

Identification of a Novel Series of Tetracyclic Terpene Hydrocarbons (C_{24} — C_{27}) in Sediments and Petroleums

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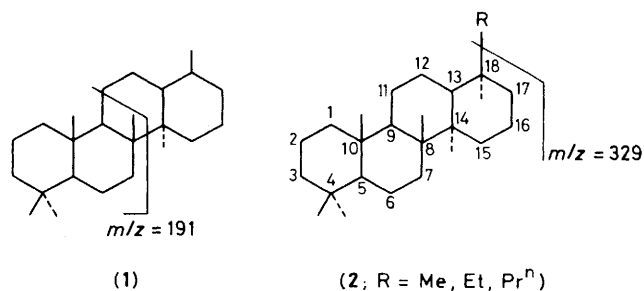
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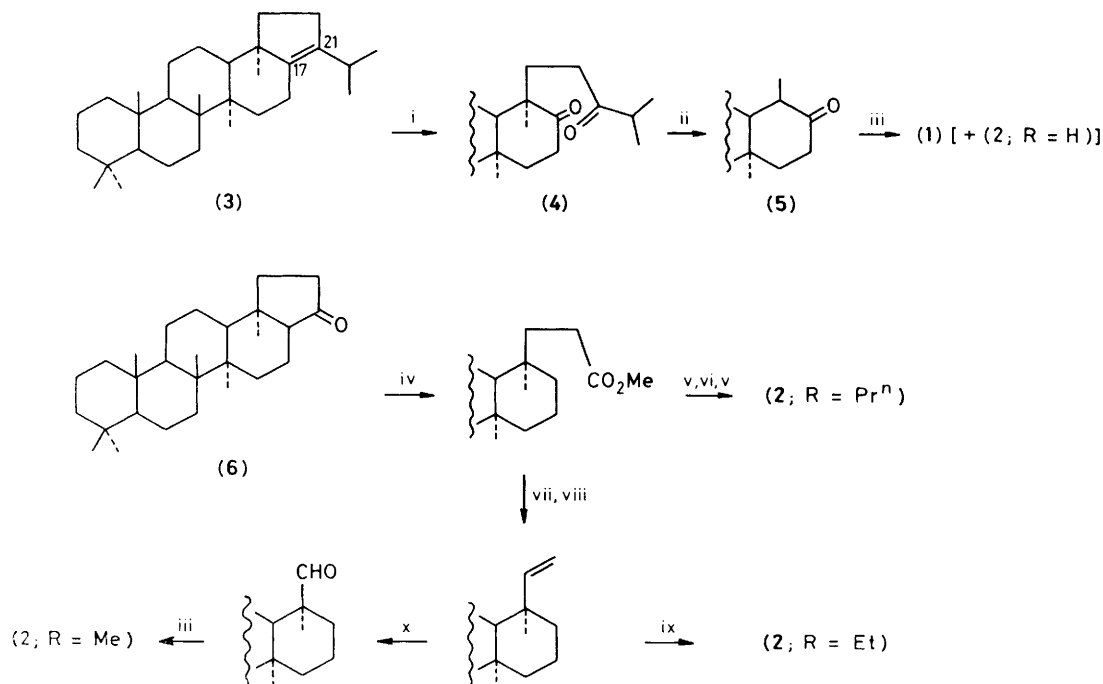
A novel series of tetracyclic terpene hydrocarbons, the 17,21-secohopanes (C_{24} — C_{27}) has been conclusively identified as a widespread constituent of sediments and petroleums; these compounds could be formed by thermal or microbial degradation of pentacyclic hopanoid precursors which commonly occur in micro-organisms, but they could also represent a novel class of bacterial lipids.

Molecular organic geochemistry has been increasingly used over the last decade in problems concerning the origin and transformation of organic matter in the subsurface,^{1,2} and its impact on related fields has been recognized.³ The precise structural elucidation of the ubiquitous pentacyclic triterpenes of the hopane series in sediments and petroleums⁴⁻⁶ could, for instance, be related to the widespread occurrence of this class of compounds in the membrane lipids of prokaryotes (bacteria, blue-green algae) and has thus induced the development of a novel field of bacterial biochemistry.^{3,7} Furthermore, the biological marker compounds, *i.e.* complex molecules derived in the subsurface from biological precursors, have been increasingly used in petroleum exploration for the study of the maturing of organic matter and of correlation of source rocks and crude oils.^{2,8-10}

In the alkane mixtures of several sediments and crude oils the occurrence of series of tricyclic^{2,11-15} and, less frequently, tetracyclic terpene hydrocarbons ('terpanes')^{11,12,15} has been



noticed recently, besides the ubiquitous pentacyclic hopane series. Both series display a base peak at $m/z = 191$, and their distribution is best studied with the help of the 191 mass fragmentogram.¹² A partial structural elucidation has been proposed recently for a tetracyclic component present in Georgia-South Carolina clays.¹⁶ However, until now the



Scheme 1. Synthesis of the C_{24} – C_{27} homologues of the tetracyclic 17,21-secohopane series. i, RuO_4 ; ii, NaOH/cotton wool, 280 °C (ref. 20); iii, Wolff-Kishner; iv, *hν*, MeOH; v, $LiAlH_4$; vi, $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{Cl}$, pyridine; vii, $KOH/MeOH$, H^+ ; viii, $Pb(OAc)_4$, $Cu(OAc)_2$, pyridine; ix, H_2 , Pd/C; x, O_3 , SMe_2 , H^+ .

precise structure and hence the origin of these compounds has not been clearly established.

