Fig. 1. Stereoscopic view of molecule (I) (upper diagram) and (II) (lower diagram) in a direction perpendicular to the mean plane of atoms C(7)–C(12).

correspond to single bonds between sp^2-hybridized C atoms, thus excluding the possibility of any significant conjugation between the phenyl ring and the N(5)–C(6) double bond.

In compound (II) the pyridyl ring is oriented about the C(1)–C(1″) bond in such a way as to minimize

non-bonded intramolecular interactions, torsion angle N(1)–C(1)–C(1″)–C(2″) −136·4 (6)°. The C(1)–C(1″) bond, although apparently slightly shorter than C(6)–C(1′), also corresponds in length to a Csp^2–Csp^2 single bond to within the limits of experimental accuracy.

In both structures intermolecular contacts are of the normal van der Waals type.

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Structure of 17α-Hydroxyprogesterone Caproate

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Abstract. 3,20-Dioxo-4-pregnen-17-yl hexanoate, $C_{27}H_{40}O_4$, $M_r = 428·61$, orthorhombic, $P2_12_12_1$, $a = 14·155$ (2), $b = 23·517$ (7), $c = 7·466$ (1) Å, $V = 2485·1$ (8) Å^3, $Z = 4$, $D_m = 1·14$, $D_x = 1·146$ Mg m^{-3}, $\lambda(Cu\ K\alpha) = 1·54178$ Å, $\mu = 5·59$ cm^{-1}, $F(000) = 936$, $R = 0·062$ for the 1263 observed $[I > 3\sigma(I)]$ reflections. Both rings B and C are in the chair conformation. Ring D assumes the form between half-chair

and envelope and ring *A* is intermediate between sofa and half-chair. Bond angles and distances are normal. The C(16)–C(17)–C(20)–O(20) torsion angle is −24 (1)°. All intermolecular contacts correspond to van der Waals interactions, the shortest one, C(18)–O(20) = 3·11 (1) Å, indicates a possible C—H···O interaction.

Introduction. The steroid 17α-hydroxyprogesterone caproate has been used for almost 30 years in pharmacotherapy as a progestational agent. The crystal structure of 17α-hydroxyprogesterone was solved (Declercq, Germain & Van Meerssche, 1972), but the structure of its caproate ester was not determined. Pharmacological activity of the title compound was widely investigated (Reifenstein, 1957; Junkmann, 1962; Kolb & Schulze, 1971; Kamamura, Nayakawa & Tanimoto, 1980; Korkhov, Boikova, Grinenko, Kadatskii, Akalaev & Andryushina, 1983) and it was found that it has better properties than 17α-hydroxyprogesterone (Junkmann, 1954). Determination of this structure might be significant for more efficient application of this pharmacologically active agent.

Experimental. Crystals suitable for X-ray determination were obtained by slow crystallization from the filtrate of a saturated solution of 17α-hydroxyprogesterone caproate (Diosynth) in castor oil (Ferak Berlin oHG). Density measured by flotation. Colourless, prismatic crystal 0·8 × 0·4 × 0·2 mm; X-ray single crystal analysis and data collection on a Philips PW 1100 diffractometer, monochromatic Cu $K\alpha$ radiation, ω scan mode. Unit-cell dimensions by a least-squares refinement on 40 reflections in the 2–40° θ range. 2885 reflections ($-14 \leq h \leq 14$, $0 \leq k \leq 23$, $0 \leq l \leq 7$) measured up to $\sin\theta/\lambda = 0\cdot50$ Å^{-1}, merged after Lp and semi-empirical absorption correction (min. = 0·998, max. = 1·060; North, Phillips & Mathews, 1968), yielding 1503 unique reflections (R_{int} = 0·02). Maximum variation in the net intensities of three standards (800, 080, 004) monitored every 4 h = 4·3%; correction for intensity variations applied. Structure solved with the *RANTAN*81 (Yao Jia-xing, 1981) procedure, full-matrix least-squares refinement on *F* performed with a locally rewritten version of the program *ORFLS* (Busing, Martin & Levy, 1962) on the 1263 reflections with $I > 3\sigma(I)$. Scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974). Anisotropic thermal parameters for non-H atoms; positions of the H atoms calculated with the program *PARST* (Nardelli, 1983), inserted with an overall isotropic *B* factor = 6 Å^2 and not refined. At convergence, R_{all} = 0·074, R_{obs} = 0·062, wR = 0·063 [$w = 1/\sigma^2(F)$], $S = 1\cdot030$, max. shift/e.s.d. = 0·133,· secondary extinction = 1·573 × 10^{-4}; the final difference Fourier map contained no peak higher than 0·24 e Å^{-3}. Atomic coordi-

Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent thermal parameters* (Å^2) *of non-*H *atoms* (*e.s.d.'s in parentheses*)

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
C(1)	1135 (5)	5207 (3)	6618 (12)	6·8 (3)
C(2)	241 (6)	4857 (3)	6779 (16)	8·0 (3)
C(3)	26 (6)	4693 (4)	8688 (17)	8·6 (4)
C(4)	372 (6)	5075 (4)	1·0027 (13)	7·9 (3)
C(5)	836 (5)	5547 (3)	9725 (11)	5·8 (2)
C(6)	1012 (6)	5964 (4)	1·1220 (12)	7·4 (3)
C(7)	2013 (6)	6197 (3)	1·1235 (11)	6·9 (3)
C(8)	2297 (5)	6425 (3)	9414 (9)	5·0 (2)
C(9)	2165 (4)	5963 (3)	7986 (9)	4·4 (2)
C(10)	1150 (5)	5732 (3)	7847 (10)	5·0 (2)
C(11)	2548 (5)	6152 (3)	6144 (10)	5·5 (2)
C(12)	3569 (5)	6372 (3)	6241 (10)	5·7 (2)
C(13)	3649 (5)	6852 (3)	7586 (9)	5·1 (2)
C(14)	3318 (5)	6625 (3)	9404 (9)	5·2 (2)
C(15)	3637 (7)	7091 (4)	1·0718 (11)	7·5 (3)
C(16)	4557 (7)	7317 (3)	9934 (13)	8·1 (3)
C(17)	4670 (6)	7043 (3)	8051 (11)	5·8 (2)
C(18)	3087 (6)	7380 (3)	6961 (12)	7·4 (3)
C(19)	439 (5)	6177 (3)	7170 (11)	6·5 (2)
C(20)	5117 (7)	7440 (4)	6693 (13)	7·6 (3)
C(21)	5534 (6)	7188 (4)	5045 (14)	9·1 (3)
C(22)	6155 (6)	6589 (5)	8520 (15)	8·5 (3)
C(23)	6605 (6)	6006 (5)	8482 (16)	9·9 (4)
C(24)	7631 (8)	5988 (6)	8998 (21)	12·7 (6)
C(25)	7798 (15)	6041 (10)	1·0741 (27)	21·0 (10)
C(26)	8000 (14)	5705 (8)	1·1982 (27)	17·7 (8)
C(27)	8189 (10)	5816 (6)	1·3840 (21)	13·9 (6)
O(3)	−442 (5)	4270 (3)	8951 (12)	13·4 (3)
O(17)	5219 (3)	6529 (2)	8217 (7)	6·2 (2)
O(20)	5073 (5)	7949 (2)	6864 (10)	10·9 (3)
O(22)	6561 (4)	7022 (3)	8648 (11)	10·2 (3)

nates and equivalent thermal factors for non-H atoms in Table 1; bond distances, uncorrected and corrected for riding motion (Busing & Levy, 1964), and angles in Table 2; Fig. 1, drawn with *ORTEP*II (Johnson, 1976), illustrates the molecular structure with the atomic numbering used in the tables, and Fig. 2 shows a projection of the unit-cell contents onto the *ab* plane.*

