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EXTENDED HOPANE DERIVATIVES IN SEDIMENTS: IDENTIFICATION BY ^{1}H NMR

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Abstract: The sedimentary C$_{32}$ hopanoic acid 3a, one of the most abundant in nature and of probable bacterial origin, has been isolated for the first time as a single component and characterised by ^{1}H NMR. The 17αH,21βH configuration of the C$_{31}$ alkane has been similarly confirmed.

Triterpenoids of, or related to, the hopane skeleton (1) are ubiquitous components of sediments[1,2] and occur as three series (17βH,21βH; 17αH,21βH; 17βH,21αH). A variety of functional classes[3] is found as a range of extended (>C$_{30}$) and degraded (<C$_{30}$) compounds. When an extended derivative of the 17βH,21βH and 17αH,21βH series occurs in sediments as one C-22 epimer, it appears to have the 22R configuration. Assignment of configuration at C-22 for extended hopanes of the 17βH,21βH series in sediments has been based on g.l.c. and g.c.-m.s. comparison with standards[4]. The C-22 configuration of standards has been assigned from ^{1}H n.m.r. data and steric considerations. For example, the main difference for the C-22 epimers of 2 is the δ value (250 MHz) of the C-22 methyl substituent, 0.80 (22S) and 0.93 (22R)[5].

For the first time extended hopane derivatives have been isolated from a sediment in sufficient purity to enable n.m.r. analysis (270 MHz). A branched and cyclic acid fraction from a predominantly Sphagnum peat (Rostherne Mere, U.K.) was vacuum distilled as the methyl esters to provide the C$_{32}$ ester (3b, >95% purity, one C-22 epimer). Table 1 lists the methyl δ values for the compound and for 22R and 22S standards synthesised by a modification of a previous method[2] from 4 via the unsaturated esters 5, followed by reduction and transesterification.

Table 1. δ Values (ppm) for the isolated C$_{32}$ methyl ester (mp 169-176^{o}C) and 22R and S standards (mp 175-180^{o}C and 147-152^{o}C respectively).

SUBSTITUENT	ISOLATED COMPOUND	22R STANDARD	22S STANDARD
C-18 methyl	0.69 (3H,s)	0.70	0.69
C-4β methyl	0.78 (3H,s)	0.79	0.79
C-4α methyl	0.81 (3H,s)	0.81	0.81
C-10 methyl	0.84 (3H,s)	0.84	0.85
C-22 methyl	0.89 (3H,d,J=8Hz)	0.90	0.80
C-8,14 methyls	0.94 (6H,s)	0.94	0.96
$-\underset{\underset{O}{\Vert}}{C}-O-CH_3$	3.66 (3H,s)	3.66	3.66

Thus, the natural acid, of probable bacterial origin[5], is the same as the synthetic isomer assigned the 22R configuration. This confirms g.l.c. and g.c.-m.s. evidence for this and other sediments. The proposed precursor is 6 with the 22R configuration.

^{1}H n.m.r. analysis of the C$_{31}$ alkane (7) isolated from a deeper peat sample, confirmed the 17αH,21βH configuration[6]. Lack of standards in sufficient quantity prevented assignment of C-22 configuration, although the alkane appeared to be the 22R epimer (C-22 methyl substituent, 0.88 ppm). These studies emphasise the important contribution bacterial organic matter makes to sediments.

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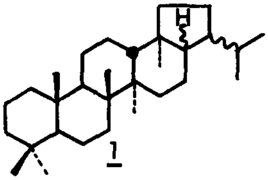

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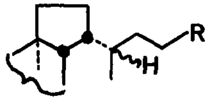
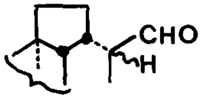


2 R = CH_2OAc
3a R = CO_2H
3b R = CO_2Me



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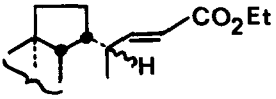
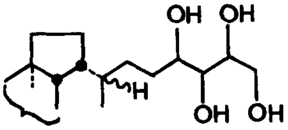


5a,b



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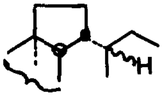

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5a E-29-ethoxycarbonylmethylidene-(22R)-hopane. mp 204-7°C; ν CCl_4 cm^{-1}: 1714,1645; nmr (100 MHz): methyl region 0.70 (3H,18α,s), 0.80 (3H,4β,s), 0.81 (3H,4α,s), 0.85 (3H,10β,s), 0.95 (6H,8β and 14α,s), 1.06 (3H,22R,d,J=6Hz), -O-CO-$\underline{CH_2}$- 4.18 (2H,q,J=7Hz), 5.68 (H,d,J=16Hz), 6.72 (H,d,J=16Hz,d,J=9Hz); ms: 496($M^{+\cdot}$,3), 481(2), 369(17), 275(46), 191(100); hrms: $M^{+\cdot}$ 496.4278, found 496.4273.

5b E-29-ethoxycarbonylmethylidene-(22S)-hopane. mp 171-4°C; ν CCl_4 cm^{-1}: 1714, 1645; nmr (100 MHz): methyl region 0.71 (3H,18α,s), 0.79 (3H,4β,s), 0.81 (3H,4α,s), 0.84 (3H,10β,s), 0.91 (3H,s), 0.93 (3H,s), 0.94 (3H,22S,d,J=6Hz), -O-CO-$\underline{CH_2}$- 4.18 (2H,q,J=7Hz), 5.71 (H,d,J=16Hz), 6.92 (H,d,J=16Hz,d,J=9Hz); ms: 496($M^{+\cdot}$,9), 481(8), 369(24), 275(46), 191(100); hrms: $M^{+\cdot}$ 496.4278, found 496.4273.

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