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Spiro-Triterpenes from Clay-Catalysed Rearrangement of Hopenes : NMR Structural Elucidation and Occurrence in a Recent Sediment

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Abstract: Acidic K-10 montmorillonite clay-catalysed rearrangement of hop-22(29)-ene **5** and of hop-17(21)-ene **6** leads to the formation of small quantities of various fernenes and of new compounds, the 14-methyl-13,15-cyclo-*B'*:*A'*-neo-26-nor-14,15-seco-18α-gammacer-7-ene **8** and its Δ^8- and $\Delta^{9(11)}$-isomers **9** and **10**, the structures of which have been established by MS and NMR spectroscopy. This novel hopane skeleton transposition also operates on bacterial sedimentary hopenes, as shown by GC-MS investigations of the alkene fraction from a recent lacustrine sediment.

Rearranged polycyclic hydrocarbon skeletons of biological origin (steroids, triterpenoids) are frequently encountered in sediments where their formation is thought to involve acidic clay catalysis, an hypothesis in many cases firmly substantiated by simulation experiments carried out on pure compounds.[1] Recently,[2] we have reported the identification in immature sediments of the two ring *B* aromatised triterpenes **1** and **4** (figure 1), and provided strong evidence that **1**, which belongs to a series extending from C_{26} (**1**) to at least C_{32} (**2**), is of bacterial origin. In this regard, the formation of these compounds would most likely proceed through a yet unrecognised rearrangement of sedimentary bacteriohopenes followed by ring *B* aromatisation.

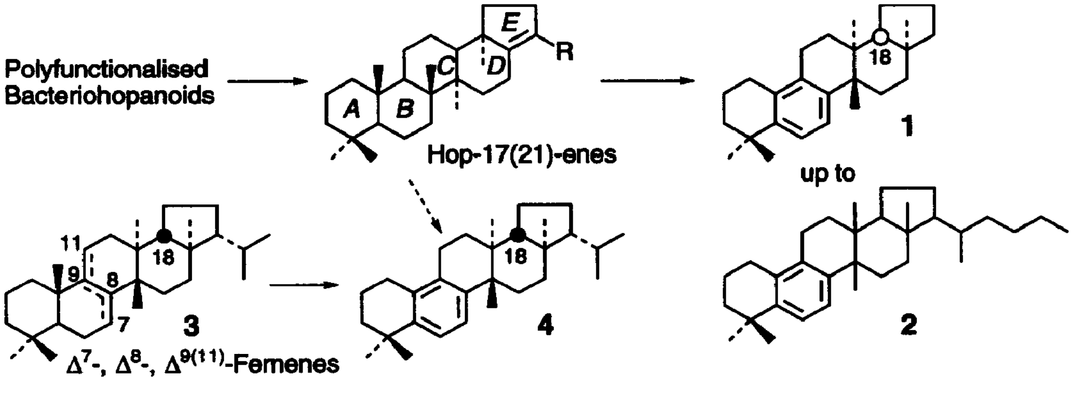
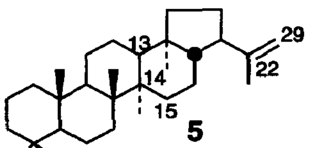


Figure 1. Probable origin of ring-*B* aromatised triterpene hydrocarbons occurring in sediments

Although hydrocarbon **4** could also result from such a sequence of processes, it appears however to have other more probable precursors such as the various isomers of fernene **3** (figure 1), widespread in ferns[3a] and reported in one case from a microbial source.[3b]

These results and the fact that the acidic rearrangement (H_2SO_4, BF_3-etherate) of hop-22(29)-ene (diploptene) **5** and of hop-17(21)-ene **6** normally stops at neohop-13(18)-ene **7**,[4] prompted us to check the behaviour of **5** and **6** in presence of clay.[5]

