Discussion. La Fig. 1 représente la molécule en perspective avec la numérotation des atomes. On observe sur l'atome C17 la présence du méthyle C18 en position β et de la chaîne diméthyl-1,5 hexyle en position α. Le groupe spatial n'admettant la présence que d'un seul énantiomère, on peut être certain que la migration stéréospécifique du méthyle C18 n'a pas été suivie de réactions d'épimérisation secondaires. L'atome C20 conserve bien la configuration 20*R* du stéroïde d'origine, ce qui confère à cette molècule la configuration absolue 17*S*, 20*R*. Dans la conformation cristalline de la molécule, le méthyle C21 se situe en position *trans* par rapport au méthyle C18. L'ensemble des quatre cycles est remarquablement plan, l'écart maximum au plan moyen des trois cycles aromatiques étant celui de l'atome C16 de $-0{,}18\,(1)$ Å [C17: $-0{,}09\,(1)$, C15 et C14: $-0{,}05\,(1)$, C13: $-0{,}04\,(1)$ Å]. Par rapport à ce même plan moyen, les méthyles C18 et C21 se situent respectivement à 1,18 (1) et $-2{,}63\,(1)$ Å. La chaîne diméthyl-1,5 hexyle se déploie en position étendue, les atomes les plus éloignés C25, C26 et C27 étant distants de $-3{,}75$, $-3{,}61$ et $-4{,}00\,(2)$ Å du plan moyen précédent. L'assemblage des molécules dans le cristal est assuré par des contacts de van der Waals normaux.

Références

DANNENBERG, H. & NEUMANN, H. G. (1964). *Justus Liebigs Ann. Chem.* **675**, 109–125.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99–149. Birmingham: Kynoch Press. (Distributeur actuel Kluwer Academic Publishers, Dordrecht.)

LUDWIG, B., HUSSLER, G., WEHRUNG, P. & ALBRECHT, P. (1981). *Tetrahedron Lett.* **22**, 3313–3316.

RICHE, C. (1982). Program *DEVIN*. Seventh European Crystallographic Meeting, Jerusalem, Abstr. p. 25.

RIOLO, J. & ALBRECHT, P. (1985). *Tetrahedron Lett.* **26**, 2701–2704.

RIOLO, J., LUDWIG, B. & ALBRECHT, P. (1985). *Tetrahedron Lett.* **26**, 2697–2700.

SHELDRICK, G. M. (1976). *SHELX76*. Programme pour la détermination des structures cristallines. Univ. de Cambridge, Angleterre.

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Stereochemical Studies. 123.* Structures of (I) *cis-transoid-cis*-Hexahydro- and (II) *cis-cisoid-cis*-Hexahydro-5,8-methano-4*H*-3,1-benzoxazine-2(1*H*)-thione

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Abstract. $C_9H_{13}NOS$, $M_r = 183·27$. The title formula has two steric structures, di-*endo* (I) and di-*exo* (II). Compound (I): triclinic, $P\bar{1}$, $a = 12·648\,(3)$, $b = 10·617\,(2)$, $c = 7·359\,(2)$ Å, $\alpha = 86·77\,(2)$, $\beta = 97·24\,(2)$, $\gamma = 110·93\,(3)°$, $V = 915·6\,(4)$ Å^3, $Z = 4$, $D_x = 1·329$ Mg m^{-3}, m.p. 438–439 K, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 2·608$ mm^{-1}, $F(000) = 392$, $T = 293$ K, final $R = 0·0395$ for 2241 observed reflections. Compound (II): monoclinic, $P2_1/c$, $a = 6·889\,(2)$, $b = 14·932\,(5)$, $c = 9·108\,(3)$ Å, $\beta = 108·71\,(2)°$, $V = 887·4\,(3)$ Å^3, $Z = 4$, $D_x = 1·371$ Mg m^{-3}, m.p. 429–431 K, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·265$ mm^{-1}, $F(000) = 392$, $T = 293$ K, final $R = 0·072$ for 1241 observed reflections. The molecules in the two compounds have the expected bond lengths and angles and form dimers connected through N—H···S hydrogen bonds with lengths and angles: N···S = 3·322 (3), H···S = 2·301 (2) Å, 157·2 (2)°, molecule *A*; and 3·348 (5), 2·466 (4) Å, 159·5 (3)°, molecule *B* in com-

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* Part 122: Kapor, Ribar, Divjaković, Stájer, Bernáth & Argay (1987).

pound (I); and 3·383 (6), 2·474 (5) Å, 141·0 (4)° in compound (II). The conformation of the 3,1-benzoxazine ring is envelope E_4 in both compounds.

