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SYNTHESIS OF RING C MONOAROMATIC STEROID HYDROCARBONS OCCURRING IN GEOLOGICAL SAMPLES

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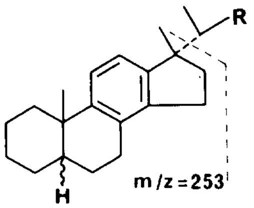
SUMMARY

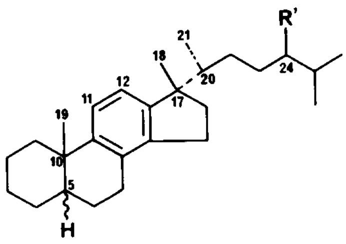
Several series of ring C monoaromatic steroid hydrocarbons (C_{21}, C_{22}, C_{27}-C_{29}) *widespread in sediments and petroleums have been identified by synthesis of the* C_{21}, C_{22} *and* C_{27} *homologues* (1 - 3) *obtained by reductive alkylation of the corresponding cyclopentanophenanthrenes.*

Steroids have been extensively used for tracing transformation reactions occurring in the subsurface[1,2]. These geochemical changes are due either to the action of microorganisms or to thermocatalytic effects in the process of petroleum formation[3]. Hydrogen transfer reactions leading to the aromatisation of molecules are quite common in the subsurface, but their nature and mechanism are still not well understood. A molecular study of components formed by aromatisation of biological precursors, such as steroids, may therefore bring quite useful information in this respect. Furthermore, since aromatic steroid hydrocarbons have found an increasing utilisation in problems related to petroleum formation and occurrence[4,5], their clear structural elucidation should induce a more rational use of these molecular parameters.

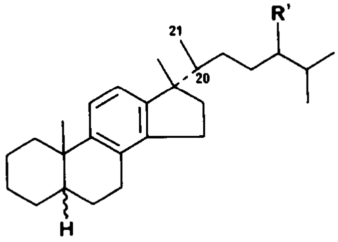
In this article we would like to report the identification by synthesis of the C_{21}, C_{22} and C_{27} homologues (1 - 3) of several series of ring C monoaromatic steroid hydrocarbons which are widespread in sediments and petroleums.



1 R = H ; CH_3
5α and 5β (H)



2 R' = H ; CH_3 ; C_2H_5
5α and 5β (H)



3 R' = H ; CH_3 ; C_2H_5
5α and 5β (H)

Ring C monoaromatic steroid hydrocarbons have been recognized in geological samples several years ago[6]. They are presumably formed in the subsurface either by rearrangement of polyunsaturated steroid precursors or by hydrogen transfer reactions undergone by more reduced species. These molecules occur as complex mixtures in the aromatic fractions and are best studied by GC-MS fragmentography of the major m/z = 253 ion formed by a highly favored cleavage of the side-chain in benzylic position. Molecular ions could only be obtained by chemical ionization MS using methane[7] or isobutane as reactant gas ; this technique showed that these series contained several isomers at C_{21}, C_{22} and C_{27}-C_{29}. The complexity of the mixtures is such that it prevented any attempt of isolation of pure compounds from geological samples for spectroscopical studies.

A rearranged structure containing a methyl group on the aromatic ring was first attributed to one series of homologues[8]. Later on, refinement of our analytical approach, structural elucidation of triaromatic steroids from geological sources[9], as well as preliminary results from a novel synthetic approach[10] led to a corrected structure where the C-18 methyl group is located on position C-17. The latter was ascribed independently at the same time on the basis of n.m.r. studies carried out on aromatic products formed during the acidic treatment of cholesta-3,5-diene[5] and by high temperature dehydrogenation reactions of saturated steranes[11].

The synthesis of ring C monoaromatic steroid hydrocarbons 1 - 3 (R=H, CH_3; R'=H) was performed with the C_{20}, C_{21} and C_{26} cyclopentanophenanthrenes 4 (20R), 5 (R=H; CH_3) and 6 (20S) as starting materials, compounds easily obtained by oxidation of the corresponding stera-3,5-dienes with phenanthrenequinone and chloranil[12] (figure 1).

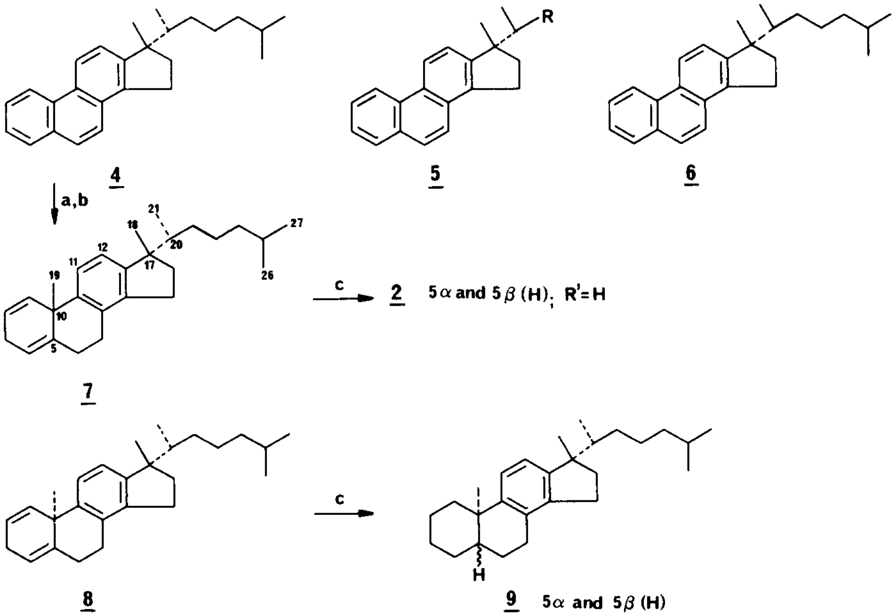


Figure 1. Synthetic scheme used for the preparation of ring C monoaromatic steroid hydrocarbons occurring in geological samples (compounds 2).
a. Li,NH_3 b. CH_3Br,THF c. Pd/C, MeOH.

