Bünger & Viertel, 1984; Engelhardt & Viertel, 1982*a*,*b*; Engelhardt & Jürgens, 1980; Engelhardt & Hartl, 1975, 1976). Allerdings sind die N—N-Abstände [im Mittel 1,391 (6) Å] bedingt durch die Konjugation mit den Carbonylbindungen deutlich kürzer als in den analogen Ringen, wo Werte zwischen 1,40 und 1,42 Å gefunden wurden. Besonders kurze intermolekulare Kontaktabstände finden sich in der Struktur nicht.

Wir danken Herrn Kollegen H. Hartl für die freundliche Hilfe bei den Intensitätsmessungen. Dem Fonds der Chemischen Industrie gilt unser Dank für finanzielle Unterstützung.

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Structure and Crystallization Pattern of (20*S*)-3β,20-Dihydroxy-20-(2-pyridyl)-21-norallopregn-16-ene with Water Molecules

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Abstract. $C_{25}H_{35}NO_2.H_2O$, $M_r = 399.57$, monoclinic, $P2_1$, $a = 10.882$ (1), $b = 7.394$ (1), $c = 14.054$ (1) Å, $\beta = 94.52$ (1)°, $V = 1127.3$ (2) Å^3, $Z = 2$, $D_x = 1.18$ g cm^{-3}, λ(Cu $K\overline{\alpha}$) = 1.54247 Å, $\mu = 5.63$ cm^{-1}, $F(000) = 436$, room temperature, $R = 0.047$ for 1745 observed reflections. The steroid molecules correspond to a (20*S*) isomer. They are hydrogen bonded head-to-tail forming hydrophobic coils parallel to the *b* axis. Each steroid molecule also forms hydrogen bonds to two water molecules related by the twofold screw axis, resulting in small hydrophilic channels along **b**.

Introduction. In our previous work (Miljković, Gaši, Kindjer, Stanković, Ribár & Argay, 1985) we described partial syntheses of 21,27-bisnordemissi-

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dine and 21,27-bisnorsolanidine and unambiguously proved the final target structures by X-ray structure analysis.

In order to develop a new synthetic strategy towards 21,27-bisnorsolanidine derivatives, we examined the action of Ac_2O upon the *N*-oxide (1). Thus, by refluxing a solution of (1) in Ac_2O an inseparable mixture of the C(20) diasteroisomeric pair of diacetates (2) and (3) was formed. Treatment of this mixture with CH_3ONa in CH_3OH–benzene afforded the corresponding diols, (4) and (5), which could subsequently be separated on silica gel. Since compound (1) was prepared from 3*β*-acetoxy-5*α*-androstan-17-one whose absolute stereochemistry has been known for a long time (Fieser & Fieser, 1967), X-ray structure analysis of the suitably crystalline diol (4) revealed its absolute configuration as (20*S*), indicating indirectly the configuration of (5) as (20*R*). Based on this absolute stereochemistry of (4) and (5), the C(20) configurations of the diacetates (2) and (3) were readily obtained by NMR spectroscopy.

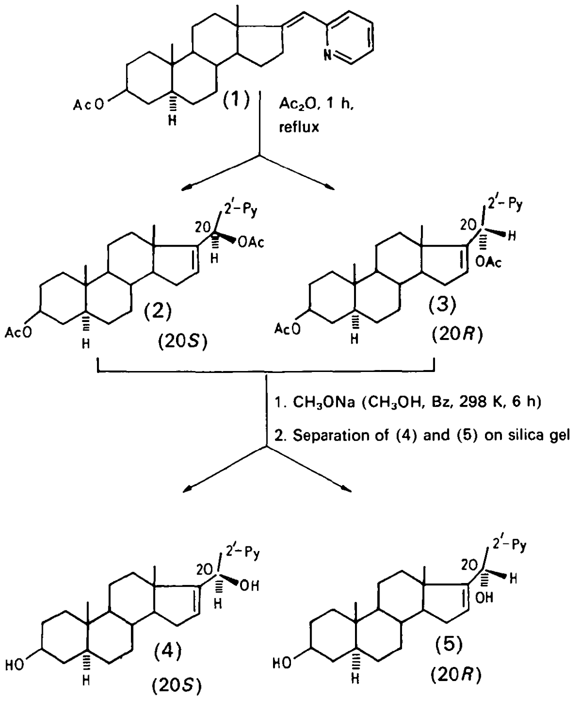

Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (× 10^3) *for non*-H *atoms*