Discussion. The *B* and *C* rings exhibit a chair conformation while the *A* ring is intermediate between sofa and half-chair: $\Delta C_s(1) = 6\cdot9°$, $\Delta C_2(1,2) = 19\cdot3°$ (Duax, Weeks & Rohrer, 1976). Ring *D* assumes a form between half-chair and envelope: $\Delta C_2(16) = 9\cdot3°$, $\Delta C_s(13) = 10\cdot8°$. The ring puckering parameters (Cremer & Pople, 1975) are: $Q = 0\cdot456$ (7) Å, $\varphi = -170$ (1)°, for *D* and $Q = 0\cdot441$ (8) Å, $\varphi = 7$ (1)°, $\theta = 56$ (1)°, for *A*. The conformation of the side chain is very similar to that found by Duax, Griffin & Rohrer (1981) in 17α-hydroxyprogesterone where the C(16)–C(17)–C(20)–O(20) torsion angle is −23°. The C(16)–C(17)–C(20)–O(20) torsion angle in the present structure is −24 (1)°.

The side chain is extended away from the steroid nucleus and there are no intermolecular interactions

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Table 2. *Bond distances* (Å), *uncorrected and corrected for riding motion* (*Busing & Levy*, 1964), *and bond angles* (°) *for non-H atoms* (*e.s.d.'s in parentheses*)

C(1)—C(2)	1·514 (11)	1·528	C(13)—C(14)	1·532 (10)	1·534
C(1)—C(10)	1·539 (10)	1·559	C(13)—C(17)	1·552 (11)	1·561
C(2)—C(3)	1·508 (17)	1·523	C(13)—C(18)	1·548 (10)	1·571
C(3)—C(4)	1·431 (15)	1·432	C(14)—C(15)	1·540 (11)	1·568
C(3)—O(3)	1·211 (12)	1·285	C(15)—C(16)	1·523 (13)	1·530
C(4)—C(5)	1·308 (12)	1·332	C(16)—C(17)	1·554 (12)	1·582
C(5)—C(6)	1·507 (12)	1·527	C(17)—C(20)	1·518 (12)	1·538
C(5)—C(10)	1·534 (11)	1·542	C(17)—O(17)	1·442 (9)	1·444
C(6)—C(7)	1·519 (12)	1·523	C(20)—C(21)	1·487 (14)	1·492
C(7)—C(8)	1·515 (10)	1·535	C(20)—O(20)	1·206 (11)	1·261
C(8)—C(9)	1·535 (9)	1·541	O(17)—C(22)	1·352 (10)	1·379
C(8)—C(14)	1·519 (10)	1·523	C(22)—O(22)	1·173 (12)	1·212
C(9)—C(10)	1·539 (9)	1·544	C(22)—C(23)	1·512 (15)	1·515
C(9)—C(11)	1·543 (10)	1·554	C(23)—C(24)	1·502 (15)	1·527
C(10)—C(19)	1·538 (10)	1·553	C(24)—C(25)	1·329 (26)	1·461
C(11)—C(12)	1·536 (10)	1·538	C(25)—C(26)	1·250 (29)	1·275
C(12)—C(13)	1·515 (10)	1·521	C(26)—C(27)	1·437 (25)	1·475