The mass spectral data obtained for the tetracyclic terpenes indicated the presence of four compounds presumably belonging to a homologous series with a constant ring system and a side chain of variable length: $C_{24}H_{42}$, $C_{25}H_{44}$, $C_{26}H_{46}$, and $C_{27}H_{48}$ ($M^+ = 330, 344, 358, \text{ and } 372$). The fragmentation pattern of the C_{24} component showed that it was clearly different from the des-*A*-lupane derivative which we have identified recently in delta sediments and terrestrial crude oils.¹⁷ As many of these sediments and petroleum displayed a concomitant high content of pentacyclic hopane derivatives it could be assumed at this stage that this tetracyclic series was related (as degradation products?) to the hopane precursors.^{12,15}

We have now synthesised four members of this series (1)–(2) and have indeed identified them as hopane-related compounds in many sediments and petroleum of various origins and ages.†

The branched and cyclic alkanes of the sediments and crude oils were obtained by chromatography followed by separation of the n-alkanes with 5 Å molecular sieves, as previously described.¹⁸ The branched and the cyclic alkanes were further analysed by glass capillary column gas chromatography (c.c.g.c.) and c.c.g.c. coupled with computerized mass spectrometry. Biodegraded oils usually yield a clearer distribution of the tri- and tetra-cyclic terpene hydrocarbons since these compounds are quite resistant to microbial attack, thereby yielding better mass spectra of the geological products.

Compounds (1) and (2) were prepared following Scheme 1 starting from hop-17(21)-ene,¹⁹ (3), and trisnorhopan-21-one,⁶

(6). The following mass spectra data were obtained (70 eV): (1): $m/z = 330 (M^+, 26\%), 315 (14), 206 (5), 191 (100), 177 (24), 163 (7), 149 (20), 137 (29), 136 (39), 123 (57), 110 (54)$; (2; R = Me): $m/z = 334 (M^+, 15), 329 (14), 206 (6), 191 (100), 177 (8), 163 (10), 150 (21), 137 (36), 136 (23), 123 (58), 109 (35)$; (2; R = Et): $m/z = 358 (M^+, 10), 343 (8), 329 (19), 205 (9), 191 (100), 177 (10), 163 (8), 149 (10), 137 (42), 123 (44), 109 (40)$; and (2; R = Pr^n): $m/z = 372 (M^+, 9), 357 (8), 329 (22), 205 (7), 191 (100), 177 (7), 163 (6), 151 (12), 137 (36), 123 (43), 109 (43)$.

The four compounds of this series were shown to be identical to those occurring in the geological samples by comparison of mass spectra and coelution in g.c. and in single ion mass fragmentography g.c.–m.s. (LKB 9000 S) on several glass capillary columns (SE 30 and SP 2250, Supelco, for single ion detection; OV 73 and Pluronic F 68, Fluka, for coelution in c.c.g.c.; 30 m × 0.25 mm). Compound (2; R = Me) was always the minor product, whereas compound (1) was present, in some samples, in quantities of the same order of magnitude as the pentacyclic hopanes. The relative distribution of the four members of the series may vary in large proportions, as may the ratio of tetracyclic to tricyclic terpene hydrocarbons, depending on the sample. This may be useful for correlation studies, although so far no clear rule has been established. Compound (2; R = H) a minor side product in the reduction of ketone (5) could not be detected in our samples; if present at some time in the past, this product may have undergone epimerisation at C-18 to the more stable isomer (1).

Among the various hypotheses which could be put forward to explain the widespread occurrence of these '17,21-secohopanes' in sediments and petroleum, at least three may be considered: (i) a thermo-catalytic degradation of pentacyclic hopane precursors during geological maturing, (ii) a microbial opening of ring E of hopanoids, e.g. oxidation of hop-17(21)-enes,⁸ at an early stage of diagenesis, followed later by a geochemical reduction to the corresponding alkanes, or (iii) a cyclisation of precursor squalene stopping at ring D, leading to tetracyclic precursors which could be further reduced by

† About 40 crude oils and rock samples (mostly from carbonates) from France (Aquitaine basin), Guatemala, Iraq, Libya, Tunisia, and the U.S.A., ranging in age from Jurassic to Tertiary. However marine petroleum from Congo, as well as several terrestrial petroleum showed only trace amounts of these tetracyclic terpene hydrocarbons.

a geochemical process. These tetracyclic terpenoids could in this case represent a novel class of bacterial constituents.

The formation of these compounds during the biodegradation of crude oils in their reservoir rock is less likely since hopanes are quite resistant to bacterial attack and seem to be altered only at a very advanced stage.¹⁴ Furthermore the tetracyclic terpene hydrocarbons are already present in the source rocks in similar proportions.

A study of the higher homologues of these 17,21-sec-hopanes on the basis of the $m/z = 329$ mass fragmentogram, corresponding to the cleavage of the side-chain, (the $m/z = 191$ fragmentogram could not be used since the elution times of the higher homologues fall in the range of the major pentacyclic hopanes) showed preliminary evidence for the presence of a series extending at least up to C₃₅, like the pentacyclic hopanes. This carbon range and the apparent absence of these tetracyclic terpanes in Recent or immature ancient sediments would seem, in a first approach, to favour one of the first two hypotheses.

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