

Fig. 2. Packing of modification I as seen along **a**. Hydrogen bonds are denoted by dashed lines.

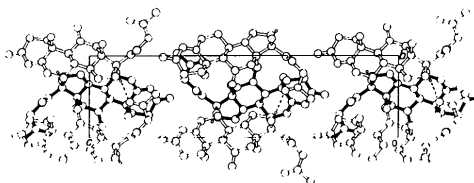


Fig. 3. Packing of modification II as seen along **a**. Hydrogen bonds are denoted by dashed lines.

Five of these six contacts involve molecules which are separated by translations along **a** or **b** and, together with the H bond that connects molecules also translated along **b**, these short contacts form a cluster of molecules parallel to the *ab* plane. The remaining contact between molecules related by the screw axis parallel to **a** connects these layers of molecules in a coil

from which the angular methyl groups project sideways.

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11 β -Hydroxy-16 α ,17 α ,21-trimethyl-5 α -pregna-1,4-diene-3,20-dione (I), C₂₄H₃₄O₃, and 11 β ,17 α -Dihydroxy-21-methyl-5 α -pregn-4-en-3,20-dione 17-Butyrate (II), C₂₆H₃₈O₅

BY JOHN C. BARNES* AND JOHN D. PATON

Chemistry Department, The University, Dundee DD1 4HN, Scotland

AND ROBERT T. LOGAN AND JAMES REDPATH

Organon Laboratories Ltd, Newhouse, Lanarkshire ML1 5SH, Scotland

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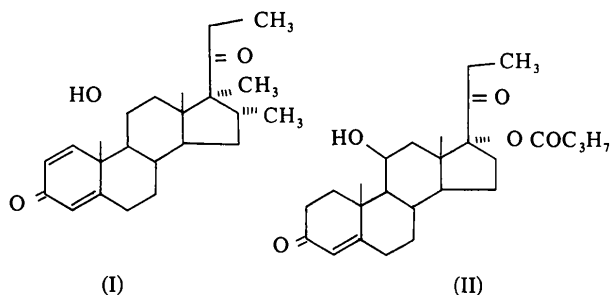
Abstract. (I) $M_r = 370.5$, monoclinic, $P2_1$, $a = 11.76$ (1), $b = 11.75$ (1), $c = 7.596$ (4) Å, $\beta = 98.85$ (8)°, $U = 1037.1$ Å³, $Z = 2$, $D_x = 1.187$ Mg m⁻³, $\text{Cu } K\alpha$, $\lambda = 1.5418$ Å, $\mu = 0.51$ mm⁻¹, $F(000) = 404$, $T = 293$ K, $R = 0.070$ for 1235 reflec-

tions. (II) $M_r = 430.6$, orthorhombic, $P2_12_12_1$, $a = 15.1065$ (11), $b = 10.6656$ (9), $c = 14.7405$ (17) Å, $U = 2374.99$ Å³, $Z = 4$, $D_x = 1.098$ Mg m⁻³, $\text{Mo } K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.05$ mm⁻¹, $F(000) = 936$, $T = 293$ K, $R = 0.044$ for 1746 reflections. Structurally (I) and (II) are typical 17-substituted steroids. In each case the molecules are linked into chains by hydrogen bonds.

* Author for correspondence.

(II) adopts the unusual staggered conformation for methyl and carbonyl groups in the EtCO side chain, while (I) has the normal almost eclipsed conformation.

Introduction. The title compounds, (I) and (II), are known by the reference numbers ORG 6216 and ORG 7417 respectively. They are of pharmacological and clinical interest as topically acting anti-inflammatory steroids (Cairns, Logan, McGarry, Roy & Woods, 1980; Cairns, McGarry, Roy & Woods, 1981; Cairns, Logan, McGarry, Roy, Stevenson & Woods, 1981), demonstrating an increase in the ratio of local to systemic effects when compared with dexamethasone (Woods, Hewett & Buckett, 1970). The presence of a 21-methyl group on the side chain has been shown (Llaurado, 1961) to eliminate the undesirable salt-retaining activity often associated with the corticosteroid molecule. In addition, the skin-thinning effects often accompanying topical application of steroids such as triamcinolone acetonide have been shown to be absent with the title compounds, making them attractive therapeutic agents for the treatment of dermatosis (Fox, Lewis, Rae, Sim & Woods, 1980).



