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NOVEL REARRANGED RING C MONOAROMATIC STEROID HYDROCARBONS IN SEDIMENTS AND PETROLEUMS

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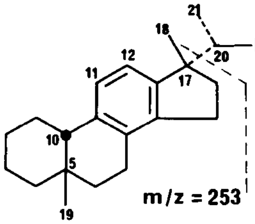
SUMMARY

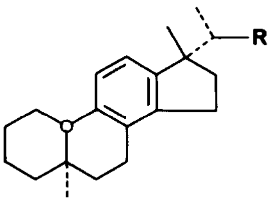
Two series of novel rearranged ring C monoaromatic steroid hydrocarbons (C_{21},C_{22}, C_{27}-C_{29}) occurring in sediments and petroleums have been characterised by synthesis of C_{21} and C_{27} homologues 1 and 2.

In the preceding article[1] we have described the synthesis of ring C monoaromatic steroid hydrocarbons occurring in geological samples. In these compounds the 19-CH_3 was preserved in the biological 10β configuration. However in many sediments and petroleums, additional components (C_{21},C_{22},C_{27}-C_{29}) often appear in the m/z = 253 and in the molecular chromatograms, as shown by chemical ionization GC-MS with apolar and polar capillary columns, using isobutane as a reactant gas. As most of these cases also correspond to the presence in substantial amounts of rearranged steranes (diasteranes)[2] in the alkane fractions, we suspected the two unknown series to be rearranged ring C monoaromatic steroid hydrocarbons bearing an angular methyl group at C-5 instead of C-10[3].

We would like to report that we have now confirmed this hypothesis by synthesis of C_{21} and C_{27} homologues of the two rearranged ring C monoaromatic steroid hydrocarbon series 1 and 2.



1



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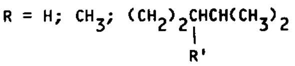

$R = H;\ CH_3;\ (CH_2)_2\underset{R'}{\underset{|}{C}}HCH(CH_3)_2$

$R' = H;\ CH_3;\ C_2H_5$

Intermediates 3 (R=H and R=isohexyl) (see preceding article) were used as starting materials (figure 1).

Typically, diene 3 (200 mg) was selectively hydrogenated to monoolefin 4, which was transformed into a mixture of epoxides 5. The latter was further treated with BF_3-Et_2O in benzene[4], which induced a methyl shift from C-10 to C-5 in approximately 50% yield. This reaction led to a 1/1 mixture of 5α and 5β-Me alcohols 6, implying that isomerisation of the chiral center at C-10 had taken place before methyl shift, due to electrophilic attack of the aromatic ring[5]. Hydrogenation of the 1(10) double bond of 6, oxidation of the alcohol and reduction of the ketone then led to a mixture of four isomers 7 which were separated into A/B cis (1 + 2) and trans (1' + 2') pairs by h.p.l.c. These pairs, easily recognisable by n.m.r., could only be distinguished by GC, the 5β-Me components being eluted first[6].

A similar approach applied to the (20R) C_{27} product 3 (R=isohexyl) led to the corresponding 5α and 5β-Me rearranged C_{27} compounds. In this case, however, removal of the alcohol function prior to hydrogenation of the 1(10) double bond allowed the separation of the 5α and 5β-Me intermediates by $AgNO_3/SiO_2$ t.l.c. (hexane). Furthermore, due to the longer side-chain the hydrogenation was totally selective in the 5α-Me series and led to the 10β(H) A/B trans component 2' exclusively.

Analytical and spectral data of final compounds and intermediates were in agreement with the described structures. Mass spectra of the rearranged standard hydrocarbons were identical with those of the non rearranged structures.

