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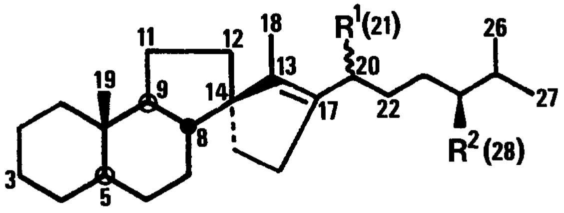
NATURALLY OCCURRING SPIRO STEROID HYDROCARBONS

T.M. Peakman, N.A. Lamb and J.R. Maxwell*
Organic Geochemistry Unit, School of Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

Abstract: The 20R and 20S isomers of 12,14α-cyclo-12,13-seco-5α(H)-cholest-13(17)-ene and the 24-methyl homologues occur widely in deep sea sediments; their presence is further evidence for the widespread occurrence of acid catalysed rearrangements in marine sediments.

The transformation pathways undergone by sterols with increasing burial depth in the sedimentary environment have been an area of interest in recent years and a wide variety of products with different skeletons and functionalities have been reported[1-7]. Steroid alkenes whose mass spectra showed a base peak at m/z 206 + 14n (n = 0-2) and an abundant ion at m/z 121 have been observed recently in Cretaceous black shales from the Deep Sea Sediment Program (DSDP Leg 50, Moroccan Basin; Leg 71, Falkland Plateau; Leg 75, Angola Basin)[8], in Miocene DSDP sediments (Leg 63, Southern California Bight)[9] and in Cretaceous black shales from northern Italy[10]. These features suggested that the compounds might be spirosterenes, since 12,14α-cyclo-12,13-seco-5α(H)-cholest-13(17)-ene (1:R^1=Me, R^2=H) and its 3β-acetoxy derivative have previously been synthesized[11,12], the stereochemistry at C-14 being inferred from mechanistic arguments. Both compounds were reported[12] to give major ions at m/z 206 (from $M^{+\cdot}$ by cleavage through C_{11}-C_{12} and C_8-C_{14}) and m/z 121 (from subsequent cleavage through C_{20}-C_{22}).

We have synthesized, therefore, the 20R (1:R^1=α-Me, R^2=H) and a mixture of the 20R and 20S (1:R^1=β-Me, R^2=H) isomers of 12,14α-cyclo-12,13-seco-5α(H)-cholest-13(17)-ene from 5α(H)-cholest-7-ene and the corresponding C_{28} homologues (1:R^1=α-Me, R^2=Me and 1:R^1=β-Me, R^2=Me) from (24S)-24-methyl-5α(H)-cholest-7-ene (5α(H)-ergost-7-ene). Treatment of an anhydrous toluene solution (0.025M) of the Δ^7-sterene with BF_3OEt_2 (20/1, v/v, 20 min., ambient) gave (cf. ref. 12) the 20R isomer in each case (1:20R, R^2=H and Me; 65% yield). Similar treatment with BF_3OEt_2 (10/1, v/v, 45 min., ambient) afforded a mixture of the 20R and 20S isomers (55:45; 20% yield, not separated). The desired products were isolated by Ag^+ thin layer chromatography on silica gel (5% $AgNO_3$, hexane developer, R_f ca. 0.2).



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The configuration at C-20 in each case was assumed by analogy with the acid catalysed formation of diasterenes[13] and by the fact that the presumed 20R isomer was the first to be formed. The mass spectra of the C_{27} compounds[14] (from gas chromatography-mass spectrometry, GC-MS, 20R isomer eluting before 20S on 50m OV1 and 30m SP2250 fused silica capillary columns) were essentially identical but the ^{1}H NMR spectra[15] showed differences in the chemical shift of the C-21 doublet which was shielded in the 20S isomer, as observed for diasterenes[13]. The key features of the methyl group resonances of the 20S isomer were obtained by computer subtraction of the spectrum of the 20R isomer from that of the mixture of 20R and 20S isomers. The C_{28} homologues were assigned by reference to the C_{27} compounds. Their mass spectra[16] were also essentially identical to each other, both being dominated by m/z 220 and 121. Their ^{1}H NMR spectra[17] exhibited, however, different chemical shifts for the protons at C-21, C-26, C-27 and C-28. The C-21 doublet again had a lower chemical shift in the 20S isomer whilst the C-28 doublet had a lower shift in the 20R isomer. The C-26 and C-27 protons were accidentally equivalent in the 20S isomer (as in both C_{27} isomers) but their magnetic inequivalence was apparent in the 20R isomer.