$$U_{eq} = \tfrac{1}{3}[(U_{11} + U_{33})\sin^{-2}\beta + U_{22} + 2U_{13}\sin^{-2}\beta\cos\beta].$$

	x	*y*	*z*	U_{eq}(Å²)
O(1)	170 (3)	1343 (8)	993 (2)	52 (1)
O(2)	−2485 (3)	4418 (2)	9097 (2)	68 (1)
C(1)	−827 (4)	484 (8)	3445 (3)	45 (1)
C(2)	−526 (4)	101 (9)	2410 (3)	48 (1)
C(3)	−93 (4)	1808 (9)	1945 (3)	43 (1)
C(4)	−1055 (4)	3293 (9)	1970 (3)	44 (1)
C(5)	−1323 (4)	3674 (8)	3016 (3)	40 (1)
C(6)	−2178 (4)	5301 (9)	3107 (3)	50 (1)
C(7)	−2296 (4)	5764 (8)	4151 (3)	47 (1)
C(8)	−2710 (3)	4140 (9)	4730 (3)	39 (1)
C(9)	−1854 (4)	2505 (8)	4592 (3)	35 (1)
C(10)	−1794 (3)	1974 (8)	3530 (3)	35 (1)
C(11)	−2116 (4)	903 (9)	5255 (3)	45 (1)
C(12)	−2101 (4)	1479 (9)	6319 (3)	46 (1)
C(13)	−3008 (4)	3033 (9)	6431 (3)	40 (1)
C(14)	−2633 (4)	4583 (8)	5790 (3)	39 (1)
C(15)	−3265 (4)	6264 (9)	6181 (3)	54 (1)
C(16)	−3146 (4)	5820 (9)	7230 (3)	54 (1)
C(17)	−2940 (4)	4050 (9)	7386 (3)	43 (1)
C(18)	−4348 (4)	2382 (9)	6204 (3)	54 (1)
C(19)	−3048 (4)	1311 (9)	3085 (3)	52 (1)
C(20)	−2704 (4)	3156 (9)	8343 (3)	48 (1)
C(21)	−3804 (4)	2029 (9)	8596 (3)	49 (1)
C(22)	−4945 (4)	2812 (11)	8652 (3)	67 (2)
C(23)	−5900 (5)	1728 (14)	8936 (4)	82 (2)
C(24)	−5680 (6)	−73 (14)	9120 (4)	85 (2)
C(25)	−4527 (6)	−760 (11)	9017 (4)	82 (2)
N	−3580 (4)	261 (9)	8773 (3)	65 (1)
O*W*	1313 (4)	4069 (9)	190 (3)	88 (1)

Experimental. 3*β*-Acetoxy-17-picolinylidene-5*α*-androstane *N*-oxide (1) was synthesized from dehydroepiandrosterone acetate in four steps (Gaši & Miljković, 1988). By refluxing (1) in Ac_2O for 1 h an inseparable mixture of the derivatives (2) and (3) was obtained with a total yield of 89.5%. The corresponding dihydroxy compounds, (4) and (5), were obtained by treatment of this mixture with CH_3ONa in CH_3OH–benzene at 298 K for 6 h. Separation on a silica gel column (benzene–ethyl acetate 2:1), followed by recrystallization from ethyl acetate–*n*-hexane (4:1) afforded pure transparent crystals of compound (4) (m.p. 451–453 K; TLC silica gel, Bz–EtOAc = 2:1, $R_f = 0.3$; calculated for $C_{25}H_{35}NO_2$: C 78.68, H 9.25%, found: C 78.16, H 9.22%) in a yield of 44% and compound (5) (m.p. 452–453 K, TLC silica gel, Bz–EtOAc = 2:1, $R_f = 0.2$; calculated for $C_{25}H_{35}NO_2$: C 78.68, H 9.25%, found: C 78.29, H 9.10%) in a yield of 37%.

The selected crystal of compound (4) with dimensions 0.26 × 0.36 × 0.60 mm was mounted on an Enraf–Nonius CAD-4 diffractometer. Crystallographic data and intensities were measured using graphite-monochromated Cu $K\bar{\alpha}$ radiation. The lattice parameters were obtained from 25 reflections with $11 < \theta < 35°$. Scan range $1 < 2\theta < 120°$, ω–2θ scan, h −12 to 12, k 0 to 8, l 0 to 15. Three standard reflections ($\bar{5}11$, $\bar{4}12$, 116) remained constant throughout the data collection. Of 1828 independent reflections, 1745 with $I > 3\sigma(I)$ were considered as observed and used for calculations. Only Lorentz and polarization corrections were applied.

