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A sedimentary fluorene derivative of bacteriohopanepolyols

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Abstract: A novel aromatised 8(14)-secohopanoid **1** ($C_{31}H_{42}$) possessing a fluorene moiety, formed from derivatives of bacteriohopanepolyols by cyclisation, aromatisation, ring opening and side-chain cleavage reactions during sediment diagenesis, has been isolated from a 150 Ma old marine sedimentary rock and identified by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.

Aromatisation is a common process during the diagenesis of biomolecules in sediments and leads to the formation of more stable 'molecular fossils', which can survive the elevated temperatures in deeply buried sedimentary rocks and even can be traced back in petroleum.[1] One of the best examples of this reaction pathway are the diagenetic products of bacteriohopanepolyols (e.g. **2**) and their derivatives, membrane rigidifiers of many prokaryotes.[2] Among the many diagenetic products formed, aromatised hopanoids are abundant. Two types have

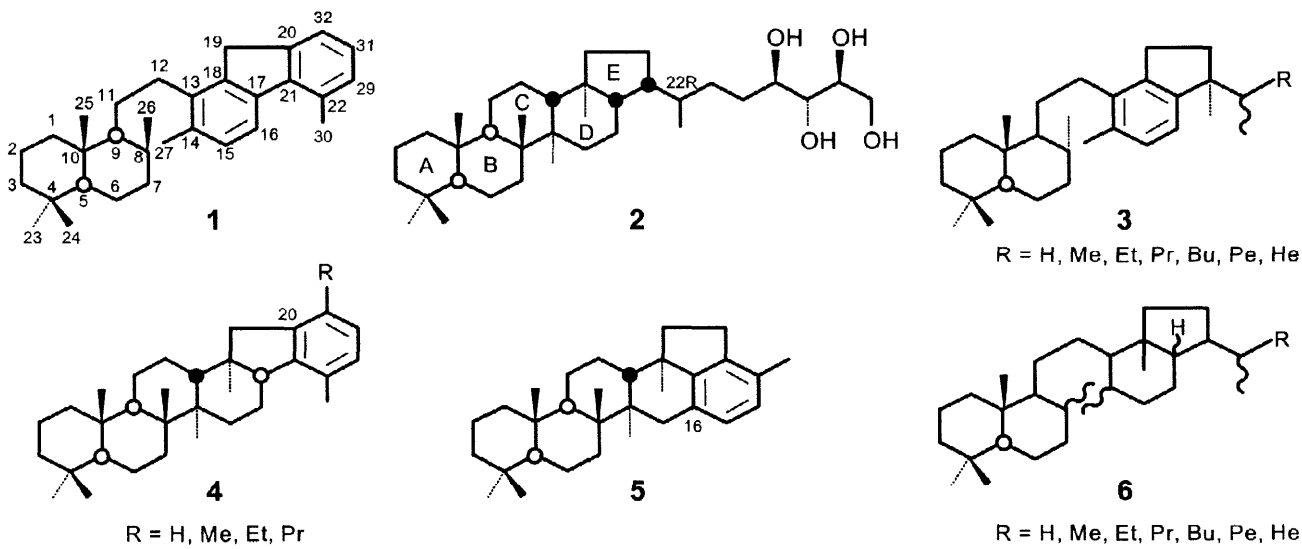

Fig. 1. Structures of compounds.

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Table 1. ^{1}H and ^{13}C Data of D-ring Monoaromatic 8(14)-secobenzohopanoid **1**.

C-number	H-shift	C-shift			
		CH_3	CH_2	CH	C
1	0.90 (α), 1,70 (β) (m, 2H)		39.58		
2	1.43, 1.51 (m, 2H)		17.52		
3	1.18 (α), 1.38 (β) (m, 2H)		42.15		
4	-				33.36
5	0.91 (α) (d, 1H)			56.80	
6	1.40, 1.54 (m, 2H)		18.48		
7	1.62 (β), 1.76 (α) (m, 2H)		34.94		
8	2.18 (α) (m, 1H)			29.74	
9	1.30 (α) (m, 1H)			54.90	
10	-				38.60
11	1.48 (′), 1.62 (′′), (m, 2H)		25.54		
12	2.48 (′, m,1H), 2.80 (′′, m, 1H)		29.82		
13	-				138.08
14	-				133.69
15	7.20 (d, J=7.2 Hz, 1H)			129.07	
16	7.67 (d, J=7.8 Hz, 1H)			120.58	
17	-				140.51
18	-				142.25
19	3.84 (bs, 2H)		35.84		
20	-				140.31
21	-				143.24
22	-				132.63
23	0.88 (s, 3H)	33.56			
24	0.81 (s, 3H)	21.58			
25	0.81 (s, 3H)	16.44			
26	1.06 (d, J=7.3 Hz, 3H)	15.66			
27	2.41 (s, 3H)	19.03			
29	2.70 (s, 3H)	20.98			
30	7.12 (d, J=7.3 Hz, 1H)			128.82	
31	7.18 (t, J=7.2 Hz, 1H)			125.84	
32	7.40 (d, J=7.2 Hz, 1H)			122.31	