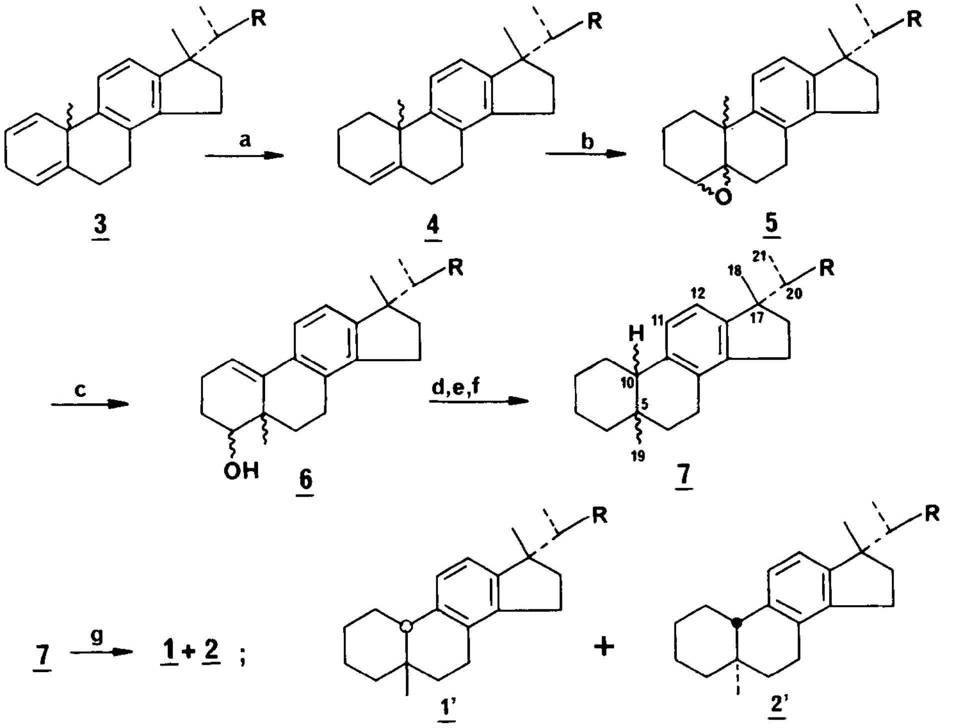

Figure 1. Synthetic scheme used for the preparation of ring C monoaromatic steroid hydrocarbons occurring in geological samples (1 and 2 ; R=H). a. $(PPh_3)_3RhCl$ b. m-CPBA c. BF_3-Et_2O, C_6H_6 d. H_2,Pd/C e. H_2SO_4,acetone f. N_2H_4,KOH g.h.p.l.c. RP18, MeOH

The following n.m.r. data were obtained (200 MHz; $CDCl_3$; δppm; JHz) :

1 + 2 (R=H) : 5,17β-dimethyl-18,19-binor-5β,10β-pregna-8,11,13-triene and 5,17β-dimethyl-18,19-binor-5α,10α-pregna-8,11,13-triene : 0.81(t,3H,J=7.5,21-CH_3); 0.88(s,3H,19-CH_3); 1.19 and 1.21(s,3H,18-CH_3); 6.86(A_2,H-11,H-12).

1' + 2' (R=H) : 5,17β-dimethyl-18,19-binor-5β,10α-pregna-8,11,13-triene and 5,17β-dimethyl-18,19-binor-5α,10β-pregna-8,11,13-triene : 0.75(s,3H,19-CH_3); 0.83(t,3H,J=7.5,21-CH_3); 1.21 (s,3H,18-CH_3); 6.89, 7.07(AB,J=8,H-12 and H-11).

1 (R=isohexyl) : 5,17β-dimethyl-18,19-binor-5β,10β-cholesta-8,11,13-triene : 0.71(d,3H,J=6.8, 21-CH_3); 0.87(d,6H,J=6.2,26-CH_3 and 27-CH_3); 0.86(s,3H,19-CH_3); 1.18(s,3H,18-CH_3); 2.65(m,4H); 6.84(A_2,H-12,H-11).

1' (R=isohexyl) : 5,17β-dimethyl-18,19-binor-5β,10α-cholesta-8,11,13-triene : 0.71(d,3H, J=6.8,21-CH_3); 0.87(d,6H,J=6.5,26-CH_3 and 27-CH_3); 0.74(s,3H,19-CH_3); 1.19(s,3H,18-CH_3); 2.65(m,4H); 6.85, 7.04(AB,J=8,H-12 and H-11).

2' (R=isohexyl) : 5,17β-dimethyl-18,19-binor-5α,10β-cholesta-8,11,13-triene : 0.68 (d,3H, J=7,21-CH_3); 0.86(d,6H,J=6.2,26-CH_3 and 27-CH_3); 0.73(s,3H,19-CH_3); 1.20(s,3H,18-CH_3); 2.66 (m,4H); 6.84, 7.05(AB,J=8.2, H-12 and H-11).