Given percentages refer to relative amounts of products obtained at the end of the described typical experiment.[5] As expected,[4] hop-17(21)-ene **6** and neohop-13(18)-ene **7** were the major compounds (~80%) of the reaction mixture. Small quantities of various kinds of fernenes **3** (diagnostic mass fragment at *m/z* 243) were rapidly formed (10 min) and their global proportion relative to other components did not significantly change with time (~5%). Thus, following increasing GC retention times, fern-8-ene, (9βH)-fern-7-ene, fern-9(11)-ene, (8βH)-fern-9(11)-ene and traces of fern-7-ene were characterised on the basis of their mass spectral fragmentation patterns,[4] relative GC retention times,[4] and also direct comparison (GC-MS coelution experiments) with reference compounds (Δ^7-, Δ^8- and $\Delta^{9(11)}$-fernenes). It should be however stressed that in absence of authentic standards, we cannot exclude the presence of (18αH)-fernenes which may have similar mass spectra to those of fernenes and also coelute with the latter. In this respect, an unidentified fernene-type product of shorter GC retention time than fern-8-ene was detected in the reaction mixture. With increasing reaction times, other compounds progressively formed. One of them[6] (~4-5%) could not be purified enough for NMR analysis and remained unidentified. Three others **8** - **10** (~7-10%), although having quite different mass spectra (figure 2a and note 7), display a common fragment at *m/z* 232 which, after NMR structural elucidation, could formally be explained by a retro Diels-Alder-like reaction involving the Δ^8 double bond (figure 2a; after double bond migration for compounds **8** and **10**).



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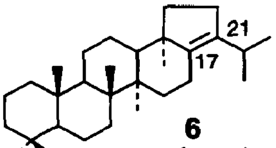

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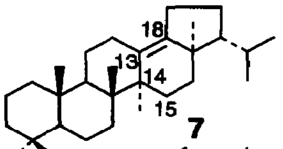

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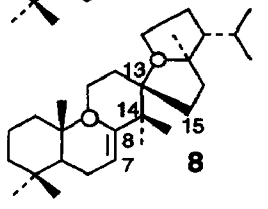

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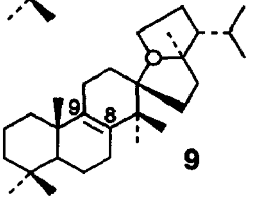

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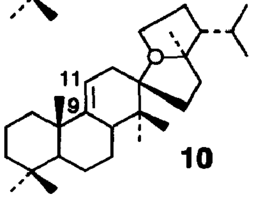

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After purification,[8] detailed 1D- and 2D-NMR studies of **8** and **9**, including ^1H-^1H PS-COSY, NOESY (τ_m = 1.5s), HMQC and HMBC (J = 7Hz) experiments were performed and led to their unambiguous structural elucidation as well as assignment of proton and carbon chemical shifts (Table 1). The basic skeleton of both products was deduced from the two and three bond heteronuclear correlation network (HMBC experiment) between methyl protons, H-18 and carbons, as shown in heavy lines for structure **8** on figure 3a. Concerning **9**, an additional connection was established as, on one hand, 26-CH_3 and 27-CH_3 diplay remote connections to one double bond quaternary carbon (C-8) and, on the other hand, 25-CH_3 correlates with the other strongly deshielded quaternary carbon (C-9). The stereochemistry of the molecules follows from the NOEs observed, the most significant being reported, for **8**, on its three-dimensional drawing (figure 3b). Hence, the NOE between H-18 and 28-CH_3 implies a *cis*-ring D/E junction, and the connections of H-18 to both 26- and 27-CH_3 afford compelling evidence that the C(14) - C(15) bond has migrated towards C-13 by the β-face of the molecule, as expected. The configuration at C-9 in structure **8** remains unchanged (NOEs between H-9/H-27 and H-9/H-5).

The third compound, **10**, was not obtained pure enough for NMR investigations. It is nevertheless clearly related to the two previous ones as shown by its mass spectrum[7] which, in addition to the characteristic *m/z* 232 fragment, display an ion at *m/z* 206 which corresponds to a retro Diels-Alder-like reaction involving the 9(11) double bond (monounsaturated D/E ring part of the molecule). Furthermore, hydrocarbon **10** (and **9**) was formed in substantial quantity during the ionic hydrogenation ($HSiEt_3/CF_3COOH$) of **8**. Its configuration at C-8 is however undetermined.