Structure solution by direct methods using *SHELXS*86 (Sheldrick, 1986). Anisotropic refinement for all non-H atoms, 31 H atoms placed at stereochemically expected positions and refined as riding groups, four H atoms [H(O1), H(O2), H(O*W*1) and H(O*W*2)] found in difference Fourier map and refined with isotropic vibration parameters. Refinement on *F*, unit weights, 278 parameters, using

Table 2. *Bond lengths* (Å), *bond angles* (°) *selected torsion angles* (°), *ring-puckering parameters* (Å, °) *and hydrogen bonds* (Å, °) *with e.s.d.'s in parentheses*

O(1)—C(3)	1.432 (5)	C(11)—C(12)	1.554 (6)
O(2)—C(20)	1.418 (7)	C(12)—C(13)	1.531 (8)
C(1)—C(2)	1.542 (6)	C(13)—C(14)	1.533 (8)
C(1)—C(10)	1.535 (7)	C(13)—C(17)	1.535 (7)
C(2)—C(3)	1.513 (9)	C(13)—C(18)	1.545 (6)
C(3)—C(4)	1.519 (8)	C(14)—C(15)	1.543 (8)
C(4)—C(5)	1.547 (6)	C(15)—C(16)	1.506 (6)
C(5)—C(6)	1.532 (8)	C(16)—C(17)	1.343 (9)
C(5)—C(10)	1.557 (8)	C(17)—C(20)	1.502 (7)
C(6)—C(7)	1.522 (6)	C(20)—C(21)	1.523 (7)
C(7)—C(8)	1.538 (8)	C(21)—C(22)	1.378 (7)
C(8)—C(9)	1.548 (8)	C(21)—N	1.349 (9)
C(8)—C(14)	1.521 (6)	C(22)—C(23)	1.395 (10)
C(9)—C(10)	1.550 (6)	C(23)—C(24)	1.374 (14)
C(9)—C(11)	1.547 (8)	C(24)—C(25)	1.372 (10)
C(10)—C(19)	1.536 (6)	C(25)—N	1.344 (9)

C(2)—C(1)—C(10)	113.8 (4)	C(12)—C(13)—C(14)	107.3 (4)
C(1)—C(2)—C(3)	110.5 (4)	C(12)—C(13)—C(17)	118.1 (4)
O(1)—C(3)—C(2)	107.2 (4)	C(12)—C(13)—C(18)	110.5 (4)
O(1)—C(3)—C(4)	112.6 (4)	C(14)—C(13)—C(17)	98.7 (4)
C(2)—C(3)—C(4)	110.7 (4)	C(14)—C(13)—C(18)	113.7 (4)
C(3)—C(4)—C(5)	109.6 (4)	C(17)—C(13)—C(18)	108.2 (4)
C(4)—C(5)—C(6)	112.6 (4)	C(8)—C(14)—C(13)	114.7 (4)
C(4)—C(5)—C(10)	112.8 (4)	C(8)—C(14)—C(15)	122.1 (4)
C(6)—C(5)—C(10)	111.8 (4)	C(13)—C(14)—C(15)	104.3 (4)
C(5)—C(6)—C(7)	110.8 (4)	C(14)—C(15)—C(16)	99.6 (4)
C(6)—C(7)—C(8)	112.6 (4)	C(15)—C(16)—C(17)	111.9 (5)
C(7)—C(8)—C(9)	109.8 (4)	C(13)—C(17)—C(16)	109.8 (5)
C(7)—C(8)—C(14)	110.7 (4)	C(13)—C(17)—C(20)	124.1 (4)
C(9)—C(8)—C(14)	107.7 (4)	C(16)—C(17)—C(20)	126.1 (5)
C(8)—C(9)—C(10)	113.0 (4)	O(2)—C(20)—C(17)	112.7 (4)
C(8)—C(9)—C(11)	112.4 (4)	O(2)—C(20)—C(21)	105.9 (4)
C(10)—C(9)—C(11)	114.2 (4)	C(17)—C(20)—C(21)	111.6 (4)
C(1)—C(10)—C(5)	106.9 (4)	C(20)—C(21)—C(22)	120.8 (5)
C(1)—C(10)—C(9)	109.8 (4)	C(20)—C(21)—N	116.1 (5)
C(1)—C(10)—C(19)	109.4 (4)	C(22)—C(21)—N	123.2 (5)
C(5)—C(10)—C(9)	106.4 (4)	C(21)—C(22)—C(23)	118.0 (6)
C(5)—C(10)—C(19)	112.5 (4)	C(22)—C(23)—C(24)	119.2 (7)
C(9)—C(10)—C(19)	111.7 (4)	C(23)—C(24)—C(25)	119.1 (7)
C(9)—C(11)—C(12)	112.4 (4)	C(24)—C(25)—N	123.0 (6)
C(11)—C(12)—C(13)	110.3 (4)	C(21)—N—C(25)	117.4 (5)

