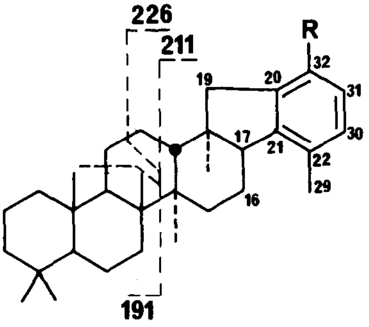
Tetrahedron Letters,Vol.25,No.11,pp 1179-1182,1984
Printed in Great Britain
0040-4039/84 $3.00 + .00

BENZOHOPANES, A NOVEL FAMILY OF HEXACYCLIC GEOMARKERS IN SEDIMENTS AND PETROLEUMS.

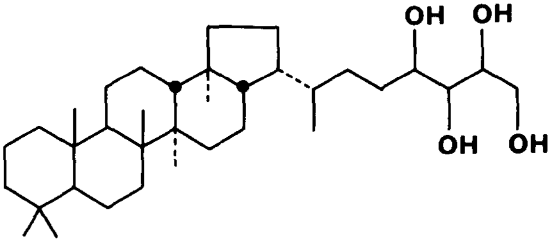
G. HUSSLER, P. ALBRECHT* and G. OURISSON
Laboratoire de Géochimie Organique, LA 31 associé au C.N.R.S.
Département de Chimie, Université Louis Pasteur,
1, rue Blaise Pascal, 67008 Strasbourg, France.
M. CESARIO, J. GUILHEM and C. PASCARD
Institut de Chimie des Substances Naturelles, C.N.R.S.
91190 Gif-sur-Yvette, France.

ABSTRACT. *A novel family of hexacyclic hopanoids, the benzohopanes* 1 *(C_{32}-C_{35}), has been identified in geological sources by X-ray crystallography. These compounds must be formed from bacterial C_{35} hopanoid precursors during early stages of sedimentation.*

Aromatisation is a widely occurring geochemical process which takes place at various stages of sedimentation in the subsurface[1]. Several steps of this process have been traced recently by defining the structure of steroid and terpenoid derived hydroaromatic compounds in sediments and petroleums[2]. In particular a series of pentacyclic hydroaromatic hopanoids showing an increasing degree of aromatisation has been identified in this laboratory a few years ago[3], but no higher condensed terpene related compounds have been detected so far. We wish to report here the conclusive structural elucidation of benzohopanes 1, a novel family of hexacyclic terpenoids related to the hopane series, extending from C_{32} to C_{35}, which occurs widely in sediments and petroleums.



1



2

a. R = H   b. R = CH_3
c. R = C_2H_5 d. R = n-C_3H_7

MS fragments correspond to 1a.

The aromatic fractions of nineteen sediment extracts and petroleums of various origins and ages[4] have been obtained by SiO_2 chromatography as previously described[5]. Subsequent analysis of these fractions by GC-MS[6] indicated the presence of four often major peaks in the high molecular weight range with molecular ions at m/z = 432, 446, 460 and 474. The mass spectral fragmentation patterns of the four compounds were similar, suggesting a homologous series based on a C_{32} skeleton bearing a side-chain of varying length[7]. The four products had the same base peak at m/z = 191, typical of a terpane moiety, likely to be of the hopane type[8],since hopane triterpanes were major components of the alkane fractions of most samples. Fragmentations at m/z = 211 + 14 n and 226 + 14 n (n = 0-3) confirmed the presence of four additional degrees of unsaturation in the right hand moiety of the molecules as compared with saturated hopanes. Furthermore the occurrence of two groups of peaks centered around m/z = 144 + 14 n and 157 + 14 n, characteristic of indene fragments, suggested that a benzene ring was condensed to the E ring of a hopane skeleton, a feature compatible with a reorganisation of the side-chain of bacterial C_{35} hopanoid precursors, such as bacteriohopane tetrol 2[9,10].

In order to obtain more accurate structural information we carried out further separation of the aromatic fractions of one rock extract and one petroleum from Guatemala by high performance liquid chromatography. Indeed,a sequence of three separations on RP 18, SiO_2 and again RP 18, using methanol, hexane and acetonitrile as respective eluents, yielded four nearly pure compounds of which 1a, 1b and 1c were crystalline (in milligram amounts from 25 g of starting petroleum)[11]. 200 MHz NMR data confirmed the most likely postulated structures 1[12]. They showed in particular the presence of one methyl group and three adjacent hydrogens on an aromatic ring in 1a, two equivalent adjacent aromatic protons in the other homologs, as well as one further methyl group on a benzene ring in 1b, replaced by an ethyl and an n-propyl substituent in 1c and 1d.

