Tetrahedron Letters,Vol.25,No.11,pp 1183-1186,1984
Printed in Great Britain

0040-4039/84 $3.00 + .00

A NOVEL SULFUR CONTAINING C_{35} HOPANOID IN SEDIMENTS.

J. VALISOLALAO, N. PERAKIS, B. CHAPPE and P. ALBRECHT*

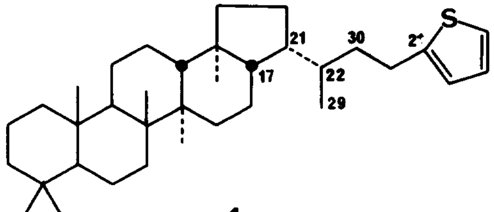
Laboratoire de Géochimie Organique, LA 31 associé au C.N.R.S.
Département de Chimie, Université Louis Pasteur
1, rue Blaise Pascal, 67008 Strasbourg, France.

ABSTRACT.

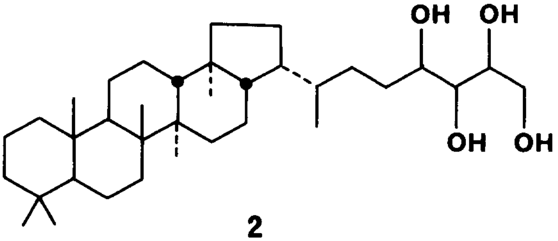
A C_{35} pentacyclic triterpenoid of the hopane series containing a thiophene ring, 30-(2'-methylene thienyl)-17β(H),21β(H)-hopane 1, has been confirmed in immature sediments by synthesis, suggesting incorporation of bacterial sulfur into geological organic matter at early stages of sedimentation.

Although sulfur often occurs in petroleums and sedimentary organic matter in high concentration (up to 10% in some high sulfur crude oils),the problem of its origin and of its stage of incorporation into the geological organic matter is still not elucidated[1-3]. With a few exceptions only relatively small or uninformative sulfur containing molecules have been characterised until recently in petroleums or sediments[4-8]. More complex molecules suspected earlier on the basis of mass spectrometry[9] may be able to deliver better information on the sulfurisation process of fossil organic matter, as illustrated recently by the discovery of novel series of terpenoid sulfides and sulfoxides in the Athabasca oil sands[10].

We wish to report here the conclusive identification of a novel sulfur containing C_{35} triterpenoid of the hopane series, 30-(2'-methylene thienyl)-17β(H),21β(H)-hopane 1, in organic rich sediments of low maturity. This molecule bears a clear relationship with bacteriohopane tetrol 2, a widespread membrane constituent of procaryotes[11], from which it could be formed during diagenesis in the subsurface under the action of bacterial H_2S.



1



2

The sediments analysed were two Cretaceous black shales from the Southern Atlantic, collected in the Angola basin during the Deep Sea Drilling Project (leg 40). The organic rich sediments were deposited during the early stages of the opening of the Atlantic Ocean in a confined environment, favouring a good preservation of the organic matter[12,13]. Typically 15 g of powdered shale were extracted with chloroform and the extract was separated by SiO_2 chromatography as described previously[12]. Analysis by coupled GC-MS[14] showed that the aromatic hydrocarbon fraction contained several compounds derived from hopanoids and steroids, reflecting the bacterial and planktonic origin of the organic matter[12]. One of the major peaks in the high molecular weight range of this fraction showed a mass spectrum compatible with structure 1 (figure 1)[15]. Indeed, this spectrum displayed a major peak at m/z = 191 (fragment b) along with a fragmentation at m/z = 369 (fragment d), which are characteristic features of hopane triterpanes[16]. The base peak at m/z = 97 (fragment a) was typical of a thiophene moiety. Furthermore fragment b was inferior in intensity to fragment c (m/z = 287), which is rather characteristic of the 17β(H),21β(H)-hopane series[17].

In order to establish this structural hypothesis we have synthesised compound 1 following the scheme described in figure 2. The starting material was homohop-30-ene 3, which was prepared previously from hop-22(29)-ene (diploptene)[18]. The final product was a mixture of two diastereomers at C-22 which were separable by high resolution gas chromatography[19]. The mass spectra of the two stereoisomers and that of the geological compound were identical. Furthermore the natural product coeluted with the least volatile isomer on two phases on capillary columns (25m x 0.25mm, SE 54 and OV 1701) ; it was therefore assumed to be 22 R by analogy with related hopanoids[20,21].

