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4,4′-Dimethyldinaphtho[*a,d*]cycloheptane, a Naturally Occurring Polyaromatic Derivative Related to Triterpenoids of the Serratane Series

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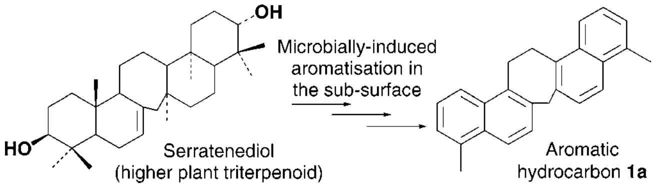
ABSTRACT



The polyaromatic hydrocarbon 4,4′-dimethyldinaphtho[*a,d*]cycloheptane (1a) has been identified by NMR studies after isolation from an Oligocene sediment. The original symmetrical structure of 1a, which bears a central seven-membered ring, is closely related to higher plant triterpenoid precursor(s) of the serratane series and is believed to have been formed in the subsurface by a microbially mediated aromatization process.

The chemical structures of molecular fossils (or biomarkers) occurring in sediments or crude oils are often specific enough to establish a correlation with the functionalized molecules they derive from. The latter can be characteristic of the different living organisms which contributed to the sedimentary organic matter and are thus frequently used as source indicators.[1] In addition, the precise structural characterization of molecular fossils gives clues to the pathways involved in the conversion of biolipids into geolipids in the subsurface.[1a,2] Hence, biomarkers are chemical tools widely used in petroleum exploration[1a,3] or for palaeoenvironmental assessment.[1a,4] The structures of many biomarkers were determined over the last 30 years, and among them, those related to higher plant triterpenoids have been shown to represent useful markers of terrigenous (as opposed to marine) organic matter in geological samples.[5]

In the course of a palaeoenvironmental reconstruction study of Oligocene sediments (ca. −30 million years) from the Rhine valley (France), GC−MS analysis of the biom-

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arkers from a series of samples deposited under fluvial/deltaic conditions and dominated by continental material revealed the presence of numerous higher plant triterpene derivatives of the lupane and amyrin series, together with an unknown compound which occurred among the predominant aromatic hydrocarbons in some of these samples. We report here on the characterization of this biomarker (**1a**), which was isolated and identified by means of structural NMR studies.[6]

The mass spectrum of the hydrocarbon **1a**[7] exhibits a molecular ion at $M^{+\bullet}$ 322 corresponding to the formula $C_{25}H_{22}$, and the presence of an intense fragment at m/z 180 ($M^+ - 142$) was interpreted as the result of the loss of a methyl naphthalene moiety. However, no other structural information could be deduced from the fragmentation pattern observed in mass spectrometry.

Consequently, NMR studies, including 1D homonuclear (^1H and ^{13}C), 2D homonuclear ($^1H-^1H$: COSY and NOESY), and 2D heteronuclear ($^1H-^{13}C$: HSQC and HMBC) correlation experiments, were performed on the isolated compound for further characterization. The interpretation of the NMR data was significantly simplified given the conspicuous symmetry of the molecule, as evidenced by the presence of only 13 signals corresponding to 13 carbon atoms in the 1D ^{13}C spectrum and of only eight signals in the ^1H spectrum. The presence of 10 aromatic protons, two benzylic methyl groups, three methylenes on quaternary carbons, and 10 quaternary carbons was deduced from the ^1H and ^{13}C spectrum and from the DEPT experiment.

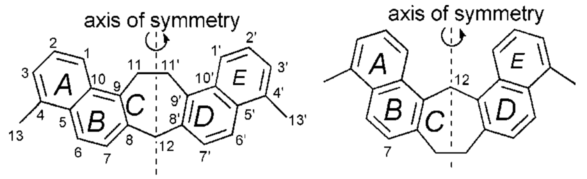
The complete carbon sequence of the hydrocarbon skeleton of the isolated hydrocarbon bearing four aromatic rings and a seven-membered ring C was completely established from the long-range $^1H-^{13}C$ experiment ($^{2,3}J_{CH}$), and all the proton and carbon chemical shifts were assigned (Table 1). However, an ambiguity remained concerning the central connection linking the two diaromatic moieties, and both structures **1a** and **1b** (Figure 1) could be envisaged.

