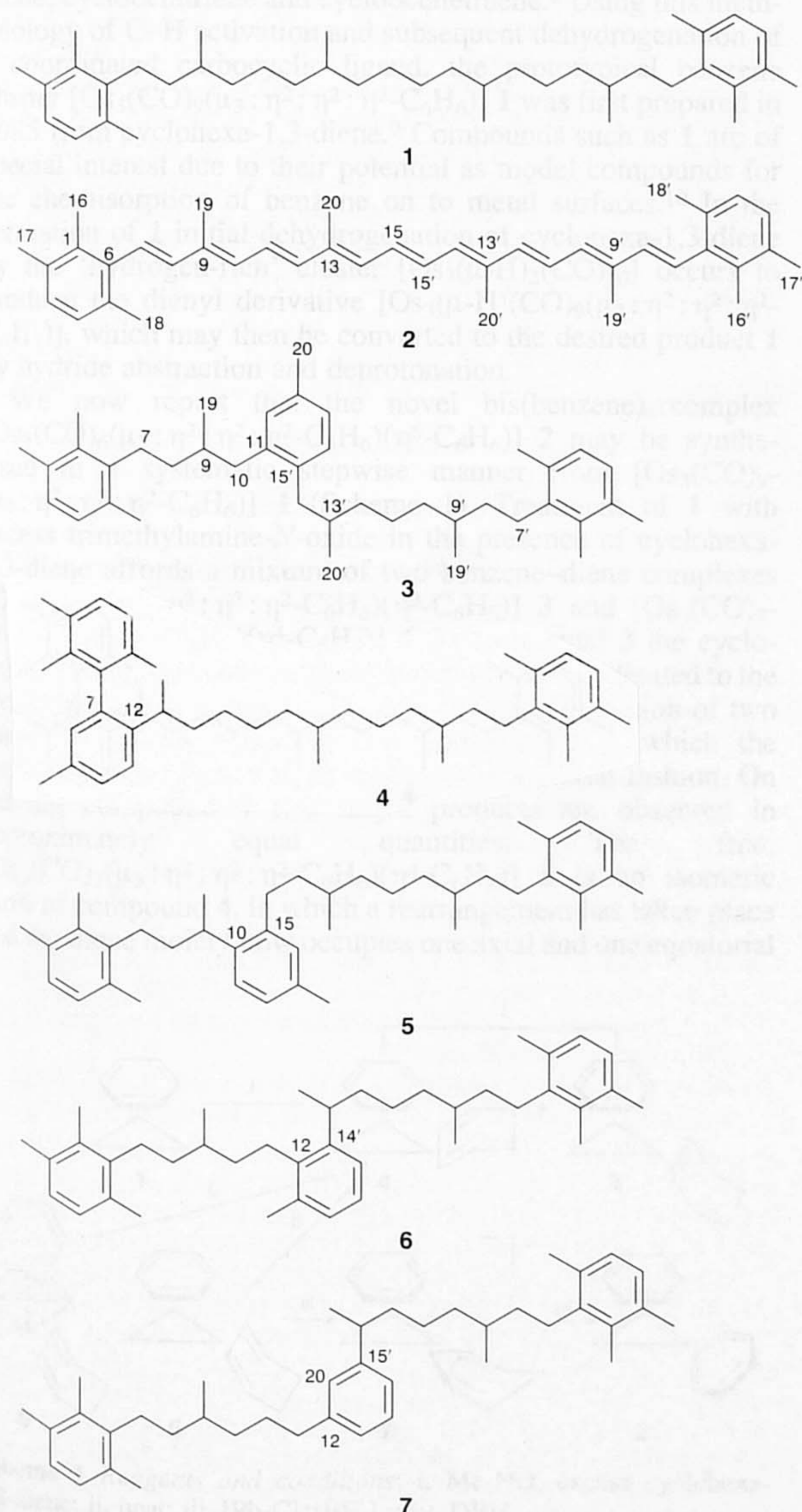


## Cyclisation and Aromatisation of Carotenoids during Sediment Diagenesis

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A novel diaryl isoprenoid with an additional aromatic ring (C<sub>40</sub>H<sub>58</sub>), 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**,<sup>1–3</sup> which is derived from the diaromatic carotenoid isorenieratene **2**, a carotenoid exclusively biosynthesized by photosynthetic green sulfur bacteria (Chlorobiaceae).<sup>4</sup> 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  $\beta$  to the aromatic ring, but instead are dominated by a fragment formed by loss of both alkyl side chains.<sup>5</sup> 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.

The genetic relationship between **1** and **3** was further established by comparison of their <sup>13</sup>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<sub>2</sub> through the reversed TCA cycle leading to biomass anomalously enriched in <sup>13</sup>C.<sup>6</sup>

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<sub>18</sub> 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 <sup>1</sup>H and <sup>13</sup>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  $\alpha$  to the aromatic rings as indicated by their chemical shifts in the range  $\delta$  1.5–1.8. Furthermore, four CH<sub>2</sub> 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 <sup>13</sup>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**  $\delta^{13}\text{C}$  (parts per thousand vs. PDB<sup>a</sup>) values of selected sedimentary components

Formation name	$\delta^{13}\text{C}$			
	<b>1</b>	<b>3</b>	Pristane	Phytane
Kimmeridge Clay	–16.6 ±0.3 <sup>b</sup>	–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

<sup>a</sup> PDB indicates PeeDee belemnite, the stable carbon isotope standard.

<sup>b</sup> Standard deviation from three replicates

with the isorenieratene carbon skeleton containing up to four additional (condensed) aromatic rings have been identified in sediments.<sup>7</sup>

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### Footnote

† Selected NMR data for **3**: <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>), 2.65 (m, CH<sub>2</sub>, C-7'), 2.58 (m, CH<sub>2</sub>, C-7), 2.55 (m, CH<sub>2</sub>, C-10), 2.41 (m, CH<sub>2</sub>, 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. <sup>13</sup>C (100 MHz; CDCl<sub>3</sub>) 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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