Introduction. The compounds studied were obtained within the framework of the synthesis of the derivatives of 1,3-oxazine, fused with norbornane and norbornene structural units, described by Stájer, Szabó, Fülöp, Bernáth & Sohár (1983). Treatment of the *endo*- and *exo*-1,3-aminoalchohols with carbon disulfide furnished the methylene-bridged tetrahydro- and hexahydro-3,1-benzoxazin-2-thiones *via* dithiocarbamates. Pharmacological investigations indicate retarded anti-inflammatory and analgesic action after the introduction of norbornane and norbornene units (Bernáth *et al.*, 1977). The determination of the structure of new synthesized derivatives can be useful in systematic pharmacological studies and as models in structure–activity relationship investigations.

Experimental. Unit-cell parameters and reflection intensities were measured by a Philips PW 1100 automatic diffractometer with graphite-monochromated Cu $K\alpha$ radiation for compound (I) and Mo $K\alpha$ radiation for compound (II). The unit-cell parameters were obtained from least-squares analysis of 18 reflections in the range $16 < \theta < 25°$ (I) and 20 reflections in the range $6 < \theta < 12°$ (II) respectively. Intensity data were collected for a colourless needle-shaped crystal 0·41 × 0·12 × 0·08 mm (I) and colourless irregular-shape crystals with approximate dimensions 0·55 × 0·27 × 0·25 mm (II). Independent reflections were measured with the θ–2θ scanning technique, scan width 1·60 (I) and 1·80° (II) and scan speed 0·04 (I) and 0·06° s^{-1} (II). 2533 reflections were collected for (I) with h: −15 to 15, k: −12 to 12, l: 0 to 8, $2\theta_{max} = 130°$; 1395 reflections were measured for (II) with h: −9 to 9, k: 0 to 20, l: 0 to 12, $2\theta_{max} = 60°$. Subsequent calculations involved 2241 (I) and 1241 (II) intensity data with $I > 2{\cdot}5\sigma(I)$ for (I) and $I > 1{\cdot}5\sigma(I)$ for (II). 3 standard reflections, no intensity variation. Neither absorption nor extinction corrections were applied. Structures were solved by *SHELX*76 (Sheldrick, 1976). Full-matrix refinement on $\sum w(\Delta F)^2$ with anisotropic non-H atoms [230 parameters in (I) and 110 parameters in (II)]. Positions of H atoms were generated from the assumed geometries, checked in Fourier maps and refined in the riding mode with an overall isotropic temperature factor of 0·0807 (I) and 0·0632 Å^2 (II). Final $R = 0{\cdot}0395$, $wR = 0{\cdot}0468$, $w = [\sigma^2(F) + 26{\cdot}26 \times 10^{-4}(F)^2]^{-1}$ (I) and $R = 0{\cdot}0718$, $wR = 0{\cdot}0746$, $w = 2{\cdot}7496[\sigma^2(F) + 1{\cdot}27 \times 10^{-4}(F)^2]^{-1}$ (II). The value of the R factor for (II) reflects the poor quality of the crystal samples. Difference Fourier maps showed no significant peaks [in (I) max. 0·21, min. −0·26 e Å^{-3}; in (II) max. 0·52, min. −0·42 e Å^{-3}]. The average shift to e.s.d. ratio Δ/σ is ≤0·108 (I) and ≤ 0·038 (II). Scattering factors as in *SHELX*76. All calculations were performed on an IBM 43/41 computer.

Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (× 10^3) *with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\textstyle\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq} (Å^2)
Compound (I)				
S(*A*)	470 (1)	1531 (1)	7172 (1)	55 (0)
N1(*A*)	1685 (2)	996 (2)	4847 (3)	43 (0)
C2(*A*)	1652 (2)	1723 (3)	6217 (4)	40 (0)
O3(*A*)	2621 (2)	2674 (2)	6886 (3)	47 (0)
C4(*A*)	3685 (2)	2502 (3)	6607 (4)	49 (1)
C4a(*A*)	3762 (2)	2272 (3)	4623 (4)	43 (1)
C5(*A*)	4091 (2)	3500 (3)	3313 (4)	50 (1)
C6(*A*)	3304 (3)	4305 (3)	3350 (5)	60 (1)
C7(*A*)	2153 (3)	3356 (4)	2410 (5)	64 (1)
C8(*A*)	2415 (3)	2120 (3)	1927 (4)	56 (1)
C8a(*A*)	2605 (2)	1331 (3)	3677 (4)	44 (1)
C9(*A*)	3653 (3)	2785 (4)	1471 (4)	65 (1)
S(*B*)	4099 (1)	9122 (1)	12444 (1)	53 (0)
N1(*B*)	3380 (2)	8952 (2)	8886 (3)	45 (0)
C2(*B*)	3130 (2)	8722 (3)	10595 (4)	43 (1)
O3(*B*)	2034 (2)	8136 (2)	10847 (3)	55 (0)
C4(*B*)	1191 (3)	8229 (4)	9352 (5)	58 (1)
C4a(*B*)	1367 (2)	7811 (3)	7534 (3)	47 (1)
C5(*B*)	954 (2)	6298 (3)	7116 (5)	55 (1)
C6(*B*)	1428 (3)	5538 (3)	8624 (5)	65 (1)
C7(*B*)	2722 (3)	6042 (3)	8367 (5)	59 (1)
C8(*B*)	2807 (2)	7001 (3)	6718 (4)	51 (1)
C8a(*B*)	2642 (2)	8294 (3)	7250 (4)	45 (1)
C9(*B*)	1664 (3)	6313 (4)	5570 (5)	65 (1)
Compound (II)				
S	5321 (2)	3889 (1)	6679 (2)	48 (0)
N1	3117 (5)	4001 (3)	3702 (5)	38 (1)
C2	3582 (6)	3551 (3)	5030 (6)	38 (1)
O3	2603 (5)	2773 (2)	5038 (4)	43 (1)
C4	1560 (7)	2367 (3)	3553 (6)	47 (1)
C4a	141 (7)	2998 (3)	2413 (6)	37 (1)
C5	−1835 (6)	3290 (3)	2746 (6)	42 (1)
C6	−3297 (7)	3648 (4)	1207 (6)	50 (1)
C7	−2207 (7)	4524 (4)	973 (6)	53 (1)
C8	−367 (6)	4599 (3)	2466 (6)	41 (1)
C8a	1228 (6)	3904 (3)	2373 (5)	36 (1)
C9	−1187 (7)	4161 (3)	3669 (6)	42 (1)

Discussion. The final atomic coordinates for non-H atoms are listed in Table 1.* Fig. 1 shows a perspective view of the molecules. The relevant bond lengths and bond angles are given in Table 2. The corresponding values for the majority of bond angles and distances are similar. The influence of the *exo* S atom on the bonds and angles around C(2) was analysed in our previous paper (Kapor, Ribár, Divjaković, Stájer, Bernáth & Argay, 1987) and the values for the present compounds agree with the previous ones. As with the structures discussed in the papers by Argay *et al.* (1985) and by Kapor *et al.* (1987) the 3,1-benzoxazine ring adopts an E_4 (Boeyens, 1978)

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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 52774 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