O(1)—C(3)—C(2)—C(1)	179.8 (4)	C(2)—C(1)—C(10)—C(19)	67.6 (5)
O(1)—C(3)—C(4)—C(5)	178.0 (4)	C(11)—C(12)—C(13)—C(18)	67.0 (5)
O(2)—C(20)—C(17)—C(13)	170.2 (4)	C(13)—C(17)—C(20)—C(21)	−70.7 (6)
O(2)—C(20)—C(17)—C(16)	−11.2 (7)	C(16)—C(17)—C(20)—C(21)	107.9 (6)
O(2)—C(20)—C(21)—C(22)	64.1 (6)	C(17)—C(20)—C(21)—C(22)	−58.9 (7)
O(2)—C(20)—C(21)—N	−114.8 (5)	C(17)—C(20)—C(21)—N	122.2 (5)

Ring-puckering parameters

Ring	Q (Å)	θ (°)	φ (°)
A	0.587 (7)	178.0 (6)	2 (9)
B	0.590 (7)	175.0 (6)	132 (7)
C	0.586 (7)	174.6 (6)	76 (7)
D	0.395 (7)	—	29 (1)

Hydrogen bonds

X	H	Y		X—H	H···Y	X···Y	X—H···Y
O(1)	H(1)	O*W*	x, y, z	0.72 (6)	1.97 (6)	2.665 (8)	165.1
O*W*	H(O*W*1)	N	$-x, \frac{1}{2}+y, 1-z$	0.98 (6)	1.99 (5)	2.902 (6)	154.0
O*W*	H(O*W*2)	O(1)	$-x, \frac{1}{2}+y, -z$	0.92 (7)	1.88 (7)	2.788 (7)	167.3
O(2)	H(2)	O(1)	$-x, \frac{1}{2}+y, 1-z$	1.03 (6)	1.90 (6)	2.905 (6)	163.8

*SHELX*76 (Sheldrick, 1976), gave $R = 0.047$; maximum and minimum peak heights in final $\Delta\rho$ map were 0.17 and -0.18 e Å^{-3}; $(\Delta/\sigma)_{\max} = 0.60$ (for water molecule 1.10). Scattering factors are as in *SHELX*76. The final atomic positions for the non-H atoms are listed in Table 1.*

Discussion. The molecule is illustrated in Fig. 1. Interatomic distances and bond angles are given in Table 2. Their values are in good agreement with those in other steroid molecules, where, in particular, C(14)—C(13)—C(17) = 99.2 (22) and C(8)—C(14)—C(15) = 119.3 (19)°, as a result of the fusion of five- and six-membered rings at the C(13)—C(14) bond (Duax, Weeks & Rohrer, 1976).

The six-membered ring *A* has an almost ideal 5α-chair conformation, while rings *B* and *C* adopt a slightly distorted chair conformation, as their ring-puckering coordinates show (Cremer & Pople, 1975; Table 2). They are all *trans* fused. The five-membered ring *D* exhibits a 14α-envelope conformation. The

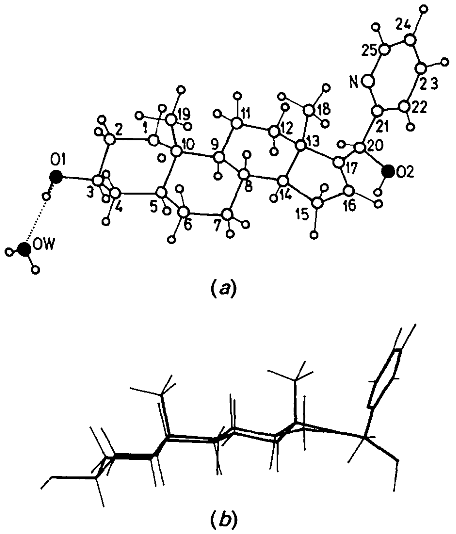

Fig. 1. (*a*) A perspective view of the hydrogen-bonded steroid and the water molecules. The numbers are for C atoms unless otherwise indicated. (*b*) The conformation of the steroid skeleton. The view of the molecule is parallel to the least-squares plane of atoms C(1)—C(17).