Finally, monocrystals of the C_{32} and C_{33} components were obtained by careful recrystallisation from a mixture of methanol and methylene chloride (2/1). These crystals were submitted to X-ray diffraction which definitely established the structure of these two products as the benzohopanes 1a and 1b, respectively 20,32-cyclo-17α(H)-bishomohopane-20,22,31-triene and 20,32-cyclo-32-methyl-17α(H)-bishomohopane-20,22,31-triene (figure 1). Both compounds are orthorhombic, space group $P\,2_1 2_1 2_1$, with Z = 4. The cell parameters are : a = 21.585(8), b = 15.538(6) and c = 7.726(5) Å for 1a and 25.263(9),14.101(7) and 7.620(5) Å for 1b; 2690 reflections were measured for 1a on an automatic diffractometer, of which 2007 were observed (respectively 2229 and 1370 for 1b). The structures were solved by direct methods[13] and the atomic coordinates and the anisotropic thermal parameters were refined to R = 0.036 and 0.085 respectively by block-diagonal least square refinement[14].

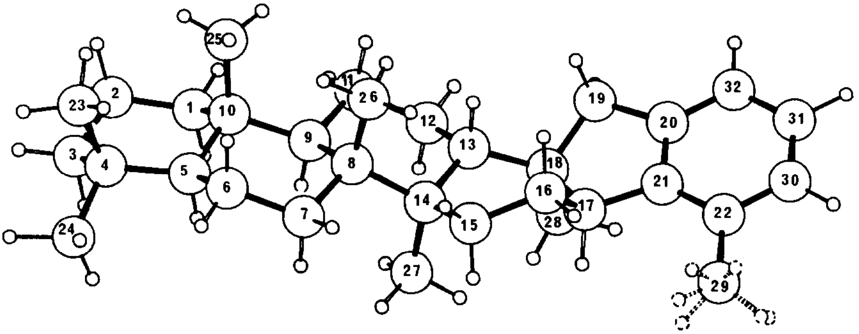
NMR and MS data of 1c and 1d can leave no doubt that these two compounds are higher homologs of the same series bearing respectively an ethyl and an n-propyl substituent at C-32.

Benzohopanes have not been detected in living organisms so far. They must therefore be considered as transformation products of hopanoid precursors which are widespread as lipidic membrane constituents of procaryots[9]. A likely precursor would be the C_{35} bacteriohopane tetrol 2 which could lead to the benzohopane series via an acid catalysed dehydration and cyclisation sequence, eventually followed by a degradation of the side-chain. That such a process, perhaps mineral matrix influenced, must take place at early stages of maturation is shown by the occurrence of benzohopanes in an immature Cretaceous black shale from the Southern Atlantic[5,15]. The benzylic 17-position has, however, already been isomerised, presumably during the cyclisation process, contrary to the hopane triterpanes and triterpene acids which mostly have the 17β(H) configuration typical of living organisms.

The benzohopanes seem to be ubiquitous in geological samples, but occur in higher concentrations in confined carbonate environments, all features compatible with the widespread occurrence of hopanoid precursors in microorganisms[9].

Acknowledgment : We thank the Société Nationale Elf-Aquitaine (SNEA) for financial support and supply of samples and Dr. J. Connan, SNEA(P), Pau, for his interest and helpful discussions.

1a



1b

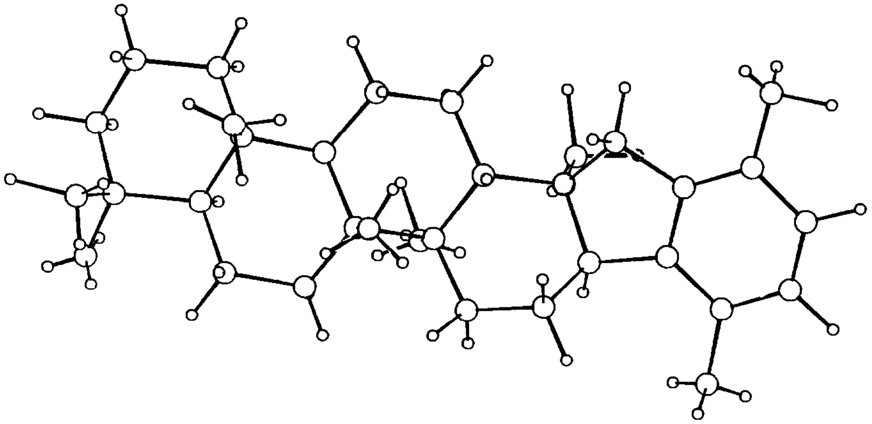


Figure 1. Perspective drawings of structures 1a and 1b obtained from X-Ray crystallography. Ring D is in a preferred boat conformation.

REFERENCES.

