Table 1. Intramolecular nonhydrogen bond distances (Å) and angles(°). Estimated standard deviations are given in parentheses.

C(1)–C(2)	1.522(4)	C(1)–C(2)–C(3)	108.2(3)
C(2)–C(3)	1.522(5)	C(2)–C(3)–C(4)	112.4(3)
C(3)–C(4)	1.514(5)	C(3)–C(4)–C(5)	111.7(3)
C(4)–C(5)	1.534(4)	C(4)–C(5)–O(5)	109.4(3)
C(5)–C(6)	1.522(6)	C(5)–O(5)–C(1)	110.8(2)
C(8)–C(9)	1.538(8)	O(5)–C(1)–C(2)	107.9(3)
C(1)–O(1)	1.384(4)	C(4)–C(5)–C(6)	110.8(3)
C(7)–O(1)	1.428(5)	O(5)–C(5)–C(6)	107.0(3)
C(2)–O(2)	1.425(5)	C(5)–C(6)–O(6)	113.2(3)
C(3)–O(3)	1.423(4)	C(1)–O(1)–C(7)	112.4(3)
C(4)–O(4)	1.421(4)	C(6)–O(6)–C(8)	115.9(4)
C(1)–O(5)	1.429(4)	O(6)–C(8)–C(9)	111.5(4)
C(5)–O(5)	1.429(4)	O(6)–C(8)–O(7)	126.2(5)
C(6)–O(6)	1.423(5)	C(9)–C(8)–O(7)	122.3(5)
C(8)–O(6)	1.295(5)	O(1)–C(1)–O(5)	106.9(3)
C(8)–O(7)	1.184(6)	O(1)–C(1)–C(2)	109.4(3)
		C(1)–C(2)–O(2)	111.2(3)
		C(3)–C(2)–O(2)	108.1(3)
		C(2)–C(3)–O(3)	107.8(3)
		C(4)–C(3)–O(3)	110.2(3)
		C(3)–C(4)–O(4)	110.6(3)
		C(5)–C(4)–O(4)	108.0(3)

determinations were carried out by a computerized application of direct methods using the weighted phase-sum formula described by Norrestam.[6] Several cycles of full-matrix least-squares refinement (anisotropic nonhydrogen and fixed isotropic hydrogen temperature parameters) gave an R-value of 0.046. The molecular structure is shown in Fig. 1. Intramolecular distances and angles are listed in Table 1. Full details of the X-ray diffraction investigation will be published elsewhere.[7]

Acknowledgements. We are indebted to Professor Peder Kierkegaard and to Professor Bengt Lindberg for their interest. The work received financial support from Riksbankens Jubileumsfond, Hierta-Retzius Stipendiefond and Statens Naturvetenskapliga Forskningsråd.

1. Borén, H. B., Garegg, P. J., Kenne, L., Pilotti, Å., Svensson, S. and Swahn, C.-G. *Acta Chem Scand. 27* (1973) 2740.
2. Lemieux, R. U. and Stevens, J. D. *Can. J. Chem. 43* (1965) 2059.
3. Lemieux, R. U. and Martin, J. C. *Carbohyd. Res. 13* (1970) 139.
4. Lindberg, B., Garegg, P. J. and Swahn, C.-G. *Acta Chem. Scand. 27* (1973) 380.
5. Bouveng, H. O. *Acta Chem. Scand. 15* (1961) 87.
6. Norrestam, R. *Acta Crystallogr. 26* (1972) 303.
7. Lindberg, K. B. *To be published.*

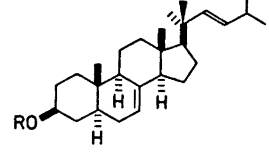
Received December 21, 1973.

Synthesis of Asterosterol, a Novel C_{26} Marine Sterol

PER M. BOLL

Department of Chemistry, Odense University, DK-5000 Odense, Denmark

Recently Kobayashi *et al.*[1,2] suggested structure *1a* for a new marine C_{26} sterol, asterosterol, isolated from several asteroids [3] and stated [1] that they had synthesized a 22-*cis* and -*trans* mixture of 24-*nor*-cholesta-7,22-dien-3β-ol, resistant to separation. Through the investigation of the sterol components of the marine sponge *Halicondria panicea* we have now found the same sterol present as a minor component.

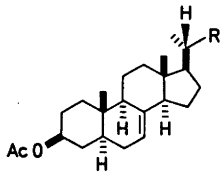


1a : R = H
1b : R = Ac

Due to the uncertainties associated with the stereochemistry at C-20 as well as the biogenetic novelty of the sidechain structure a final proof

of structure was desirable and a partial synthesis of asterosterol from 5α,6-dihydroergosterol has been developed.