No isomerisation at C-22 was effective in these sediments, confirming their low degree of thermal stress[12]. Although other sulfur compounds related to terpenoids seem to be present, higher or lower homologues of 1 were not detectable. Stereoisomers of 1, presumably at C-17 (fragment c much smaller than fragment b) and C-21 were detected, however, along with 1, in a slightly more mature sediment from Tunisia[22].

As sulfur containing triterpenoids have rarely been reported in living organisms[23], it is more reasonable to assume that the thienylhopane 1 has been formed by a diagenetic process during early stages of sedimentation in the subsurface. A likely biological precursor would be bacteriohopane tetrol 2, a surrogate of sterols in bacterial membranes[24], which bears the same carbon number as 1. This compound which has been reported in recent muds[21] and is a well recognised precursor of fossil hopanoids[11], could have undergone a cyclisation reaction, perhaps mineral matrix catalysed, with H_2S, which is widely produced in the subsurface by sulfate reducing bacteria[25]. The latter must have indeed played an active role in confined environments such as the black shales at their time of deposition. This hypothesis is now being checked by simulation experiments with model compounds.

Acknowledgments.

We thank the Institut Français du Pétrole for financial support and supply of samples ; Professor G. Ourisson for his interest and helpful discussions, Dr. F. Leyendecker for helpful discussions, J.M. Trendel for a sample of diploptene, Dr. G. Teller and R. Hueber (Univ. Louis Pasteur, Strasbourg) for the mass spectrometrical analysis.

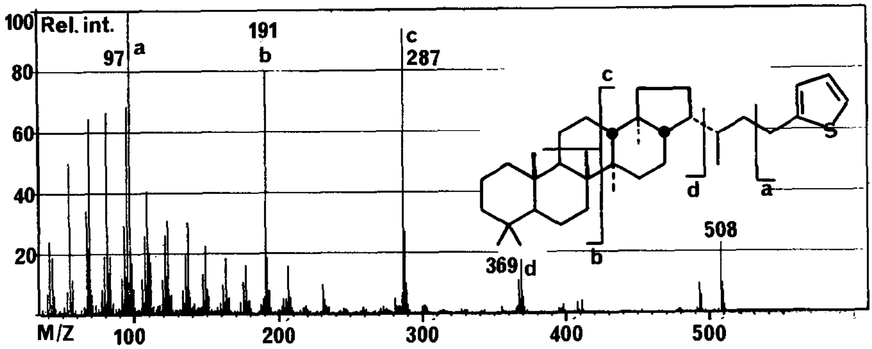


Figure 1. Mass spectrum of thienylhopane 1 (70eV ; LKB 9000 S GC-MS).

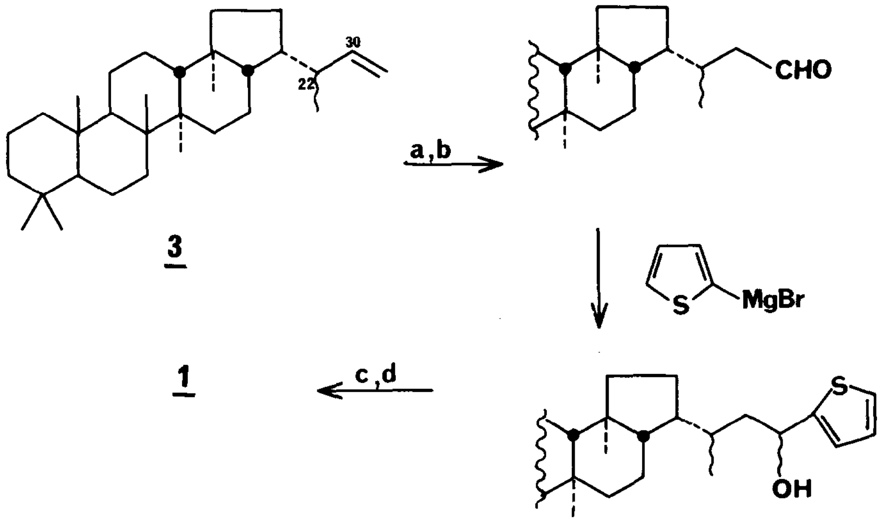


Figure 2. Synthesis of thienylhopane 1 as a mixture of diastereomers at C-22.

a : B_2H_6 ; NaOH, H_2O_2 ; b : PDC, CH_2Cl_2 ;

c : MnO_2, CH_2Cl_2 ; d : N_2H_4 ; KOH.