Table 1. ^1H and ^{13}C NMR Chemical Shift Data of Compound **1a** (Bruker ARX 500; in CD_2Cl_2)

C no.	δ ^{13}C (ppm)	δ ^1H (ppm)	J (Hz)
1/1′	121.80	8.00	d; 9.0
2/2′	126.06[a]	7.37	dd; 9.0; 7.0
3/3′	126.08[a]	7.25	d; 6.5
4/4′	135.31		
5/5′	132.35		
6/6′	122.76	7.81	d; 8.5
7/7′	128.30	7.44	d; 8.5
8/8′	137.10		
9/9′	134.85		
10/10′	132.87		
11/11′	27.95	3.72	
12	42.12	4.50	
13/13′	19.96	2.65	

[a] Assignments interchangeable.

Finally, the presence of nuclear Overhauser effects (NOEs) between H-7/CH_2-12 and H-1/CH_2-11 (Figure 2) was observed, allowing discrimination between the two structures proposed above (cf. Figure 1) and unambiguous establishment that the aromatic hydrocarbon corresponds to compound **1a**.



1a **1b**

Figure 1. Plausible structures proposed on the basis of the 1D ^1H and ^{13}C NMR spectra.

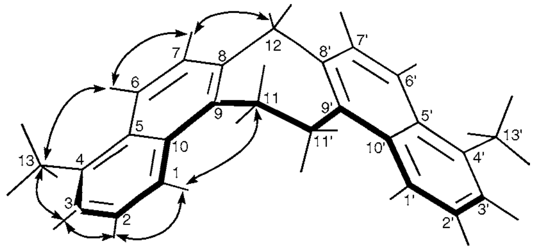


Figure 2. NOEs observed for compound **1a**.

The hydrocarbon skeleton of compound **1a**, which contains a rather uncommon seven-membered ring C, is related to higher plant triterpenoids of the serratane series, like, for example, serratenediol **2** (Figure 3). Since the identification of the latter,[8] numerous studies were carried out on this group of triterpenoids, and several derivatives belonging to this series of compounds were isolated from different land plants such as ferns, club moss, and spruce.[9] It is, however, noteworthy that serratane derivatives are only seldom reported to occur in angiosperms. In the Oligocene sedimentary series investigated, higher plant triterpenoids indicative of angiosperm contributions are generaly predominant.

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(6) A crushed sediment (ca. 3300 g) was extracted by stirring at 40 °C with acetone (1000 mL, × 2) and with a mixture of CH_2Cl_2/CH_3OH (1:1 v/v; 1000 mL, × 2). The organic extracts were combined and the solvents removed under reduced pressure, yielding ca. 720 mg of solvent extract, the nonpolar hydrocarbons of which being recovered by gross liquid fractionation on silica gel eluting with a mixture of CH_2Cl_2/hexane 1:1 v/v. The latter fraction was refractionated on silica gel eluting with an increasing proportion of CH_2Cl_2 in hexane (from 0% to 20%). One of the most polar fractions recovered was shown by GC to contain **1a** as a predominant hydrocarbon which was subsequently isolated by reversed-phase HPLC (Zorbax ODS, 250 mm by 9.4 mm; 5 μm; CH_3OH/acetone 7:3 v/v; 5 mL min^{-1}), affording ca. 2 mg of pure **1a** (>90% by GC).

(7) MS data for **1a** (EI, 70 eV): 322 (M^+, 100), 307 (77), 292 (50), 180 (43), 165 (17), 146 (13).

