Cyclisation and Aromatisation of Carotenoids during Sediment Diagenesis

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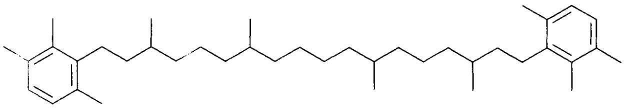
A novel diaryl isoprenoid with an additional aromatic ring ($C_{40}H_{58}$), formed from the diaromatic carotenoid isorenieratene by cyclisation and aromatisation during sediment diagenesis, is identified in carbonaceous sedimentary rocks.

A number of carbonaceous sediments contain substantial amounts of the diaryl isoprenoid isorenieratane **1**,[1–3] which is derived from the diaromatic carotenoid isorenieratene **2**, a carotenoid exclusively biosynthesized by photosynthetic green sulfur bacteria (Chlorobiaceae).[4] Upon GC analyses of the polyaromatic fractions of extracts of a number of sediments (*e.g.* Kimmeridge Clay, Schistes Cartons, Calcaires en Plaquettes, Allgäu Formations) compound **3** elutes just before **1** and possesses a mass spectrum [*m*/*z* 538(20), 173(12), 134(36), 133(100), 119(22%)], suggesting that it is isorenieratane **1** with an additional aromatic ring formed by cyclisation and aromatisation of the isoprenoidal acyclic part of **1**. The MS, however, does not reveal any strong indications for the position of the additional ring. This is not surprising since MS of 1,2-dialkylbenzenes hardly contain fragment ions due to cleavage of one of the alkyl side chains β to the aromatic ring, but instead are dominated by a fragment formed by loss of both alkyl side chains.[5] Indeed, the MS of **3** contains a fragment ion at *m*/*z* 119, which is more abundant than in the MS of **1** (22 *vs.* 10%), suggesting the presence of a trialkylbenzene moiety.



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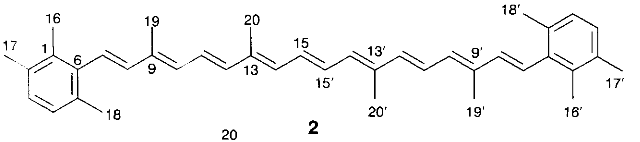

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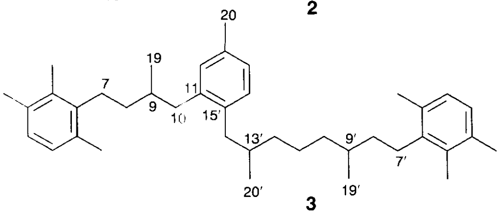

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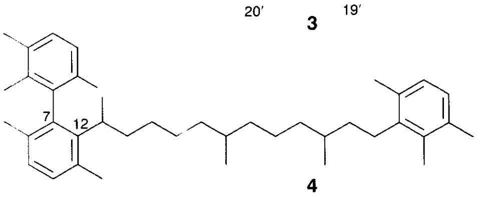

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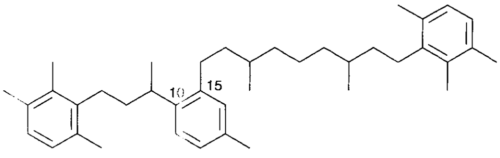

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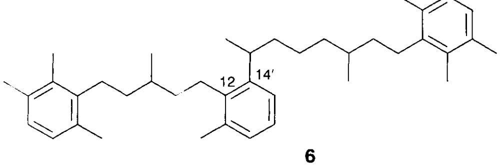

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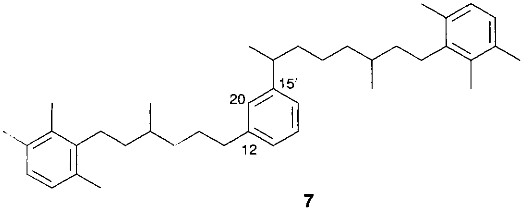

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The genetic relationship between **1** and **3** was further established by comparison of their ^{13}C content in two sediments (Table 1) as determined by isotope ratio monitoring-GC-MS. Both **1** and **3** are uniquely enriched by *ca.* 14 parts per thousand relative to lipids derived from algae. This is consistent with their derivation from photosynthetic green sulfur bacteria since these organisms fix CO_2 through the reversed TCA cycle leading to biomass anomalously enriched in ^{13}C.[6]

To fully determine the structure of **3**, it was isolated from the sedimentary rock extract of the Lower Jurassic Allgäu Formation by column chromatography and subsequent reversed phase HPLC using a Polygosil C_{18} preparative column eluting with MeOH–EtOAc (90–10; *v*/*v*). The purest fraction (2.3 mg) consisting of 74% of **3** (other 26% consisted of a complex mixture of hydrocarbons, none representing more than 3% of the total fraction) was analysed by ^1H and ^{13}C NMR.† These data allowed discrimination between the five possible isomers **3**–**7**, which can be formed by cyclisation and aromatisation of **1**. From the COSY spectrum of **3** it was deduced that all three aliphatic methyl groups were coupled with protons attached to carbon atoms not α to the aromatic rings as indicated by their chemical shifts in the range δ 1.5–1.8. Furthermore, four CH_2 groups next to an aromatic ring were clearly revealed in the COSY spectrum. Since **3** is the only structure which shows these features, its identity was established. Other shifts are in agreement with this assignment.

The similarity in structure and ^{13}C content of **1** and **3** establishes a direct link between these sedimentary components and their precursor, isorenieratene **2**. The identification of **3** is the first evidence for the process of cyclisation and aromatisation of carotenoids during sediment diagenesis. In fact, the formation of **3** is only one step in this process since components

Table 1 $\delta^{13}C$ (parts per thousand *vs.* PDB[a]) values of selected sedimentary components

	$\delta(^{13}C)$			
Formation name	1	3	Pristane	Phytane
Kimmeridge Clay	−16.6 ±0.3[b]	−16.3 ±0.2	−30.0 ±0.3	−30.1 ±0.5
Allgäu	−19.0 ±0.4	−19.0 ±0.3	−33.5 ±0.8	−33.5 ±0.2

[a] PDB indicates PeeDee belemnite, the stable carbon isotope standard.
[b] Standard deviation from three replicates

with the isorenieratene carbon skeleton containing up to four additional (condensed) aromatic rings have been identified in sediments.[7]

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Footnote

† *Selected NMR data* for **3**: ^{1}H (400 MHz, $CDCl_3$), 2.65 (m, CH_2, C-7′), 2.58 (m, CH_2, C-7), 2.55 (m, CH_2, C-10), 2.41 (m, CH_2, C-14′), 2.23 (s, Me, C-20), 1.86 (m, CH, C-9), 1.68 (m, CH, C-13′), 1.52 (m, CH, C-9′), 1.00 (d, *J* 6.7 Hz, Me, C-19), 0.97 (d, *J* 6.7 Hz, Me, C-19′), 0.85 (d, *J* 6.7 Hz, Me, C-20); Shifts for C-8, C-8′, C-10′ and C-12′ were not determined. ^{13}C (100 MHz; $CDCl_3$) 19.6 (Me, C-19′), 19.5 (Me, C-19), 19.5 (Me, C-20′); these assignments may be interchanged, 21.0 (Me, C-20).

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