Reduction of 4 (200 mg) with lithium in ammonia, followed by alkylation with methyl bromide according to a procedure described for phenanthrene[13] was totally regiospecific (yield : 70%) ; it led to the introduction of a methyl group at C-10 exclusively, the 10-β configuration being favored (10β/10α = 65/35). The two stereoisomers 7 and 8 were easily separated on $AgNO_3/SiO_2$ using hexane/ethyl acetate (9/1) as an eluent. They could be distinguished in n.m.r. spectroscopy by the chemical shifts of the C-18 and C-21 methyl groups which are differently affected by the dienic system in ring A, as confirmed on Dreiding models (10β isomer : 18-CH_3, δ=1.20 ppm ; 21-CH_3, 0.67 ; 10α isomer : 18-CH_3, 1.15, 21-CH_3, 0.73). Subsequent hydrogenations of 7 and 8 led to 2 [R'=H; 5α and 5β(H); 5:95] and 9 [5α and 5β(H); 70:30] respectively, which were separated by thin layer chromatography, using hexane as an eluent, into four compounds pure by GC.

Analytical and spectroscopical data of final compounds and intermediates were in agreement with the described structures. Compounds 2 and 9 displayed identical mass spectra : m/z = 143 (11%); 253 (100%).

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

2 (R'=H) : 17β-methyl-18-nor-5α-cholesta-8,11,13-triene : 0.69(d,3H,J=6.9,21-CH_3); 0.86 (d,6H,J=6.6,26-CH_3 and 27-CH_3); 1.08(s,3H,19-CH_3); 1.19(s,3H,18-CH_3); 2.63(m,4H); 6.84, 7.09(AB,J=8.2,H-12 and H-11).

2 (R'=H) : 17β-methyl-18-nor-5β-cholesta-8,11,13-triene : 0.68(d,3H,J=6.8,21-CH_3); 0.86 (d,6H,J=6.6,26-CH_3 and 27-CH_3); 1.20(s,3H,18-CH_3); 1.25(s,3H,19-CH_3); 2.61(m,4H); 6.85, 7.09(AB,J=8.1,H-12 and H-11).

9 (R'=H): 17β-methyl-18-nor-5α,10α-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); 1.21(s,3H,18-CH_3); 1.23(s,3H,19-CH_3); 2.62(m,4H); 6.85, 7.10(AB,J=8.2,H-12 and H-11).

9 (R'=H): 17β-methyl-18-nor-5β,10α-cholesta-8,11,13-triene : 0.72(d,3H,J=6.7,21-CH_3); 0.87(d,6H,J=6.2,26-CH_3 and 27-CH_3); 1.07(s,3H,19-CH_3); 1.20(s,3H,18-CH_3); 2.67(m,4H); 6.86, 7.12(AB,J=8.1,H-12 and H-11).

Compounds 2 [R'=H; 5α and 5β(H)] were identified with those occurring in geological samples by the following criteria : identical mass spectra ; coelution on SP 2250, SE 30 and OV 73 capillary columns (18m, 25m and 50m respectively) in GC-MS using single ion fragmentography (m/z = 253); coelution on OV 1 (25m) and Pluronic F 68 (50m) capillary columns in chemical ionisation GC-MS with isobutane as a reactant gas, using the m/z = 253 and 367 ($M+1^+$) fragmentograms. Homologues 2 (R'=CH_3; C_2H_5) were tentatively identified by extrapolation from mass spectral and retention data. Compounds 9 bearing the C-19 methyl group in the 10α-position were not detected in geological samples[14].

The same synthetic approach applied to cyclopentanophenanthrenes 5 and 6 led to the identification of the corresponding C_{21}, C_{22} and C_{27}(20S)[15] equivalents 1 (R=H; CH_3) and 3 (R'=H) which were shown to be present in geological samples following the same criteria. Again the presence of homologues 3 (R'=CH_3; C_2H_5) was inferred from mass spectral and retention data. In all cases the 10α isomers were not detected in subsurface samples.

Ring C monoaromatic steroid hydrocarbons are formed at a relatively early stage of sedimentation, but their distributions can vary depending on the mineral matrix, as shown by the predominance of rearranged structures bearing a methyl group at C-5 in certain types of environments[16]. Other changes, such as isomerisations at chiral centers [e.g. $5\alpha(H) \rightarrow 5\beta(H)$ more stable] or further aromatisation to triaromatic counterparts[5], take place due to thermocatalytic effects during maturation and can be used to reconstruct the thermal history of sediments.

Furthermore, this study constitutes a novel pathway for the synthesis of ring C monoaromatic steroids (possibly functionalised in ring A), which have mostly been prepared so far by rearrangement of precursors bearing a functionality at C-17[17].

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