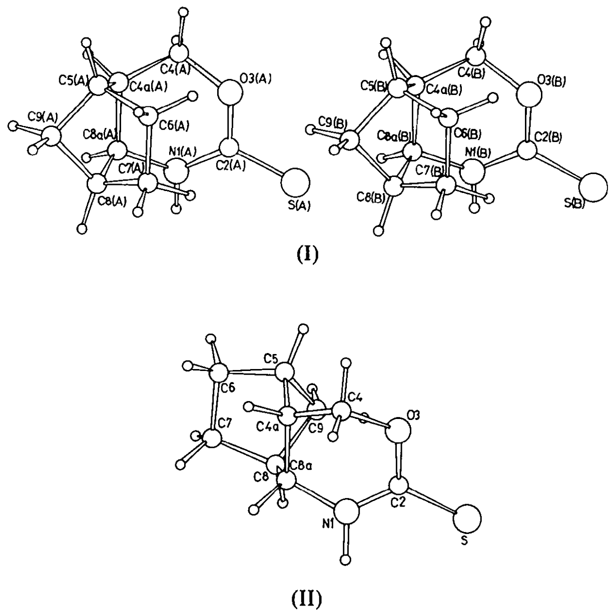
	(I*A*)	(I*B*)	(II)
S—C(2)	1·674 (2)	1·675 (3)	1·671 (5)
C(2)—O(3)	1·336 (3)	1·334 (2)	1·344 (5)
C(2)—N(1)	1·317 (3)	1·324 (4)	1·330 (7)
O(3)—C(4)	1·462 (2)	1·457 (4)	1·446 (6)
N(1)—C(8a)	1·464 (3)	1·468 (3)	1·473 (5)
C(4)—C(4a)	1·515 (4)	1·500 (4)	1·507 (6)
C(4a)—C(5)	1·541 (4)	1·537 (4)	1·549 (4)
C(4a)—C(8a)	1·550 (3)	1·546 (2)	1·552 (6)
C(5)—C(6)	1·529 (3)	1·523 (4)	1·536 (7)
C(5)—C(9)	1·532 (4)	1·532 (4)	1·535 (7)
C(6)—C(7)	1·546 (4)	1·563 (3)	1·557 (8)
C(7)—C(8)	1·533 (4)	1·528 (5)	1·537 (7)
C(8)—C(8a)	1·537 (4)	1·539 (4)	1·533 (5)
C(8)—C(9)	1·542 (3)	1·531 (4)	1·531 (6)
S—C(2)—O(3)	117·9 (3)	118·4 (3)	118·2 (5)
S—C(2)—N(1)	124·1 (3)	124·2 (3)	124·0 (6)
O(3)—C(2)—N(1)	118·0 (4)	117·4 (4)	117·8 (6)
C(2)—O(3)—C(4)	117·1 (3)	117·5 (4)	117·2 (6)
C(2)—N(1)—C(8a)	125·8 (4)	126·0 (4)	126·1 (6)
O(3)—C(4)—C(4a)	113·1 (3)	113·9 (4)	113·6 (6)
C(4)—C(4a)—C(5)	118·5 (4)	118·6 (4)	117·2 (6)
C(4)—C(4a)—C(8a)	111·4 (4)	112·0 (4)	110·5 (6)
C(5)—C(4a)—C(8a)	103·3 (3)	102·7 (3)	102·7 (6)
C(4a)—C(5)—C(6)	111·0 (4)	111·2 (4)	106·2 (6)
C(4a)—C(5)—C(9)	99·8 (4)	100·7 (4)	103·1 (6)
C(6)—C(5)—C(9)	101·6 (4)	101·6 (4)	101·3 (6)
C(5)—C(6)—C(7)	103·2 (4)	102·7 (4)	102·3 (6)
C(6)—C(7)—C(8)	103·6 (4)	103·1 (4)	103·7 (6)
C(7)—C(8)—C(8a)	110·1 (4)	110·3 (4)	107·7 (6)
C(7)—C(8)—C(9)	101·1 (4)	101·6 (4)	102·3 (6)
C(8a)—C(8)—C(9)	100·1 (4)	100·0 (4)	100·7 (6)
N(1)—C(8a)—C(4a)	112·8 (3)	111·9 (3)	111·8 (6)
N(1)—C(8a)—C(8)	113·7 (4)	114·2 (3)	110·4 (6)
C(4a)—C(8a)—C(8)	103·2 (3)	103·5 (3)	103·2 (6)
C(5)—C(9)—C(8)	94·4 (4)	94·2 (4)	94·5 (6)

