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18,19-BISNOR-13βH,14αH-CHEILANTHANE: A NOVEL DEGRADED TRICYCLIC SESTERTERPENOID-TYPE HYDROCARBON FROM THE ATHABASCA OIL SANDS

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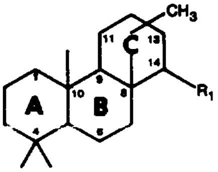
Abstract: The Athabasca oil sand bitumen contains a homologous series of tricyclic terpanes containing 19-30 C atoms per molecule. The structure of the most abundant member, the C_{23} tricyclane, has now been elucidated.

Recently, we reported[1] the occurrence, in the Athabasca oil sand bitumen, of a homologous series of tricyclic terpanes having basic structure I (R_1 = H to R_1 = $C_{11}H_{23}$) and containing 19-30 C atoms per molecule.



I

We have now isolated the most abundant component of the series having the formula $C_{23}H_{42}$ (peak 5b, Fig. 1) by preparative g.c. (>90% purity) from a concentrate of the tricyclic terpanes separated from the native bitumen.[1] We also isolated this compound and its isomer (peak 5a) from the pyrolyzate (300°C) of the resin fraction of the bitumen. The latter tricyclane was present in relatively high concentration in the resin pyrolyzate (2.13 mg/g of saturates) but occurred in much lower amounts in the corresponding fraction of the natural bitumen (0.17 mg/g). All three compounds were analyzed by mass spectrometry (direct-inlet insertion probe) and both samples of component 5b by H^1 n.m.r.

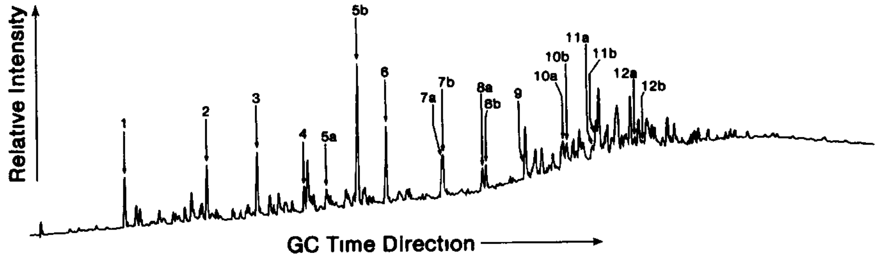
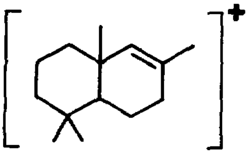
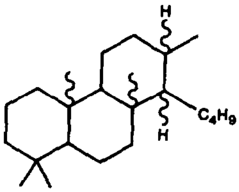


Fig. 1. GC of a concentrate of the tricyclic terpanes [peak 1 ($C_{19}H_{34}$) - peak 12 ($C_{30}H_{56}$)] of the Athabasca oil sands.[2]

Peak 5b displays $C_{23}H_{42}$ [M^+, 318 (29%), M^+-15, 303 (20%), M^+-C_4H_9, 261 (20%), M^+-C_9H_{19}, 191 (100%)], indicating a tricyclic structure with a butyl side chain. On the basis of the intense ion at m/e 191, corresponding to II which is characteristic of many polycyclic terpanes,[3] the tentative structure III is an obvious choice for this compound.[4]



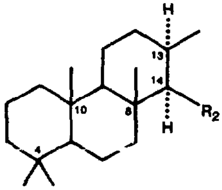
II



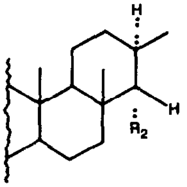
III

The mass spectrum, gas liquid chromatographic retention time and PMR of the compound represented by peak 5b from the resin pyrolyzate[1] were identical to those of the corresponding component in the natural bitumen (peak 5b, Fig. 1) thus confirming that they are the same compound.[5]

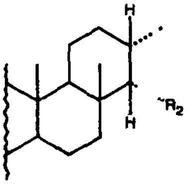
The mass spectrum of peak 5a features $C_{23}H_{42}$ [M^+, 318 (25%), M^+-15, 303 (15%), M^+-C_4H_9, 261 (58%), M^+-C_9H_{19}, 191 (63%), 57 (100%)]. These data support the overall structure III but indicate a more facile loss of the butyl substituent under electron impact. This may be related to an energetically unfavourable conformation in component 5a, which is most probably due to the stereochemistry at the point of attachment of the alkyl substituent to the C ring. Hence, assuming that the A, B and C rings are *trans*-fused, three possible structures, IV, V, VI, reflecting destabilizing interactions between neighbouring/coplanar methyl and butyl substituents of ring C, can be envisioned for component 5a.



