cis-Isomer of the C_{26} Marine Sterol 24,24-Dimethyl-5α-chol-22-en-3β-ol

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Summary The Δ^{22} *cis*- and *trans*-C_{26} sterols (**1**) and (**2**) from a Wittig synthesis have been separated; the properties of the *cis*-isomer (**1**) may be explained by the obstruction to the free rotation of the side chain.

THE Wittig reaction between isobutyltriphenylphosphonium bromide and 20*S*-3β-acetoxy-5α-bisnorcholan-20-al (butyl-lithium, heptane–ether 3:5) gives two 20*R*-C_{26} sterols in the proportion 3:2.[1] The minor sterol has been identified as 24,24-dimethyl-5α-chol-*trans*-22-en-3β-ol (**2**) m.p. 121—123°, $[\alpha]_D^{20} + 6 \pm 2°$.[1]†

The most abundant C_{26} sterol, has now been identified as the *cis*-isomer (**1**) m.p. 161—163°, $[\alpha]_D^{20} - 6{\cdot}5 \pm 2°$.† The mass spectra of the propionate shows the expected mole-

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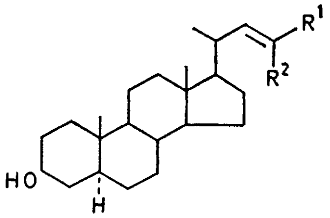
† Perkin-Elmer 141 polarimeter in $CHCl_3$.

cular ion at *m/e* 428, and the same fragmentations as for the propionate of (**2**), particularly concerning the side chain, due to the C(22) unsaturation. The i.r. spectrum is in agreement with the *cis*-structure (760 cm^{-1}, KBr). The only differences observed between the n.m.r. spectra of (**1**) and (**2**) are related to the 18-methyl (δ 0·70 instead of 0·67), the 21-methyl (δ 0·95 instead of 1·00), and the protons 22-H and 23-H which give signals at δ 4·95 and 5·10 (AB system *J* 2 Hz) instead of 5·22 and 5·30.



(1) R^1= H, R^2= Pr^i

(2) R^1= Pr^i, R^1= H

Reduction (H_2–Pd) leads to the corresponding stanol, identical in all respects with the stanol produced from (**2**) or from 24,24-dimethylchola-5,23-dien-3β-ol;[2] $[\alpha]^{20}_{D}$ + 10 ± 2°. †The observed differences in the rotatory powers of (**1**) and (**2**) are thus related to the stereochemistry at C(22) and C(23).

Molecular models indicate obstruction to free rotation of the side chain in the *cis*-isomer. It is supposed that the marked differences in the physical properties of (**1**) and (**2**) are connected with this observation. The separation of the two isomers (propionates) by t.l.c. on Al_2O_3–$AgNO_3$ may be related to the formation of different Ag complexes, the *cis*-isomer having the lower R_F value.

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[1] A. Métayer and M. Barbier, *Compt. rend., Ser C*, 1973, **276**, 201.
[2] A. Métayer, J. Viala, A. Alcaide, and M. Barbier, *Compt. rend., Ser. C.*, 1972, **274**, 662.