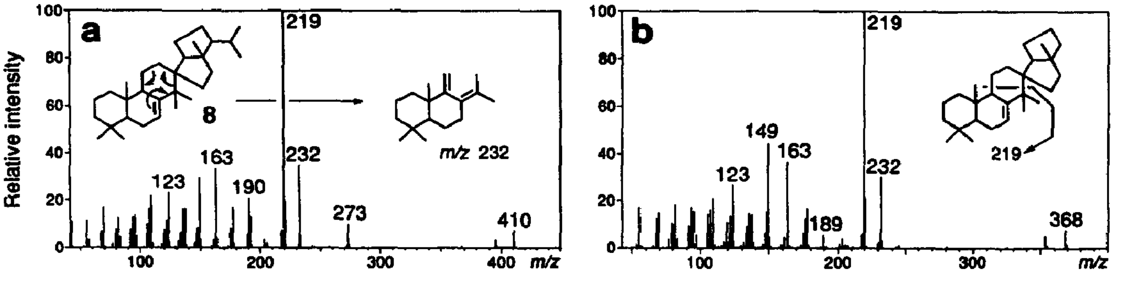

Figure 2. Mass spectra (EI, 70 eV) of (a) compound **8** and of (b) its sedimentary 22,29,30-trinor equivalent

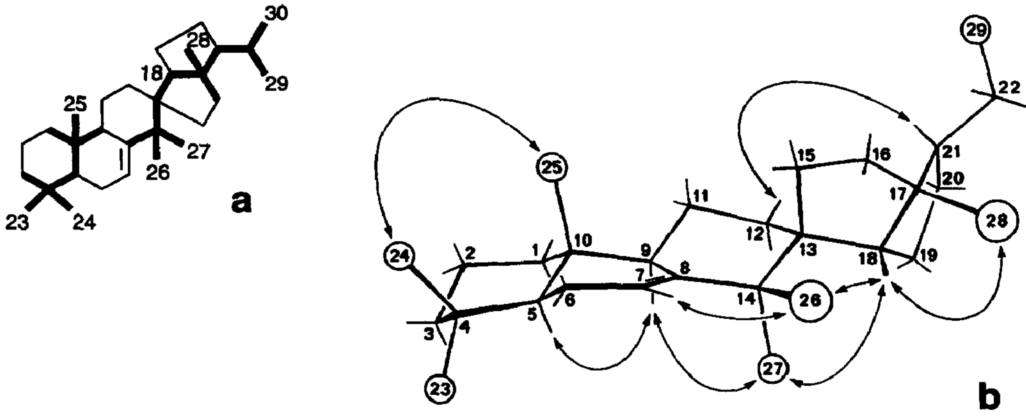

Figure 3. (a) carbon sequence (in heavy lines) established for **8** from the HMBC experiment
(b) 3D drawing of **8** showing the most important NOEs observed

Under the experimental conditions used, formation of the various fernenes **3** is quite immediate, but their ulterior interconversion with hop-13(18)-ene **7** - the proportion of which raised relative to hop-17(21)-ene **6** and the fernenes **3** throughout the reaction - is not established (rapid modification of the catalyst activity?). In contrast, the appearance of spiro-triterpenes **8** - **10** is progressive and implies the protonation of hop-13(18)-ene **7** by the α face. Noteworthy is the fact that, apparently, formation of 18α-fernenes - if any - does not occur to appreciable extent (or these compounds might be converted back immediately to hop-13(18)-ene). From the presence in sediment of hydrocarbon **1**, it is however obvious that formation of 18α-fernenes takes place - at least to some degree - in natural conditions under which, for instance, traces of 18α-fernene-type derivatives could be 'trapped' by aromatisation processes.

From the geochemical view point, GC-MS investigations of the alkene fraction from a recent lacustrine sediment (Lac du Bouchet, Haute Loire, France) where the 22,29,30-trinorhop-17(21)-ene is by far the major compound of the fraction, showed that this novel hopane skeleton transposition also naturally operates on sedimentary hopenes. Indeed, the three trinor equivalents of alkenes **8** - **10** were unambiguously recognised from their characteristic mass spectra (figure 2b and note 9) which exhibit the same fragmentation patterns as **8** - **10**, with ions from the right part of the molecules showing a shift of 42 daltons according to the loss of the isopropyl group. Furthermore, we may now expect the occurrence in geological samples of either the saturated or the ring-*B* aromatised counterparts of all these alkenes which may turn out to be useful biomarkers in petroleum geochemistry, in particular diagnostic of clay-rich depositional environments.