been rigorously identified. Firstly, D-ring aromatic 8,14-secohopanoids **3**[3] in which the bond between C-8 and C-14 has been cleaved resulting from aromatisation. The second type of aromatised hopanoids (**4** and **5**)[4-5] is formed by a cyclisation at C-20 or C-16 involving the functionalised side chain, followed by aromatisation of the formed ring. Here we provide evidence that these two aromatisation processes may also co-occur during early diagenesis and lead to the formation of a hopanoid fluorene derivative, which may act as a precursor of alkylated fluorenes in more mature sediments and petroleum.

During examination of the aromatic hydrocarbon fraction of a solvent extract of a mudstone from the Jurassic Kimmeridge Clay Formation by GC-MS, we encountered an abundant (5.6 mg/g organic C) aromatic component **1** with a mass spectrum[6] dominated by a molecular ion at m/z 414 and by fragment ions at m/z 207, 208 and 123 suggesting a triterpenoid derivative. To establish the structure of **1**[7] it was isolated by column chromatography and subsequent preparative TLC using SiO_2 plates by elution with hexane. A fraction (1.7 mg) consisting of 87% of **1** (other 13% consisted of a complex mixture of hydrocarbons, none representing more than

1% of the total fraction) was analysed by high field ^{1}H and ^{13}C NMR[8] (Table 1) which led to complete assignment of proton and carbon chemical shifts. Carbon multiplicities were established by APT and DEPT spectra and revealed that **1** contains 31 carbon atoms with 7 aromatic and 2 aliphatic C, 5 aromatic and 3 aliphatic CH, 8 CH_2 and 6 CH_3 units. The proton spectrum showed 5 aromatic protons, 2 CH_3 units attached to an aromatic system and a singlet at δ=3.84 ppm representing two isochronous protons. Comparison with ^{1}H NMR data of fluorene[9], which shows a singlet at δ=3.76 for its aliphatic CH_2 unit, strongly suggested that **1** comprised a dimethylfluorene moiety. This would also be in agreement with the most abundant m/z 207 ($C_{16}H_{15}$) fragment ion in the mass spectrum of **1**, which is formed by cleavage of the C-C bond in the alkyl side chain β to the dimethylfluorene moiety. ^{1}H-^{1}H COSY, one dimensional NOE experiments (Table 2) and inverse direct and long range (^{2}J and ^{3}J) ^{1}H-^{13}C correlation experiments (Fig. 2) established the aromatic substitution pattern of **1**. The remaining aliphatic part of the chemical structure of **1** was identified as a *trans*-decalin moiety substituted at C-9 and containing 4 methyl substituents by comparison of ^{1}H and ^{13}C NMR data with those of related components **3** and **5**.[3,5] These assignments were fully confirmed by ^{1}H-^{1}H COSY, one dimensional NOE experiments (Table 2) and inverse direct and long range (^{2}J and ^{3}J) ^{1}H-^{13}C correlation experiments (Fig. 2). The NOE interactions of H-25 and H-26 and H-8 and H-9 (Table 2) unequivocally established the stereochemistry of **1** to be 8α(H),9α(H).