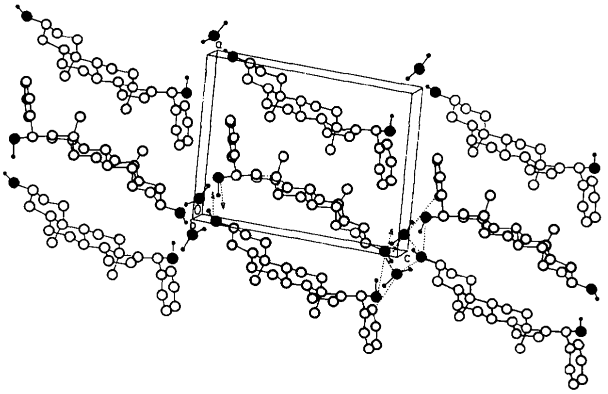

Fig. 2. The packing arrangement looking down the *b* axis. Hydrogen bonds are indicated by dotted lines.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54517 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distance of C(14) with respect to the plane formed by C(13), C(15), C(16) and C(17) is 0.604 (4) Å. The atoms C(13), C(16), C(17) and C(20) lie in the same plane. O(2) is displaced 0.230 (2) Å from this plane and the pyridine ring plane is almost perpendicular to it [at 81.0 (1)°]. The torsion angles (Table 2) around C(20) define a (20*S*) isomer of the steroid molecule (Fig. 1*b*). The twist along the length of the steroid molecule is negligible [C(19)—C(10)···C(13)—C(18) = 1.8 (4)°].

The packing arrangement (Fig. 2) shows screw-axis-related steroid molecules with head-to-tail hydrogen bonds through O(2)—H(2)···O(1). The columns thus formed, parallel to **b**, are hydrophobic. At the same time O(1) and O*W* are linked through hydrogen bonds forming a hydrophilic column up the *b* axis.

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Structure of the Head-to-Tail *cis-anti-cis* Photodimer of 2-Methylbenzo[*b*]thiophene 1,1-Dioxide

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Abstract. *r*-1,*c*-2,*t*-3,*t*-4-Di(2′,3′-benzothiophene 1,1-dioxide)-1,3-dimethylcyclobutane (alternative name: 5a,10a-dimethyldibenzo[*d*:*d*′]cyclobuta[1,2-*b*:4,3-*b*′]-dithiophene 5,5,10,10-tetraoxide), $C_{18}H_{16}O_4S_2$, $M_r = 360.4$, monoclinic, $P2_1/a$, $a = 6.918\ (1)$, $b = 12.270\ (1)$, $c = 9.283\ (1)$ Å, $\beta = 104.13\ (2)°$, $V = 764.1\ (2)$ Å^3, $Z = 2$, $D_x = 1.56$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1.54178$ Å, $\mu = 3.29$ mm^{-1}, $F(000) = 376$, $T = 293$ K, $R = 0.051$ for 1357 observed reflections. The molecular structure shows no significant differences in bond lengths and bond angles between the two benzo[*b*]thiophene groups. A crystallographic centre of symmetry coincides with the cyclobutane ring and this dimer possesses a *cis-anti-cis* structure.

Introduction. Photodimerization of 2-methylbenzo[*b*]thiophene 1,1-dioxide in benzene solution was first reported by Hopkinson, Schloman, Plummer, Wenkert & Raju (1979) and El Amoudi El Faghi, Geneste & Olivé (1981). Two photodimers were identified as being of the cyclobutane type and a specific stereochemistry, head-to-head and head-to-tail *cis-anti-cis*, was assigned to each dimer on the basis of ^{1}H and ^{13}C NMR. The first X-ray structure of a head-to-tail dimer, the *cis-syn-cis* isomer, was reported by El Amoudi El Faghi, Geneste, Olivé, Rambaud & Declercq (1987). This photodimer was obtained from irradiation of 2-methylbenzo[*b*]thiophene 1,1-dioxide in the solid state. In this article we report the X-ray structure of the head-to-tail dimer, *cis-anti-cis*, obtained by photodimerization of the same reactant in solution (Hopkinson *et al.*, 1979; El Amoudi El Faghi *et al.*, 1981).

Experimental. Colourless prismatic shaped crystals from chloroform at room temperature. Lattice

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