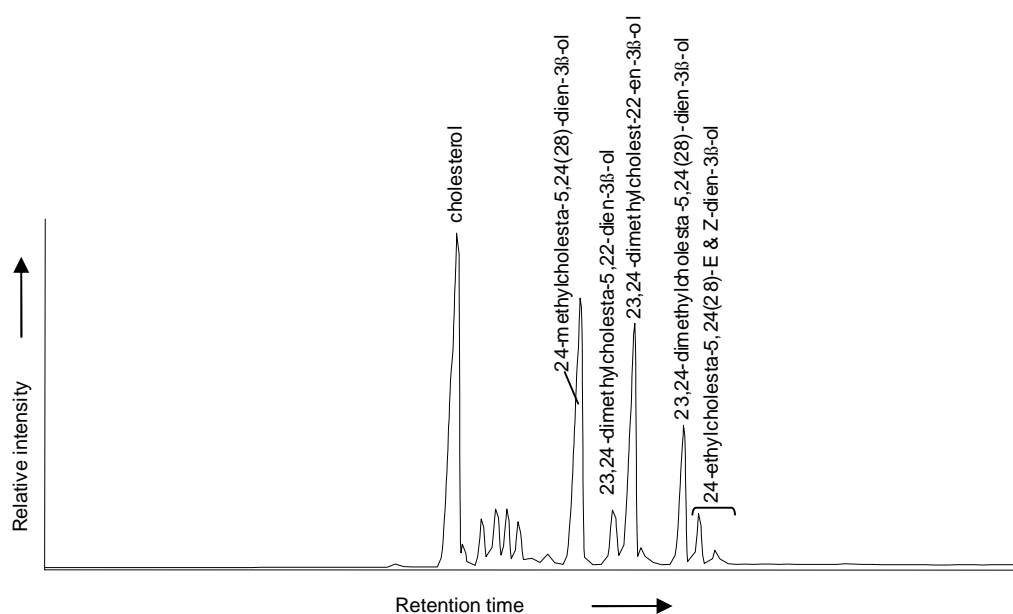


Figure 1. FID chromatogram of the sterol fraction of *Ditylum brightwellii*

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