All four compounds occurred in Cretaceous black shales from the Angola Basin (DSDP Leg 75; e.g. Fig. 1a and b) as shown by GC-MS coinjection using single ion monitoring (m/z 121, 206 and 220) on two fused silica capillary columns (50m OV1, 50-275 @ 2^{o} min^{-1}; 30m SP2250, 50-220 @ 2^{o} min^{-1}). The C_{29} pseudo homologues were assigned from single ion monitoring (m/z 121 and 234), interpretation of mass spectra and retention times (Fig. 1c).

In these and other deep sea sediments the spirosterenes presumably arise by an acid catalysed rearrangement involving clay minerals[18] (cf. the formation of diasterenes from Δ^4- and Δ^5-sterenes[2], A-ring monoaromatic steroid hydrocarbons[3] and B-ring monoaromatic anthrasteroids[4]). Their precise origin is not certain, but they could arise in these sediments from Δ^7- or $\Delta^{8(14)}$-sterenes, although these alkenes have not been reported in marine sediments. Alternatively, they may result as minor products of the backbone rearrangement to diasterenes of Δ^4- and Δ^5-sterenes. The latter co-occur with the spiro compounds and with diasterenes; also they occur as minor products in the backbone rearrangement in the laboratory[19].

In two suites of Cretaceous black shales (Moroccan Basin and Falkland Plateau, see above) the 20R isomer, initially present alone, isomerises gradually to its 20S counterpart with increasing burial depth. Analogous behaviour was observed in the laboratory by treating the C_{27} and C_{28} Δ^7-sterenes with anhydrous TsOH/AcOH at 70^{o}C and monitoring, by GC, the spirosterene isomer abundances. An R to S ratio of ca. 1.2 was reached after 7 days.

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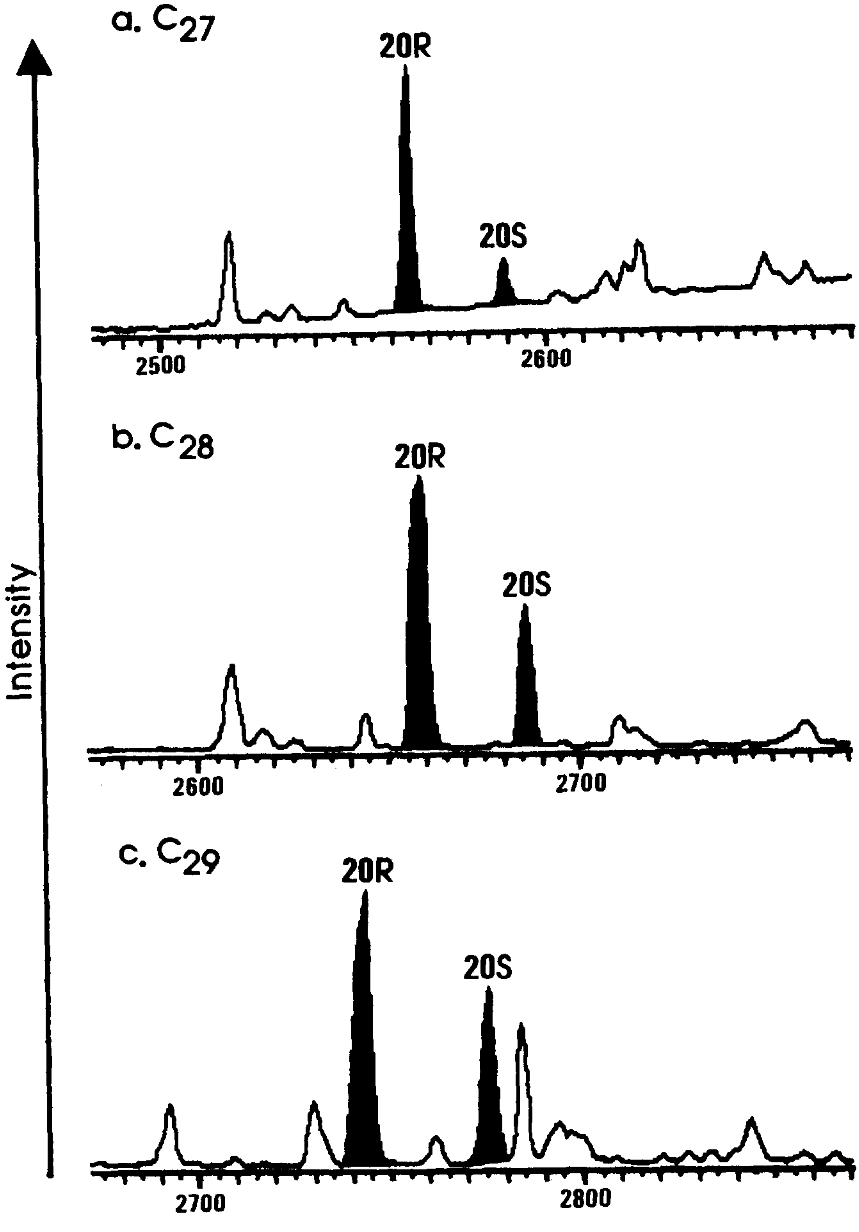