1. B. Tissot and D.H. Welte, Petroleum formation and occurrence. Springer, Berlin, 1978.
2. C. Spyckerelle, A. Greiner, P. Albrecht and G. Ourisson, J.Chem.Res.(S), 330, (M) 3746 (1977); B. Ludwig, G. Hussler, P. Wehrung and P. Albrecht, Tetrahedron Lett.,22, 3313 (1981); A.S. Mackenzie, C.F. Hoffman and J.R. Maxwell, Geochim.Cosmochim. Acta, 45, 1345 (1981); W.K. Seifert, R.M. Carlson and J.M. Moldowan, in Advances in Organic Geochemistry 1981, M. Bjørroy et al., eds., Wiley,London, 710 (1983); A.S. Mackenzie, S.C. Brassell, G. Eglinton and J.R. Maxwell, Science, 217, 491 (1982).
3. A. Greiner, C. Spyckerelle and P. Albrecht, Tetrahedron, 32, 257 (1976); A. Greiner, C. Spyckerelle, P. Albrecht and G. Ourisson, J.Chem.Res.(S), 334, (M) 3829 (1977).
4. The samples ranged in age from Cretaceous to Miocene and included 9 petroleums from carbonate basins (Aquitaine, France; Guatemala; Iraq; Tunisia; Italy; Spain); 2 petroleums of continental origin (Nigeria; New Zealand); 7 sediments from carbonate basins (Aquitaine; Tunisia; Guatemala) and 1 black shale from the Angola basin.
5. G. Hussler, B. Chappe, P. Wehrung and P. Albrecht, Nature, 294, 556 (1981).
6. LKB 9000 S GC-MS, SE 30, 25m x 0.25mm, 100-300°C, 3°C/min.
7. MS data (70eV, source temperature 230°C).
   1a : m/z = 432 (42%,M^+), 417(9), 226(44), 211(35), 191(100), 171(9), 170(11), 169(9), 158(25), 157(28), 156(30), 145(23), 144(30), 143(20), 95(28), 81(28), 69(30).
   1b : m/z = 446 (48%,M^+), 431(10), 240(59), 225(39), 191(100), 185(8), 184(9), 183(8), 172(32), 171(36), 170(43), 159(32), 158(52), 157(28), 95(30), 81(30), 69(32).
   1c : m/z = 460 (39%,M^+), 445(8), 254(56), 239(34), 199(7), 198(8), 197(7), 191(100), 186(33), 185(33), 184(44), 173(33), 172(51), 157(19), 95(32), 81(33), 69(37).
   1d : m/z = 474 (46%,M^+), 459(10), 268(55), 253(33), 213(7), 212(8), 211(8), 200(33), 199(27), 198(39), 191(100), 187(27), 186(43), 185(16),157(25),95(27),81(29),69(29).
8. A. Ensminger, A. Van Dorsselaer, C. Spyckerelle, P. Albrecht and G. Ourisson, in Advances in Organic Geochemistry 1973, B. Tissot and F. Bienner eds., Technip, Paris, 245 (1974).
9. G. Ourisson, P. Albrecht and M. Rohmer, Pure Appl.Chem., 51, 709 (1979).
10. M. Rohmer, M. Dastillung and G. Ourisson, Naturwissenschaften, 67, 456 (1980).
11. Waters HPLC, Si 100 and Si 100-C_{18}, 10µ, 25 x 0.73 cm, eluent 6 ml/min, detection UV (254 nm) and RI.
12. Analytical data of benzohopanes. Mps 1a : 203-205; 1b : 207-208.5, 1c : 174.5-176°C.
    UV (isooctane) : λmax(ε), 1a : 274.5(470), 266.5(430), 262.5(300); 1b : 264.5(290); 1c : 265(220).
    MS HR 1a, $C_{32}H_{48}$, calc. 432.3756, mes. 432.3748; 1b, $C_{33}H_{50}$, c. 446.3913, m. 446.3904; 1c, $C_{34}H_{52}$, c. 460.4069, m. 460.4071; 1d, $C_{35}H_{54}$, c. 474.4225, m. 474.4212.
    NMR (200 MHz, $CDCl_3$ + CCl_4, δppm, J Hz).
    1a : 7.07-6.85(m,3H); 2.87 and 2.72(AB, J=15, 2H,H-19); 2.67(dd,J=12 and 3,1H,H-17); 2.28 (s,3H, H-29); 1.12(s,3H); 1.00(s,3H); 0.87(s,6H); 0.81(s,6H).
    1b : 6.81(s,2H); 2.71(s,2H,H-19); 2.66(dd,J=12 and 3,1H,H-17); 2.25(s,3H,H-29); 2.17(s,3H, H-33); 1.13(s,3H); 0.99(s,3H); 0.90(s,3H); 0.87(s,3H); 0.81(s large,6H).
    1c : 6.90(s,2H); 2.75(s,2H,H-19); 2.67(dd,J=12 and 3, 1H,H-17); 2.52(q,J=7.5,2H,H-33); 2.26(s,3H,H-29); 1.17(t,J=7.6,3H,H-34); 1.12(s,3H); 0.99(s,3H); 0.89(s,3H); 0.86(s, 3H); 0.82(s,3H); 0.81(s,3H).
    1d : 6.88(s,2H); 2.75(s,2H,H-19); 2.67(dd,J=12 and 3,1H,H-17); 2.52-2.42(m,2H,H-33); 2.26 (s,3H,H-29); 1.12(s,3H); 0.99(s,3H); 0.95(t,J=7.3, 3H,H-35); 0.89(s,3H); 0.86(s,3H); 0.82(s,3H); 0.81(s,3H).
13. C. Riche, 7th European Crystallographic Meeting, Jerusalem, Abstracts, p. 25 (1982).
14. G. Sheldrick, SHELX 76. A program for crystal structure determination. University of Cambridge, England. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.
15. G. Hussler and P. Albrecht, Nature, 304, 262 (1983).

(Received in UK 2 December 1983)