Table 3. *Puckering parameters and asymmetry factors*

	Q(Å)	θ(°)	φ(°)	fC_s(Å)	^cN_d
Benzoxazine ring					
(I*A*)	0·455 (3)	72·1 (4)	167·6 (4)	0·076 (16) [N(1)]	$E_4 > {}^3S_4$
(I*B*)	0·451 (4)	74·5 (4)	168·1 (5)	0·073 (16) [N(1)]	$E_4 > {}^3S_4$
(II)	0·464 (5)	70·5 (6)	180·5 (6)	0·0030 (7) [N(1)]	$E_4 > B_{4,1}$
Five-membered ring C(4a)—C(5)—C(9)—C(8)—C(8a)					
(I*A*)	0·613 (4)		71·2 (3)	0·008 (1) [C(9)]	*E*
(I*B*)	0·608 (4)		72·3 (3)	0·0030 (5) [C(9)]	*E*
(II)	0·583 (5)		79·1 (4)	0·072 (12) [C(9)]	*E*
Five-membered ring C(5)—C(6)—C(7)—C(8)—C(9)					
(I*A*)	0·588 (4)		144·4 (3)	0·0050 (8) [C(9)]	*E*
(I*B*)	0·590 (4)		145·1 (3)	0·011 (2) [C(9)]	*E*
(II)	0·584 (6)		148·7 (6)	0·048 (8) [C(9)]	*E*
Six-membered ring C(4a)—C(5)—C(6)—C(7)—C(8)—C(8a)					
(I*A*)	0·923 (4)	89·6 (2)	240·1 (2)	0·0010 (1) [C(5)] 0·0050 (6) [C(6)—C(7)]	$^{2,5}B$
(I*B*)	0·923 (4)	89·7 (2)	239·2 (2)	0·011 (1) [C(5)] 0·011 (1) [C(6)—C(7)]	$^{2,5}B$
(II)	0·980 (7)	91·0 (3)	234·6 (3)	0·074 (8) [C(5)] 0·076 (8) [C(6)—C(7)]	$^{2,5}B$

envelope conformation in both compounds. Puckering parameters (Cremer & Pople, 1975) and asymmetry factors (Kálmán, Czugler & Simon, 1982) for the benzoxazine ring and for rings in norbornene unit, are given in Table 3.

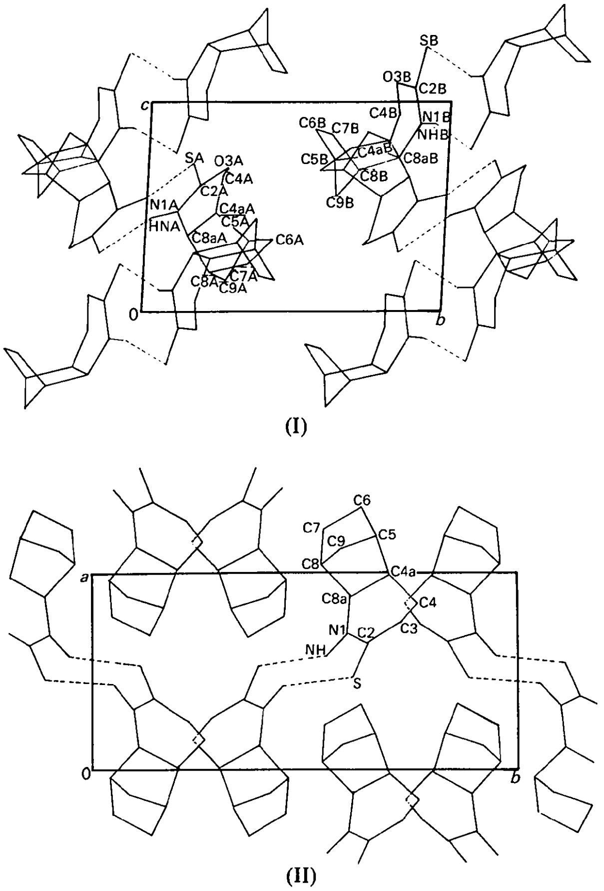
Previous spectroscopic analyses (^{1}H and ^{13}C NMR spectra) of derivatives (Stájer *et al.*, 1983) indicated a difference between di-*endo* and di-*exo* analogues in the values of torsion angle H(8a)—C(8a)—C(8)—H(8) of about 50° in di-*endo* compounds,



(I)

(II)

Fig. 1. A perspective view of the molecules showing atom numbering. The H atoms are shown but not labelled.



(I)

(II)

Fig. 2. The crystal structures projected along the *a* (I) and *c* (II) axes. Hydrogen bonds are shown by broken lines.

and about 90° in the analogous di-*exo* compounds. The calculated value of this torsion angle is 43·0 (5) (*A*), 43·8 (5)° (*B*) in (I) and −70·8 (8)° in (II). This confirms estimates from spectroscopic results of the values of these angles for di-*endo* (I) and di-*exo* (II) derivatives. The difference in torsion angles causes different molecular conformations in the di-*endo* and di-*exo* molecules, the latter isomer being more planar; this can substantially influence structurally specific action at receptor sites.