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Table 1 ^{13}C- and ^{1}H-NMR Data for **8** and **9** (125.8 and 500.1 MHz, CD_2Cl_2, δ in ppm relative to TMS)

C-atom	**8** δ(C)	**8** δ(H)		**9** δ(C)	**9** δ(H)	
1	40.53	0.99 (α)	1.83 (β)	38.59	1.13 (α)	1.75 (β)
2	19.39	1.41 (α)	1.53 (β)	19.80	1.57 (β)	1.46 (α)
3	42.62	1.16 (α)	1.41 (β)	42.28	1.15 (α)	1.38 (β)
4	32.96			33.71		
5	49.96^{a}	1.01		50.67	1.09	
6	24.30	1.89	1.89	19.63	1.69 (α)	1.45 (β)
7	118.07	5.51		25.94^{c}	1.99 (α)	2.20 (β)
8	145.82			134.10		
9	49.34	1.90		136.85		
10	36.00			38.02		
11	21.28	1.34 (β)	1.55 (α)	20.71	1.94 (β)	2.08 (α)
12	28.30	1.28 (β)	1.65 (α)	25.11	1.36 (β)	1.62 (α)
13	49.98^{a}			48.64		
14	42.22			39.76		
15	33.01	1.51 (β)	1.68 (α)	32.55	1.71 (α)	1.47 (β)
16	40.23	1.31 (α)	1.53 (β)	40.78	1.38	1.54
17	52.80			52.37		
18	59.56	2.06		59.18	2.00	
19	25.57	1.52 (β)	1.47 (α)	25.92^{c}	1.42 (α)	1.46 (β)
20	34.15	1.37 (α)	1.87 (β)	34.55	1.36 (α)	1.88 (β)
21	58.78	1.10		60.24	1.10	
22	29.75	1.47		29.48	1.47	
23	33.73	0.860		33.27	0.869	
24	22.53^{b}	0.909		21.84	0.835	
25	15.21	0.807		20.44	0.950	
26	22.53^{b}	1.051		22.98	0.952	
27	27.74	0.919		26.18	0.881	
28	23.77	0.930		24.13	0.922	
29	23.22	0.816 *J*=6.5Hz		22.48	0.879 *J*=6.5Hz	
30	22.57^{b}	0.859 *J*=6.5Hz		23.17	0.859 *J*=6.5Hz	

$^{a-c}$ Assignments interchangeable

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5. K-10 Montmorillonite (Fluka) was activated at 120°C for 4 h before use. Typically, for an analytical scale experiment, the catalyst (10 mg) was added to a solution of pure hop-17(21)-ene **6** (3.5 mg) in anhydrous cyclohexane (2 ml) and the mixture was stirred under argon at room temperature for 14 h. Evolution of the reaction was monitored by GC analysis of regularly taken small aliquots of the mixture. After filtering over celite, the reaction products (starting weight quantitatively recovered) were analysed by GC-MS (DB-5 J&W 60 m x 0.25 mm x 0.1 μm, He; Finnigan MAT TSQ 70, 70 eV).
6. MS data, *m/z* (rel. int.) : 410(M^+, 33%), 395(92), 271(10), 257(100), 245(24), 231(49), 163(14), 137(20).
7. MS data, *m/z* (rel. int.); **9** : 410(M^+, 6%), 395(3), 243(3), 232(100), 217(40), 189(17), 175(9), 149(4), 147(7), 121(8), 119(6); **10** : 410(M^+,3%), 395(3), 232(11), 206(100), 204(5), 189(4), 163(51), 147(5), 121(11).
8. The mixture was first fractionated over 10% silver nitrate impregnated silica gel (hexane) and purification of hydrocarbons **8** (98% by GC) and **9** (94% by GC) was finally achieved by reverse phase HPLC (semipreparative Du Pont 250x9.4mm; Zorbax ODS, 8μm, 80Å; methanol-chloroform 85:15, 5ml/min; and then analytical Vydac 250x4.6mm; 201TP, 5μm, 300Å; methanol-chloroform 85:15, 1ml/min)
9. MS data, *m/z* (rel. int.); Δ^{8} : 368(M^+, 22%), 353(69), 243(7), 232(100), 217(36), 189(29), 175(15), 149(15), 147(13), 121(19), 119(23); $\Delta^{9(11)}$: 368(M^+, 1%), 353(2), 232(5), 204(5), 189(4), 164(100), 149(11), 121(14).

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