5α,6-Dihydroergosterol acetate (*2b*) was ozonized at −70° in methylene chloride in the presence of pyridine followed by reductive work-up (Zn-AcOH). Preparative layer chromatography (hexane-ethyl acetate 9:1) gave 19 % unchanged starting material (*2b*) and 28 % of the pure aldehyde (*2a*) which showed, in the



2a : R = CHO
2b : R = trans-CH:CH·CHEt·CHMe$_2$

NMR spectrum,* the aldehyde proton as a doublet at 9.54 ppm. Acid work-up gives according to Barton *et al.*[4] an epimerized product with the aldehyde proton as two doublets at 9.55 and 9.60 ppm in the ratio of 4:1. Wittig reaction of the (20*S*)-aldehyde with isobutyltriphenylphosphonium bromide (butyllithium, heptane-ether 3:1) gave 46 % of the acetates of 22-*trans*-24-*nor*-5α-cholesta-7,22-dien-3β-ol (*1b*) and its 22-*cis*-isomer in the proportions 1:5. The separation of the two isomers was accomplished by TLC in hexane-benzene (3:1) on SiO_2-20 % $AgNO_3$.

The NMR spectrum of the synthetic 22-*trans*-isomer (*1b*), m.p. 171 − 173°, $[\alpha]_D^{25}$ −21.0° (lit.[2] m.p. 134 − 136.5°, $[\alpha]_D$ −2.8°), showed signals of 18-H_3 (δ 0.533, s), 19-H_3 (0.803, s), 26,27-H_6 (0.903, d, *J* 6.7), 21-H_3 (1.01, d, *J* 6.7), acetyl (2.00), 3-H (4.67, m) and 7-H, 22-H and 23-H (5.14, ill-defined). All NMR values were within the experimental error of those reported by Kobayashi *et al.*[2] The mass spectrum of the synthetic compound (*1b*) was identical with that published [2] and the IR spectrum, also as reported, was superimposable on that of 5α,6-dihydroergosterol acetate including the finger print region and showed absorption at 965 cm^{-1} (*trans*-disubstituted sidechain double bond). Hydrolysis of *1b* gave *1a* as needles from MeOH, m.p. 171 − 172°, $[\alpha]_D^{25}$ −23.9°, which displayed physical constants distinctly different from those reported (lit.[2] 129 − 130°, $[\alpha]_D \pm 0°$). Even taken into consideration the discrepancies in m.p. and specific rotation, the synthesis just reported clearly indicates that the structure assigned to asterosterol by Kobayashi *et al.*[2] is correct.

* Chloroform was used for NMR and optical rotation measurements. IR spectra were measured in KBr. All new compounds gave correct analyses.

The synthetic sterol acetate (*1b*) was identical with the acetylated natural material isolated from *Halicondria panicea*.

The mass spectrum of the 22-*cis* C_{26} sterol acetate, m.p. 145 − 145.5°, $[\alpha]_D^{25}$ −31.3°, showed the expected molecular ion at *m/e* 412. The fragmentation was the same as that of *1b*, also with respect to the side chain-fragments. The IR spectrum is in agreement with the *cis*-structure (766 cm^{-1}). The only differences observed between the NMR spectra of *1b* and its *cis*-isomer are related to 18-H_3 (0.559), 21-H_3 (0.969, d, *J* 6.4), 26, 27-H_6 (0.927, d, *J* 6.4), 22-H and 23-H (AB, 4.95, 5.07, *J* 2.1). Hydrolysis gave the free sterol, m.p. 137 − 138.5°, $[\alpha]_D^{25}$ −35.9°.

Reduction (H_2-Pd) of *1b* or its isomer leads to the same compound, the corresponding stanol, m.p. 129 − 134°, $[\alpha]_D^{25}$ +8.6° (lit.[5] 128 − 135°). The observed differences in the rotatory powers of *1b* and its isomer are thus related to the stereochemistry at C-22 and C-23.

Acknowledgement. The author is grateful to Dr. E. Caspi for helpful discussions during this work, which was carried out at the Worcester Foundation of Experimental Biology, Shrewsbury, Mass. He is also thankful to the Worcester Foundation and the Danish Science Research Council for support.

1. Kobayashi, M., Tsuru, R., Todo, K. and Mitsuhashi, H. *Tetrahedron Lett.* (1972) 2935.
2. Kobayashi, M., Tsuru, R., Todo, K. and Mitsuhashi, H. *Tetrahedron 29* (1973) 1193.
3. Smith, A. G., Rubinstein, I. and Goad, L. J. *Biochem. J. 135* (1973) 443.
4. Barton, D. H. R., Davies, P. J., Kempe, U. M., McGarrity, J. F. and Widdowson, D. A. *J. Chem. Soc. Perkin Trans. 1* (1972) 1231.
5. Métayer, A., Viala, J., Alcaide, A. and Barbier, M. *C. R. Acad. Sci. Ser. C 274* (1972) 662.

Received January 31, 1974.