Experimental. All calculations performed on Dundee University DEC10 computer using *SHELX76* (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978) program packages. Atomic scattering parameters from *International Tables for X-ray Crystallography* (1974). Refinements minimized $\sum w(|F_o| - |F_c|)^2$.

Compound (I). Crystals of ORG 6216 supplied by Organon Laboratories Ltd as colourless laths elongated along **b**, 0.3 × 0.5 × 0.2 mm. Unit-cell parameters refined (from 15 reflections) and intensity data collected on locally rebuilt Wooster four-circle diffractometer controlled by LSI 11 microcomputer (Barnes, Golnazarians, Iball & Paton, 1983). Diffractometer operated in fixed χ mode, collecting all unobscured planes with $0 < 2\theta < 150^\circ$ and $90 < \chi < 180^\circ$. $-14 \leq h \leq 14$, $0 \leq k \leq 12$, $0 \leq l \leq 8$. 2961 planes gave non-zero counts, 1953 unique, 1235 with $|F| > 5\sigma_F$ used in refinement. Structure solved using direct-methods routine *TANG* for non-centrosymmetric space group *P2₁*. *E* map showed two cyclohexane rings and adjacent parts of molecule. After least-squares refine-

ment (*R* 0.44), difference Fourier map showed remaining ring atoms and all but three exocyclic carbon and oxygen atoms. Convergence at *R* 0.070, anisotropic thermal parameters for carbon and oxygen atoms. Except as noted below, all hydrogen atoms included on calculated positions with refined isotropic thermal parameters. All hydrogen atoms gave acceptable thermal parameters except for hydroxyl H(1111), which is involved in hydrogen bonding to O(31) and methyl group C(161) attached to ring system at C(16). None of these four hydrogens could be located on a difference electron density map. It was decided to place H(1111) on the line of the hydrogen bond joining O(111) to O(31) of the adjacent molecule, at 1.08 Å from O(111). The methyl group is disordered or rotating but was included in the final calculation as a fixed group in a staggered conformation relative to the ring system. Final refinement: 265 refined parameters, *R* = 0.070, *wR* = 0.085, $w = 1.1831/[\sigma(F)^2 + 0.008833F^2]$, mean $\Delta/\sigma = 0.051$, max. $\Delta/\sigma = 0.196$, max. difference peak = 0.24 e Å⁻³.

Compound (II). Crystals of ORG 7417 supplied by Organon Laboratories Ltd as colourless laths, 0.3 × 0.2 × 0.15 mm. Unit-cell parameters refined using 20 reflections with θ ca 20° and intensity data collected on Enraf-Nonius CAD-4F diffractometer. One octant of data collected to θ limit of 25°. Intensity and orientation checks during data collection showed no variation. 2389 reflections measured, 1746 observed with $|F| > 5\sigma_F$, $0 \leq h \leq 17$, $0 \leq k \leq 12$, $0 \leq l \leq 17$. Structure solved using direct-methods routine *TANG* for non-centrosymmetric space group *P2₁2₁2₁*. *E* map showed two cyclohexane rings and adjacent parts of molecule. After least-squares refinement (*R* 0.20), difference electron density map showed both cyclic carbon atoms and exocyclic carbon and oxygen atoms. Convergence at *R* 0.044 with anisotropic thermal parameters for carbon and oxygen atoms. Most hydrogen atoms determined by analysis of electron density difference maps; exceptions were those attached to C(174), C(175) and C(176), which were included on calculated positions with refined isotropic parameters. All hydrogen atoms gave acceptable thermal parameters except for: hydroxyl H(1111), which is involved in intermolecular hydrogen bonding to O(31'); H(2111) at the terminal end of the propanal group attached to C(17); and some hydrogen atoms of the butyrate group O(171)–C(176). Final refinement: 432 refined parameters, *R* = 0.044, *wR* = 0.0467, $w = 0.8866/[\sigma(F)^2 + 0.001548F^2]$, mean $\Delta/\sigma = 0.137$, max. $\Delta/\sigma = 0.195$, max. difference peak = 0.63 e Å⁻³.*