IV

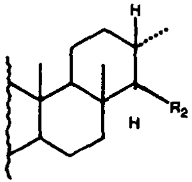


V



VI $(R_2 = \underline{n}\text{-}C_4H_9)$

The C-8 and C-10 methyl groups would be axially oriented in all three structures (chair-chair-chair) Thus, while IV and V suffer from three 1-3 diaxial methyl interactions (C-4β/C-10, C-8/C-10, C-8/C-13) VI is destabilized by only two (C-4β/C-10, C-8/C-10). The severe crowding in IV arising from the 1-3 diaxial bonds is further accentuated by *syn* axial-equatorial repulsions of neighbouring bulky substituents (C-8 Me/C-14 Bu, C-13 Me/C-14 Bu) Therefore, of the three possible structures for compound 5a, IV is the least likely, and VI is the most plausible. It then follows that VII is a possible structure of a more thermodynamically stable isomer of component 5a, i.e. component 5b This structure also possesses two 1-3 diaxial bonds but is expected to be relatively less destabilized because the C-14 butyl group is in the thermodynamically more stable β, equatorial position[6] This tentative structure of component 5b is supported by PMR data.



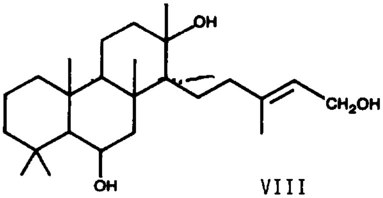
VII

The 400 MHz PMR ($CDCl_3$) of peak 5b displays signals for 4 angular methyls (3H singlet at δ 0.76, 6H singlet at δ 0.80, 3H singlet at δ 0 84) and one secondary Me (3H doublet at δ 0 83, J ≈ 7c/s) These data confirm the presence of 5 ring methyls (4 tertiary and 1 secondary) in VII. The most downfield resonance (0 84 ppm) is assigned to the C-4 α-Me which is the most deshielded of the angular methyls. On biogenetic grounds, the position of the secondary Me is either C-13 or C-14.[7,8] However, since this Me has almost identical chemical shift with the C-4 α-Me, its location on the C ring should be environmentally equivalent to that of the tertiary Me. Hence, it should be located at C-13 and with α-stereochemistry. We are then left with 3 unassigned Me resonances at δ 0.76 (3H) and 0.80 (6H) which we tentatively designate as follows δ 0.76 (C-4 β-Me), 0 80 (C-8 β-Me and C-10 β-Me).

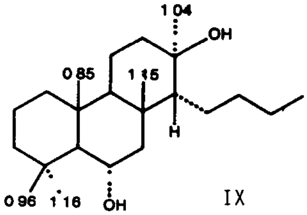
A reference natural product which could be correlated with VII is the tricyclic sesterterpenoid, cheilanthatriol, VIII which affords signals for five quaternary ring methyls at δ 0.86 (6H singlet) and δ 1.02, 1.12, 1.16 (3H singlet each).[7] We have evaluated the effects of 6α-hydroxyl (equatorial) and 13β-hydroxyl (axial) substituents on the Me resonances of VII by comparison with literature data for corresponding Me protons in compounds with analogous functionalization as well as identical ring junction configurations, Table 1. The five tertiary methyls of the hypothetical dihydroxy compound IX should resonate at ca 1 16, 1.15, 1.04, 0 96 and 0.85 ppm (3H each) which are in close agreement with the chemical shifts attributed to the ring methyls of cheilanthatriol (vide supra). The cause of the deviation of the anticipated resonance of the β-Me at C-4 in IX (0.96 ppm) from the corresponding signal for VIII (0.86 ppm) is not understood However, the possible effects of a 3-methyl-penten-2-ol C ring substituent on methyl resonances of IX were not taken into account in computing the chemical shifts Nevertheless, it is significant that zeorin X, which has the same trans-anti-trans geometry for the A,B,C rings as inferred for VII affords chemical shifts for the C-4 and C-10 methyls at 0.86, 0 98 and 1.17 ppm[9] which are almost identical to those predicted above for the corresponding ring methyl protons of the hypothetical dihydroxy tricyclic compound

Table 1 The effects of 6α-hydroxyl and 13β-hydroxyl substituents on the chemical shifts of the methyl protons of VII (C_{23} tricyclane).