It is likely that the novel hopanoid fluorene derivative **1** is formed through diagenetic reactions of bacteriohopanepolyols (e.g. **2**) or its derivatives. These reactions would involve (i) cyclisation at C-20 involving the polyfunctionalised side-chain, (ii) aromatisation of the newly formed ring with concomitant loss of the propyl side-chain C-33 - C-35 and (iii) aromatisation of ring-D with concomitant loss of methyl C-28 and cleavage of the bond between C-8 and C-14. The occurrence of these diagenetic reactions have been described before,[3,4,10-13] but the combination of these different diagenetic pathways is unprecedented. Furthermore, this is the first time that the stereochemistry of a sedimentary 8(14)-secohopanoid has been fully established. Hopanoid fluorene derivative **1**, isolated from a thermally relatively immature sediment (R_0 = ca. 0.35), possesses the same stereochemistry as its precursor(s) (e.g. **2**), i.e. 8α(H),9α(H) and, thus, possesses an axially substituted methyl group (C-26) at C-8. This assignment is somewhat in contradiction with the reported stereochemistry of **3**[3], which contains an equatorially substituted methyl group at C-8. This may either be caused by the slight ambiguity in the assessment of the stereochemistry of **3** or by the fact that upon further burial in the sediment isomerisation occurs to the presumably thermodynamically more stable 8ß(H),9α(H) 8(14)-secohopanoids. This latter explanation would be consistent with the fact that petroleum contains a complicated mixture of stereoisomers of 8(14)-secohopanes **6**.[10,11] In the mudstone from which **1** was isolated only traces of stereoisomers of **1** were encountered. In contrast to the benzohopanes **4**, which generally are composed of a series of four homologs,[3,4]

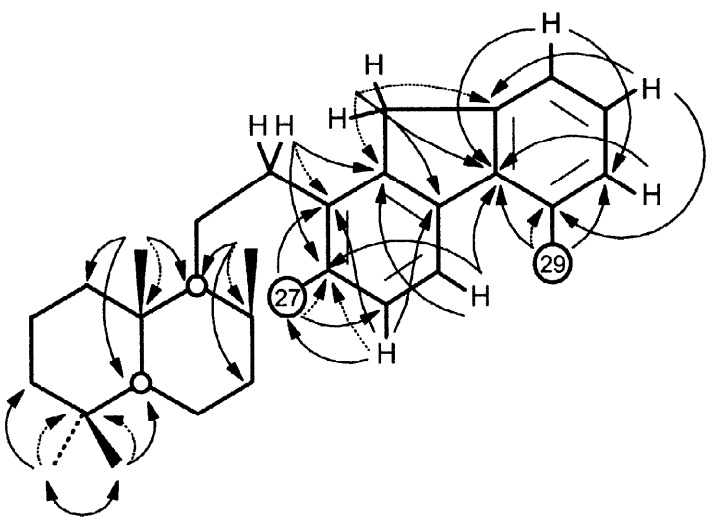

Fig. 2: Connectivities from an inverse long range [^{2}J (stippled lines) and ^{3}J (solid lines)] ^{1}H-^{13}C correlation experiment.

Table 2: One dimensional NOE interactions observed for **1**.

H irradiated	NOE observed	H irradiated	NOE observed
6β	26	19	12′, 12′′, 32
7α	5α, 8α	26	6β, 7β, 8α, 25, 27
8α	7α, 9α, 12′′, 26	27	12′′, 15, 26
9α	8α	29	16, 30

only traces of a homologue of **1** (presumably with an additional methyl group at C-32) could be identified. At present it is not clear whether this is related to the specific diagenetic pathway leading to formation of **1**, which may involve a specific intermediate or precursor, or whether in other depositional settings a similar homologous series may be encountered. In this context it should be emphasised that the concentration of **1** in 13 samples from the Dorset Kimmeridge Clay covering total organic carbon (TOC) contents of 0.6-52.1% varied widely from 0 to over 5000 μg/g TOC. Only three samples contained concentrations >150 μg/g TOC and these were restricted to mudstones and oil shales from the "mid-TOC range" (i.e. 5-12%), indeed suggesting that specific depositional conditions favour the formation of **1** from its precursor(s).

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6. Selected mass spectral data for **1**: MS (70 eV) *m/z* 414(100), 208(48), 207(70), 193(22), 192(25), 191(10), 123(33), 109((8), 95(13), 81(15), 69(30), 55(23)
7. Note that the numbering of **1** in Fig. 1 is adopted from the numbering of hopanoid derivatives and that consequently C-28 is missing.
8. NMR experiments were performed on a Bruker ARX400; field strength 400 and 100 MHz for ^{1}H and ^{13}C; respectively, solvent $CDCl_3$
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