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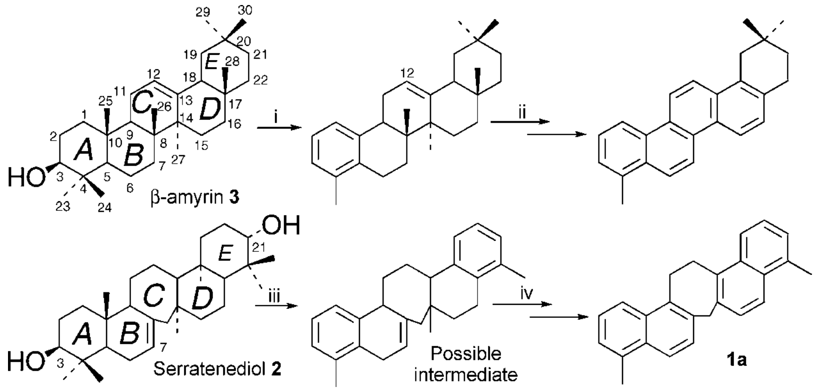

Figure 3. Aromatization pathway undergone by higher plant triterpenoids in the subsurface. Key: (i) aromatization of ring A triggered by the presence of a functional group at C-3; (ii) progression of the aromatization from ring A to ring D; (iii) aromatization of ring A and ring E triggered by the presence of functional groups at C-3 and C-21; (iv) progression of the aromatization from ring A to ring B and from ring E to ring D.

In contrast, when the serratane derivative **1a** is present, it usually occurs as a major compound whereas angiosperm biomarkers are almost absent. This suggests that drastic floral changes occurred, possibly triggered either by environmental changes or by climatic variations.

The formation of the polyaromatic hydrocarbon **1a** from a parent molecule like **2** (or from other related functionalized triterpenoids of the serratane series) involves an aromatization process and implies the loss of several methyl groups. This pathway fits into the scheme of the most important geochemical transformations undergone by higher plant triterpenoids in the subsurface.[10] In a general way, such a process either starts with the loss of ring A, followed by aromatization from ring B to ring D,[10a,11] or aromatization starts directly in the ring A, triggered by the presence of an oxygenated functionality at C-3, and proceeds gradually toward ring D where it usually stops.[10] The latter process leads to the formation of mono- and polyaromatic hydrocarbons, as illustrated in Figure 3 in the case of β-amyrin **3**. The presence of an endocyclic double bond, which is a common feature in the case of numerous higher plant triterpenoids, is thought to favor this diagenetic pathway.

Aromatization reactions have been shown to occur at the earliest stages of diagenesis[12] and to be microbially mediated.[13] The formation of a compound with the structure of **1a** would be in excellent agreement with such a transformation pathway. Indeed, compound **1a** could originate from a parent molecule like serratenediol **2** (Figure 3), which is functionalized at both C-3 and C-21 positions. Since the partial structure of rings A and E from serratenediol **2** is identical to that of ring A from most of the functionalized higher plant triterpenoids like, for example, β-amyrin **3** (Figure 3), the oxygenated functionalities would induce the biologically mediated aromatization which would start at each end of the molecule (i.e., in rings A and E) and progress to ring B and D. The presence of the seven-membered ring (ring C) would prevent complete aromatization, leading to compound **1a** as the end-product.

Derivatives related to the serratane series are almost unknown in the sedimentary record. The fact that compound **1a** occurrs among the predominant aromatic hydrocarbons in the sediments investigated in the present study likely indicates that a specific higher plant precursor, which remains to be identified, was thriving in the catchment area of the sediments. The significance of the presence of compound **1a** in terms of paleoecology remains to be determined, but it may have implications for palaeobotanical and/or paleoclimatic studies.

On a structural point of view, dinaphtho[*a*,*d*]cycloheptane derivatives have never been observed as natural products, nor prepared by synthesis. Quite a few functionalized dibenzo counterparts have, however, been synthesized as they display various pharmacological activities.[14] Furthermore, these highly flexible structures have also been studied for their conformational aspects.[15] In this respect, further NMR studies will be carried out on compound **1a** in order to investigate the effect of the two naphthalene subunits on the central seven-membered ring system.

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Supporting Information Available: NMR data (^1H and ^{13}C spectra; $^1H-^1H$ COSY and NOESY spectra; $^1H-^{13}C$ HSQC and HMBC spectra). This material is available free of charge via the Internet at http://pubs.acs.org.

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