C(2)—C(1)—C(10)	113·6 (6)	C(12)—C(13)—C(14)	107·7 (6)
C(1)—C(2)—C(3)	112·5 (8)	C(17)—C(13)—C(18)	108·3 (6)
C(2)—C(3)—O(3)	118·3 (10)	C(14)—C(13)—C(18)	113·0 (6)
C(2)—C(3)—C(4)	115·5 (9)	C(14)—C(13)—C(17)	100·8 (6)
C(4)—C(3)—O(3)	126·1 (11)	C(8)—C(14)—C(13)	113·8 (6)
C(3)—C(4)—C(5)	125·7 (9)	C(13)—C(14)—C(15)	103·1 (6)
C(4)—C(5)—C(10)	123·0 (7)	C(8)—C(14)—C(15)	119·7 (6)
C(4)—C(5)—C(6)	120·5 (8)	C(14)—C(15)—C(16)	104·7 (6)
C(6)—C(5)—C(10)	116·3 (6)	C(15)—C(16)—C(17)	107·0 (7)
C(5)—C(6)—C(7)	113·3 (7)	C(13)—C(17)—C(16)	103·1 (6)
C(6)—C(7)—C(8)	111·6 (7)	C(16)—C(17)—O(17)	109·0 (6)
C(7)—C(8)—C(14)	111·5 (6)	C(16)—C(17)—C(20)	113·1 (7)
C(7)—C(8)—C(9)	109·9 (6)	C(13)—C(17)—O(17)	106·2 (6)
C(9)—C(8)—C(14)	109·3 (5)	C(13)—C(17)—C(20)	114·6 (7)
C(8)—C(9)—C(11)	111·8 (5)	C(20)—C(17)—O(17)	110·4 (6)
C(8)—C(9)—C(10)	114·2 (5)	C(17)—C(20)—O(20)	121·2 (8)
C(10)—C(9)—C(11)	111·7 (5)	C(17)—C(20)—C(21)	118·2 (8)
C(5)—C(10)—C(9)	108·0 (6)	C(21)—C(20)—O(20)	120·3 (9)
C(1)—C(10)—C(9)	109·7 (5)	C(17)—O(17)—C(22)	117·0 (6)
C(1)—C(10)—C(5)	108·2 (6)	O(17)—C(22)—C(23)	108·4 (7)
C(9)—C(10)—C(19)	113·2 (5)	O(17)—C(22)—O(22)	125·8 (8)
C(5)—C(10)—C(19)	107·7 (6)	O(22)—C(22)—C(23)	125·5 (8)
C(1)—C(10)—C(19)	109·9 (6)	C(22)—C(23)—C(24)	115·3 (10)
C(9)—C(11)—C(12)	112·7 (6)	C(23)—C(24)—C(25)	114·9 (13)
C(11)—C(12)—C(13)	110·6 (6)	C(24)—C(25)—C(26)	135·0 (21)
C(12)—C(13)—C(18)	111·0 (6)	C(25)—C(26)—C(27)	130·0 (19)
C(12)—C(13)—C(17)	115·7 (6)		
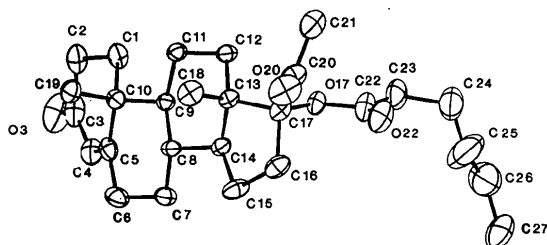
Fig. 1. *ORTEP perspective view of the molecule, showing the atomic numbering.*

Fig. 2. Molecular packing (projected along **c**).

between the side chain and steroid nucleus. Two questionable interatomic distances, C(25)—C(26) = 1·25 (3) Å and C(26)—C(27) = 1·44 (2) Å (1·27 and 1·47 Å respectively when corrected for riding motion), can be attributed to an unresolved side-chain disorder. The short intramolecular distance O(20)—C(18) = 3·11 (1) Å indicates a possible C—H···O interaction (Berkovitch-Yellin & Leiserowitz, 1984); unfortunately, the position of the H atom involved (which belongs to a methyl group) could not be obtained from a difference Fourier synthesis.
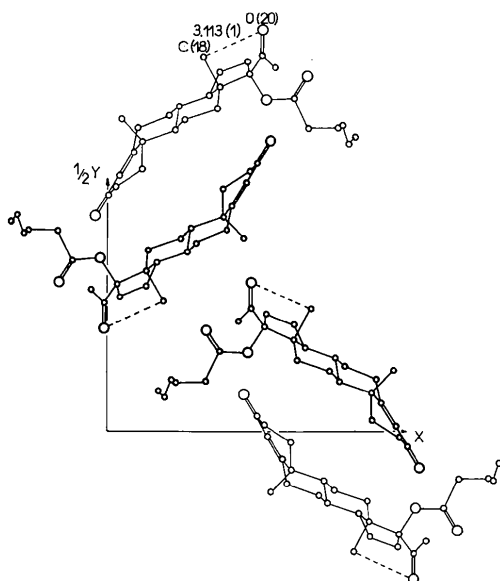
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