REFERENCES.

1. B. Tissot and D.H. Welte, Petroleum formation and occurrence. Springer, Berlin (1978).
2. W.L. Orr, in Oil sand and oil shale chemistry, O.P. Strausz and E.M. Lown eds., Verlag Chemie, New York, pp. 223-243 (1978) and refs therein.
3. G. Constantinides and G. Arich, in Fundamental aspects of petroleum geochemistry, B. Nagy and U. Colombo eds., Elsevier, Amsterdam, pp. 109-175 (1967).
4. W. Carruthers and H.N.M. Stewart, J. Chem. Soc.(C), 560 (1967).
5. J.K. Whelan, J.M. Hunt and J. Berman, Geochim.Cosmochim.Acta, 44, 1767 (1980).
6. T.S. Bates and R. Carpenter, Geochim.Cosmochim.Acta, 43, 1209 (1979).
7. C.M. White and M.L. Lee, Geochim.Cosmochim.Acta, 44, 1825 (1980).
8. J. Rullkötter, H. Von der Dick and D.H. Welte, in Initial reports of the Deep Sea Drilling Project, vol. 63, B. Haq, R.S. Yeats et al. eds, U.S. Government Printing Office, Washington, pp. 819-836 (1981).
9. H. Castex, J. Roucache and R. Boulet, Rev. Inst.Franç. Petrole, 29, 3 (1974).
10. J.D. Payzant, D.S. Montgomery and O.P. Strausz, Tetrahedron Lett., 24, 651 (1983).
11. G. Ourisson, M. Rohmer and P. Albrecht, Pure Appl.Chem., 51, 709 (1979).
12. G. Hussler, B. Chappe, P. Wehrung and P. Albrecht, Nature, 294, 556 (1981).
13. G. Hussler and P. Albrecht, Nature, 304, 262 (1983).
14. Conditions : SE 30, 25m x 0.25mm, 100-300°C, 3°C/min ; LKB 9000 S computerised GC-MS.
15. A similar spectrum has been reported recently without further structural investigations for a compound occurring in Cretaceous black shales from Italy (G. Van Grass, Ph.D. Thesis, Technische Hogeshool Delft, 1982)and in a Miocene claystone (J. McEvoy, G. Eglinton and J.R. Maxwell, in Initial Reports of the Deep Sea Drilling Project, Vol. 63, B. Haq, R.S. Yeats et al. eds., U.S. Government Printing Office, Washington, pp. 763-774, 1981).
16. A. Van Dorsselaer, Thèse de Doctorat ès Sciences, Université Louis Pasteur, Strasbourg (1975).
17. 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, pp. 245-260 (1974).
18. A. Ensminger, P. Albrecht, G. Ourisson, B.J. Kimble, J.R. Maxwell and G. Eglinton, Tetrahedron Lett., 3861 (1972).
19. NMR data of 1 (200 MHz ; $CDCl_3$, δppm, J Hz) : 0.68(s,3H); 0.80(s,3H); 0.82(s,3H); 0.85 (s,3H); 0.89(d, J=6.5, H-29, 22 S); 0.96(s,6H); 1.00(d, J=6.2, H-29, 22 R); 2.78(m,2H); 6.78-7.33(m,3H).
20. M. Dastillung, P. Albrecht and G. Ourisson, J. Chem. Res. (S),158; (M),2353 (1980).
21. M. Rohmer, M. Dastillung and G. Ourisson, Naturwissenschaften, 67, 456 (1980).
22. H. Belayouni, Thèse de Doctorat ès-Sciences, Université d'Orléans (1983).
23. A. Kjaer, Pure Appl.Chem., 49, 137 (1977) ;
    M. De Rosa, A. Gambacorta and L. Minale, Chem. Commun., 392 (1975).
24. M. Rohmer, P. Bouvier and G. Ourisson, Proc. Natl. Acad. Sci. USA, 76, 847 (1979).
25. J.R. Postgate, The sulphate-reducing bacteria. Cambridge University Press, Cambridge (1979).

(Received in UK 2 December 1983)