Only the compounds bearing an A/B cis junction 1 and 2 were identified with those occurring in geological samples. Indeed they are obviously more stable and easily formed by epimerisation of the benzylic position at C-10[7] from the corresponding trans isomers. The following criteria were used for their identification : identical mass spectra ; coelution on SE 30 (25m) capillary column in single ion fragmentography GC-MS (m/z = 253) and on Pluronic F 68 (50 m) in chemical ionization GC-MS with isobutane as a reactant gas,using the m/z = 253, 283 and 367 ions. The presence of homologues 1 (R=CH_3; R'=CH_3; C_2H_5) and 2 (R=CH_3; R'=H; CH_3; C_2H_5) was inferred from mass spectral and retention data.

An enriched fraction of C_{29} isomers from a carbonate sample containing only rearranged structures furnished further evidence for the identification of these series, since its n.m.r. spectrum displayed an identical signal for the H-11 and H-12 aromatic protons[8].

5β-Me rearranged ring C monoaromatic steroid hydrocarbons may be formed in the subsurface by aromatisation of rearranged sterenes occurring in many immature shales as a result of backbone rearrangement of Δ^4 or Δ^5-sterenes catalysed by clay minerals[9] (or during the rearrangement itself). On the other hand, their formation by a hydride abstraction from non rearranged structures during maturation cannot be excluded ; it would explain why in certain samples rearranged monoaromatics occur in the absence of rearranged steranes. In that respect, it is interesting to observe that treatment of non-rearranged monoaromatic standards with montmorillonite clay showed evidence for isomerisation of the chiral centers at C-5, C-10, C-17 and C-20 as a result of electrophilic attack of the aromatic ring, but no conversion into rearranged structures. The latter and the lack of 10α-Me products in geological samples make the occurrence of such a mechanism in the subsurface quite unlikely. The 5α-Me series may be formed from the 5β-Me isomers by a favored hydride abstraction at C-10 in the tertiary benzylic position and subsequent equilibration *via* spiro intermediates.

Tentative evidence for the presence of C_{27}-C_{29} 20S epimers of the rearranged monoaromatics may be inferred from the general occurrence of 20S epimers in other series and from retention data of products formed in simulation experiments with clay minerals which isomerise the various chiral centers. However, more conclusive evidence for the presence of 20S 5β-Me isomers has been obtained by other authors from n.m.r. data of aromatic products formed by dehydrogenation-isomerisation experiments of cholestane[10].

The occurrence of 5β-Me rearranged components is quite variable in sediments and crude oils, as compared with non rearranged structures. The 5α-Me rearranged products seem to be restricted to certain types of lithologies corresponding, in particular, to evaporitic carbonates. Further work on the geochemical significance of the relative distribution of the various families[1] (figure 2) is in progress.

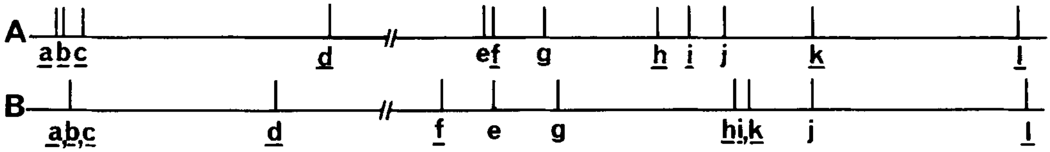

Figure 2.

Schematic GC distribution of C_{21} and C_{27} isomers of ring C monoaromatic steroids occurring in geological samples on polar and non polar column, as deduced from chemical ionization GC-MS ($i\text{-}C_4H_{10}$) :

A. CP Wax 57 CB, 51m x 0.32mm, 150-250°C, 1.5°C/min. B. OV 1, 25m x 0.32mm, 150-250°C, 3°C/min. a)$^*C_{21}$(5β,10β), b)$^*C_{21}$(5α,10α), c) C_{21}(5β), d) C_{21}(5α), e)$^*C_{27}$(20S,5β,10β), f) C_{27}(20S,5β), g)$^*C_{27}$(20S,5α,10α), h)$^*C_{27}$(20R,5β,10β), i) C_{27}(20R,5β), j)$^*C_{27}$(20R,5α,10α), k) C_{27}(20S,5α), l) C_{27}(20R,5α).(underlined letters = compounds identified by synthesis ; *rearranged structures).

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