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NOVEL TRICYCLIC TERPANES (C_{19},C_{20}) IN SEDIMENTS AND PETROLEUMS.

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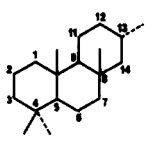
Summary : Three homologs (1-3 , C_{19},C_{20}) of a tricyclic terpane series (C_{19}-C_{30}) widely occurring in sediments and petroleums have been identified as probable degradation products of tricyclohexaprenane 13, a yet unknown tricyclic terpane skeleton.

Tricyclic and tetracyclic terpanes have been recognized recently as widely occurring constituents of many sediments and crude oils[1]. Although partial structures have been proposed for both series, only lately have the tetracyclic terpanes been conclusively identified as hopane related components (17,21-secohopanes , C_{24}-C_{27})[2]. The tricyclic series usually extends from C_{19} to C_{30} and is best studied by computerized gas chromatography - mass spectrometry with the help of the mass fragmentogram m/z = 191, typical of a terpane moiety (usually the base peak), mass spectra of better quality being obtained on biodegraded petroleums[2]. It was of major geochemical interest to elucidate the origin of these widely occurring substances, in particular to see whether they could also be related to pentacyclic hopanoid precursors From the mass spectral fragmentation and gas chromatographic behaviour of the various members of the series, a common tricyclic ring system bearing an isoprenoid side chain of variable length was postulated for which synthetic confirmation is being sought.

We have now synthesized several short chain tricyclic terpanes (1 - 10 , C_{19}-C_{21}, see below) and have identified three of them (1 - 3) as members of the major tricyclic series of many sediments and petroleums of various origins and ages[3,4] The compounds 4 - 10 were not detected in significant amounts in our samples.



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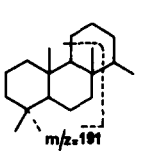

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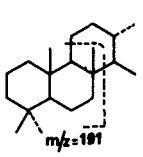

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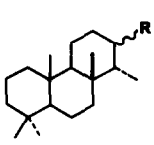
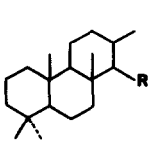


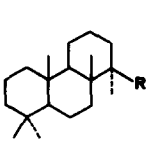
4 R=H

5a R=αCH_3
b R=βCH_3



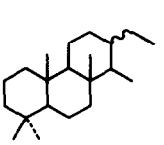
6 R=H

7 R=CH_3



8 R=CH_3

9 R=C_2H_5



10 a+b
(α+β at C-13)

The branched an cyclic alkanes of the sediments and petroleums were obtained by previously described methods[5] and analyzed by all glass capillary column gas chromatography (CCGC) and CCGC coupled with computerized mass spectrometry. Molecular ions were obtained for the tricyclic series at m/z = 262, 276, 290. 416, corresponding to compounds ranging from $C_{19}H_{34}$ to $C_{30}H_{56}$ which were present in variable amounts depending on the sample The C_{23} homolog was usually major, reaching sometimes the same order of magnitude as the ubiquitous pentacyclic hopanes. In some samples the higher homologs (> C_{25}) were less abundant, but we do not know yet whether this indicates a formation of the series from different biological precursors (C_{25},C_{30}) or reflects the paleoenvironmental conditions A significant fragmentation at m/z = 261 was observed for these compounds, indicating the probable presence of a side chain of variable length on a C_{19} basic skeleton The C_{22} and C_{27} members of the series were usually less abundant, which suggests a branching at these positions (see below) and the probable presence of an isoprenoid side chain. In the gas chromatograms doublets displaying identical mass spectra were observed for homologs above C_{24}, reflecting the probable presence of an epimerized chiral center at C-22, a feature of mature samples, especially in the pentacyclic hopane series. Furthermore there were two C_{19} isomers in the series, only one of which gave a strong fragmentation at m/z = 191 On the basis of these considerations a C_{18} tricyclic ring system, common to structures 1 - 10, was most plausible, with a methyl group and an isoprenoid side chain positioned at C-13 or C-14, keeping in mind that at least one substituent must be present at C-14 in order to induce the strong 191 fragmentation

Compounds 1 - 3 were prepared following the synthetic schemes described in figure 1[6] Because of the relationship between the tetracyclic series and the pentacyclic hopanoids[2], the syntheses were first oriented toward plausible hopane related compounds such as 2, 8 and 9[7,8].

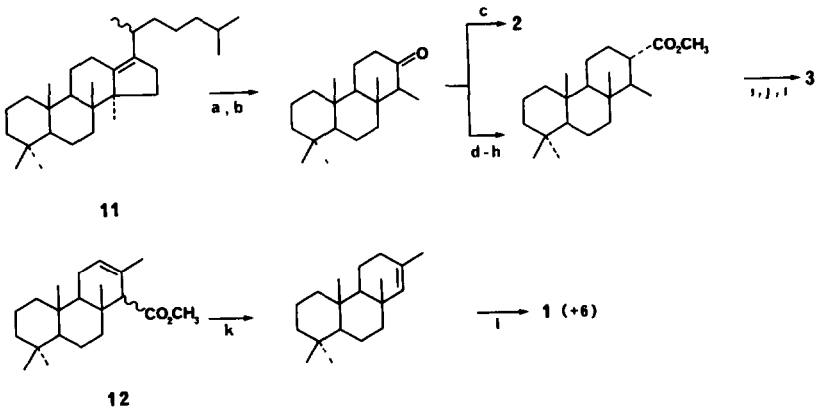


Fig.1 : Synthesis of the tricyclic C_{19} and C_{20} terpanes 1-3 (ref.6). Dammarenes 11 were obtained from dipterocarpol and methylisoanticopalate 12 from manool, after refs. 7 and 8.