Figure 1 Mass chromatograms (50m OV1) showing spirosterenes (shaded) in a Cretaceous black shale, plotted against pseudo retention index: a. m/z 206 (C_{27}); b. m/z 220 (C_{28}); c. m/z 234 (C_{29}).

References and Notes

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14. $M^{+\cdot}$ 370 (1%); m/z 355 (<1%, $M^{+\cdot}$-Me); m/z 219 (15%, cleavage from $M^{+\cdot}$ through C_9-C_{11} and C_8-C_{14} ?); m/z 206 (100%, cleavage from $M^{+\cdot}$ through C_{11}-C_{12} and C_8-C_{14}); m/z 121 (63%, cleavage from m/z 206 through C_{20}-C_{22}).
15. δ ppm (200 MHz, $CDCl_3$). 20R isomer: 0.75 (3H, s, C-19); 0.84 (6H, d, J = 6½ Hz, C-26, 27); 0.93 (3H, d, J = 7 Hz, C-21); 1.47 (3H, s, C-18); *ca.* 2.5 (1H, m, C-20). 20S isomer: as for 20R isomer except 0.92 (3H, d, J = 7 Hz, C-21) instead of 0.93.
16. $M^{+\cdot}$ 384 (1%); m/z 369 (<1%, $M^{+\cdot}$-Me); m/z 233 (13%, cleavage from $M^{+\cdot}$ through C_9-C_{11} and C_8-C_{14} ?); m/z 220 (100%, cleavage from $M^{+\cdot}$ through C_{11}-C_{12} and C_8-C_{14}); m/z 121 (82%, cleavage from m/z 220 through C_{20}-C_{22}).
17. δ ppm (200 MHz, $CDCl_3$). 20R isomer: 0.75 (3H, s, C-19); 0.75 (3H, d, J = 6½ Hz, C-26); 0.77 (3H, d, J = 7 Hz, C-27); 0.82 (3H, d, J = 7 Hz, C-28); 0.94 (3H, d, J = 7 Hz, C-21); 1.47 (3H, s, C-18); *ca.* 2.5 (1H, m, C-20). 20S isomer: 0.75 (3H, s, C-19); 0.77 (6H, d, J = 7 Hz, C-26, 27); 0.83 (3H, d, J = 7 Hz, C-28); 0.93 (3H, d, J = 7 Hz, C-21); 1.47 (3H, s, C-18); *ca.* 2.5 (1H, m, C-20).
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