The molecules of the two compounds are connected through hydrogen bonds of N—H···S type to form dimers. The corresponding bond lengths and angles are H···S = 2·301 (2) (*A*), 2·466 (4) (*B*), N(1)···S = 3·322 (3) (*A*), 3·348 (5) Å (*B*), ∠N—H···S = 157·2 (2) (*A*), 159·5 (3)° (*B*) (I) and H···S = 2·474 (5), N(1)···S = 3·383 (6) Å, ∠N—H···S = 141·0 (4)° (II). These results are in agreement with the lengths of hydrogen bonds in similar molecules (Kapor *et al.*, 1987). Molecular packing in the crystal is shown in Fig. 2.

References

ARGAY, GY., KÁLMÁN, A., KAPOR, A., STÁJER, G. & BERNÁTH, G. (1985). *J. Mol. Struct.* **131**, 31–43.
BERNÁTH, G., GERA, L., GÖNDÖS, GY., HERMANN, M., SZENTIVÁNYI, M., ECSERY, Z. & JANVÁRY, E. (1977). German Patent No. 2,643,384; *Chem. Abstr.* **87**, No. 168078b.
BOEYENS, J. C. A. (1978). *J. Cryst. Mol. Struct.* **8**, 317–320.
CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
KÁLMÁN, A., CZUGLER, M. & SIMON, K. (1982). In *Molecular Structure and Biological Activity*, edited by J. F. GRIFFIN & W. L. DUAX, pp. 367–376. New York: Elsevier Biomedical.
KAPOR, A., RIBÁR, B., DIVJAKOVIĆ, V., STÁJER, G., BERNÁTH, G. & ARGAY, GY. (1987). *Acta Cryst.* C**43**, 1347–1350.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
STÁJER, G., SZABO, E. A., FÜLÖP, F., BERNÁTH, G. & SOHÁR, P. (1983). *J. Heterocycl. Chem.* **20**, 1181–1185.

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Structure of 6*α*-Methyl-3,20-oxo-1,4,9(11)-pregnatrien-17*α*-yl Acetate

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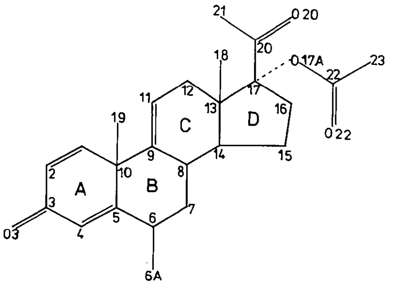
Abstract. $C_{24}H_{30}O_4$, $M_r = 382{\cdot}5$, orthorhombic, $P2_12_12_1$, $a = 13{\cdot}091$ (2), $b = 19{\cdot}711$ (1), $c = 8{\cdot}242$ (1) Å, $V = 2126{\cdot}7$ (5) Å^3, $Z = 4$, $D_x = 1{\cdot}195$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54184 Å, μ(Cu $K\alpha$) = 0·56 mm^{-1}, $F(000) = 824$, $T = 295$ K. Final $R = 0{\cdot}045$ for 2446 unique reflections. The planar *A* ring is bent relative to the rest of the steroid skeleton. The *B* ring has a typical chair conformation and the *C* and *D* rings assume 13*β*,14*α*-half-chair and 13*β*-envelope conformations, respectively. The conformation of the progesterone side chain is similar to the conformation observed in other 17*α*-ester pregnanes: C16—C17— C20—O20 torsion angle −27·4 (3)°.

Introduction. As is well known, a number of steroid hormones have a progesterone-like side chain at the C17 position. It is highly probable that the conformation of the side chain is responsible for control over the interaction of these hormones with their receptors (Duax, Cody, Griffin, Rohrer & Weeks, 1978). The 17*α*-ester substituents were found to have a restricting influence on the side-chain conformation (Duax, Griffin & Rohrer, 1981). The crystal structure of the title compound (I) has been determined as part of an effort to establish intramolecular features responsible for the progesterone side-chain conformation.



(I)

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