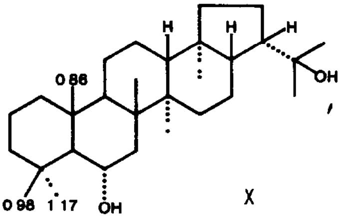
Methyl position	Inferred chemical shift (ppm)	Estimated shift due to 6α-OH (ppm)	Estimated shift due to 13β-OH (ppm)	Σ δ (ppm)	Structurally analogous interactions
4α	0.84	0 31	0 01	1 16	6α-OH/23 Me, olean-12-ene,[9] 3α-OH/18 Me, 5α 14α-androstanes[10]
4β	0.76	0.19	0 01	0.96	6α-OH/24 Me, olean-12-ene,[9] 4β-OH/18 Me, 5α 14α-androstanes[10]
8β	0 80	0 03	0.32	1 15	6α-OH/26 Me, olean-12-ene;[9] 2β-OH/25 Me, olean-12-ene [9]
10β	0.80	0 03	0.02	0 85	6α-OH/25 Me, olean-12-ene;[9] 2β-OH/26 Me, olean-12-ene [9]
13α	0.83	0	0 21	1.04	cf 6α-OH/27 Me, olean-12-ene,[9] 4β-OH/C-4α Me, 5α-selinanes[11,12]



VIII



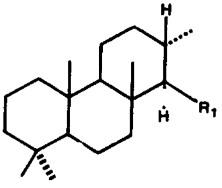
IX



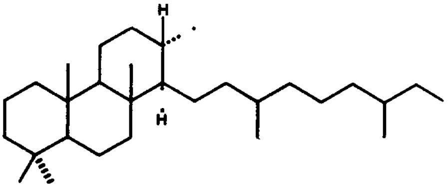
X

Therefore, peak 5b can be considered to represent a tricyclic alkane having the structure VII and is accordingly named 18,19-bisnor-13βH,14αH-cheilanthane. Its isomer, peak 5a, VI, is then 18,19-bisnor-13βH,14βH-cheilanthane. The basic carbocyclic structure of the entire tricyclane homologous series[1] then becomes XI with XII representing the C_{30} member.

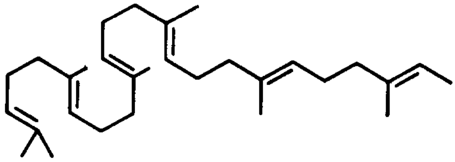
The most obvious biotic precursors of the C_{23} tricyclanes are therefore sesterterpenoids such as cheilanthatriol. However, in view of the fact that $>C_{25}$ tricyclic terpanes have now been detected from several different geological sources,[1,13] a common tricyclic triterpenoid precursor(s) for at least the C_{26}-C_{30} homologs cannot be ruled out at this stage. Specifically, we note that the carbon skeleton of structure XII, which is tentatively proposed for the C_{30} member occurring in the Lower Cretaceous Athabasca petroleum[1] can arise from the cyclization of the hexaisoprenoid XIII, synthesized either _via_ head to tail coupling of six isoprene units, or head to tail dimerization of two C_{15} units (cf. squalene biosynthesis[14]).



XI R_1 = H to R_1 = $C_{11}H_{23}$



XII



XIII

In a recent study Albrecht and coworkers[15] reported the identification of the lower members of tricyclic terpanes occurring in sediments and petroleums These were the 13β(H) monomethyl, 14α(H) monomethyl and 13β(H), 14α(H) dimethyl derivatives of the tetramethyl perhydrophenanthrane skeleton, in essential agreement with our own conclusions

Further work is in progress to determine the structure of functionalized tricyclic terpenoid derivatives isolated from the same Athabasca bitumen [16]

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