Comparison of the synthesized compounds with those occurring in the geosphere were made by mass spectrometry and coelution by CCGC-MS in single ion mass fragmentography (LKB 9000 S , m/z = 191, except for 1 where m/z = 262 was used) on two glass capillary columns (SE 30 , SP 2250, Supelco, 30m x 0 25mm) On this basis only the C_{19} and C_{20} compounds 1, 2

and 3 were identified as belonging to the major geological series of tricyclic terpanes. The compounds 4 - 10, although displaying mass spectral fragmentations very similar to the geological terpanes, could be eliminated by their different retention times.

The following mass spectral data were obtained for compounds 1-3 (CCGC-MS , 70eV) :

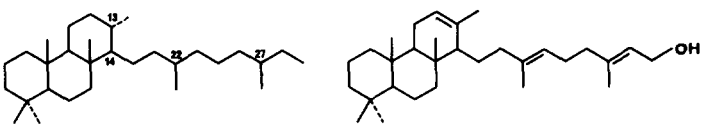
1 m/z = 262(M^+,36%), 247(67), 191(9), 177(12), 163(8), 149(35), 137(20), 123(100), 111(32), 109(47), 95(57), 81(67), 69(69), 55(50)

2 m/z = 262(M^+,47), 247(36), 206(9), 192(21), 191(100), 177(10), 163(5), 149(33), 137(19), 123(36), 109(31), 95(31), 81(24), 69(19), 67(12).

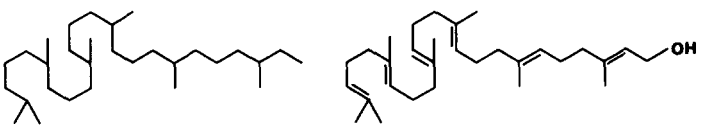
3 m/z = 276(M^+,52), 261(28), 220(4), 192(20), 191(100), 177(5), 163(33), 149(4), 123(49), 109(27), 95(44), 82(20), 81(24), 69(32), 55(19).

Of particular significance was the absence in our samples of compounds 8 and 9, which were the most likely tricyclic components derivable from pentacyclic hopane precursors, showing that, unlike the tetracyclic series[2], the tricyclic terpane series is not related to the hopanoids

The conclusive identification of compounds 1-3 and the absence of the other substances, in particular of 10, implies that the variable isoprenoid side chain must be located at position β C-14, which is also the more likely in terms of terpene biosynthesis From the spectroscopic and GC considerations outlined above (e g branching at C-22 and C-27 , epimers at C-22 separable in GC above C_{24}) we can now admit, with a high degree of certainty, that the tricyclic series culminates in a yet unknown C_{30} basic tricyclic triterpane skeleton, the tricyclohexaprenane 13, from which it is (as least partly) derived[9]. A related tricyclic sesterterpene, cheilanthatriol, has been identified in the case of a fern[10] and luteone, another related degraded C_{23} tricyclic terpenoid, in a mollusc feeding on sponges[11], but there is no report of such compounds extending over C_{25} A likely biological precursor of structure 13 would be the tricyclohexaprenol 14, which could be formed anaerobically from regular hexaprenol 15, a universal cell constituent (it is a precursor of the dolichols)[12], by a favored all-chair, trans-anti-trans cyclisation process[13] The saturated counterpart of 15, regular hexaprenane 16, has been reported in petroleums[14] and recently in the lipids of archaebacteria[15]



13 14



16 15

It appears from the molecular dimensions of 14 that this compound would again be a suitable stabilizing constituent of membranes of microorganisms, much in the same way as hopanoids and sterols in procaryots and eucaryots[16] The confirmation of this hypothesis would be one more example of the predictive potential of molecular organic geochemistry[17].

Further work aiming at the conclusive identification of the higher homologs of the tricyclic terpane series is in progress[18].

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3 About 40 crude oils and rock samples (mostly from carbonates) from France (Aquitaine basin), Guatemala, Iraq, Libya, Tunisia and U.S A, ranging in age from Jurassic to Tertiary. The tricyclic terpanes are apparently absent in recent sediments, suggestion their formation in a later stage of maturation

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1 is separable from the major epimer 6 by GC Analytical and spectral data were in agreement with the proposed structures The synthesis of compounds 4 - 10 will be reported elsewhere

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18. This study was supported by the Centre National de la Recherche Scientifique, France. We thank the Société Nationale Elf-Aquitaine for financial support and supply of samples , Dr. Teisseire, Société Roure Bertrand-Dupont for supply of manool. One of us, F R.A.N., on leave from the Universidade Federal do Rio de Janeiro, thanks the Conselho Nacional de Desenvolvimento Cientifico Tecnologico (CNPq, Brazil) for a research grant.

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