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters for (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42000 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *ORG 6216*: coordinates ($\times 10^4$) and U_{eq} values ($\text{\AA}^2 \times 10^3$) for non-hydrogen atoms with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^\dagger
C(1)	9498 (5)	3937	9100 (9)	46 (2)
C(2)	10157 (6)	3019 (9)	9426 (9)	54 (2)
C(3)	10340 (6)	2252 (9)	7977 (10)	57 (2)
C(4)	9718 (6)	2530 (8)	6209 (10)	53 (2)
C(5)	9049 (6)	3427 (7)	5890 (9)	42 (2)
C(6)	8406 (6)	3682 (8)	4075 (8)	47 (2)
C(7)	7122 (5)	3631 (8)	4151 (8)	47 (2)
C(8)	6737 (5)	4362 (7)	5632 (8)	40 (2)
C(9)	7495 (5)	4118 (7)	7430 (8)	42 (2)
C(10)	8820 (5)	4247 (8)	7368 (8)	46 (2)
C(11)	7072 (5)	4718 (8)	9009 (9)	50 (2)
C(12)	5792 (6)	4496 (8)	9022 (9)	52 (2)
C(13)	5006 (6)	4743 (7)	7259 (9)	48 (2)
C(14)	5486 (5)	4085 (7)	5824 (8)	44 (2)
C(15)	4567 (5)	4183 (8)	4179 (9)	50 (2)
C(16)	3422 (6)	4282 (9)	4893 (10)	60 (2)
C(17)	3726 (6)	4298 (8)	6963 (10)	49 (2)
O(31)	10956 (5)	1405 (6)	8227 (7)	73 (2)
C(19)	9198 (6)	5447 (8)	6887 (10)	59 (2)
O(111)	7262 (4)	5928 (6)	8999 (7)	66 (1)
C(18)	4972 (6)	6042 (7)	6872 (10)	52 (2)
C(161)	2515 (7)	3406 (12)	4094 (14)	93 (4)
C(171)	3600 (7)	3103 (9)	7775 (12)	69 (3)
C(20)	2929 (6)	5085 (8)	7771 (10)	56 (2)
C(21)	2929 (9)	5102 (12)	9767 (11)	89 (4)
C(211)	2309 (11)	6034 (13)	10463 (14)	104 (5)
O(201)	2202 (5)	5681 (8)	6888 (8)	85 (2)

$$\dagger U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

Discussion. Atomic coordinates are given in Tables 1 and 2, with bond lengths and angles in Tables 3 and 4. In general the bond lengths and angles have values that are typical for steroids. The *A* ring in (II), for example, is in a distorted sofa conformation consistent with that of other α,β -unsaturated steroids such as cyproterone acetate, chlormadinone acetate, 17 α -acetoxyprogesterone and medroxyprogesterone acetate, as shown by X-ray measurements (Duax, Cody & Hazel, 1977). (Figs. 1 and 2 show the atomic numbering for the title compounds.)

The main unexpected observation is the difference in stereochemistry between (I) and (II) in the C_2H_5CO side chain at C(17). Theoretically two low-energy conformations of this side chain might be expected. The minimum potential energy of ketones occurs when the carbonyl bond eclipses with the adjacent $C_\alpha-C_\beta$ bond (Suter, 1979). Following this rule, a minimum-energy conformation occurs in steroid side chains when the C(20)-carbonyl bond eclipses either with the C(17)-C(16) bond or with the C(17)-C(13) bond. Occasionally both conformations are found (Duax, Griffin, Strong, Funder & Vlick, 1982), but more usually the conformational preference is for the C(20)-carbonyl bond to eclipse partly with the C(17)-C(16) bond. This has been shown to be the case in 84 out of 88 reported X-ray structure determinations (Duax, Griffin, Rohrer & Weeks, 1980).

In both (I) and (II), the side-chain carbonyl group occupies the predicted position, eclipsing with the C(17)-C(16) bond, but whereas (I) has the methyl group C(211) almost eclipsed with the carbonyl group,

Table 2. *ORG 7417*: coordinates ($\times 10^4$) and U_{eq} values ($\text{\AA}^2 \times 10^3$) for non-hydrogen atoms with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^\dagger
C(1)	8203 (2)	3142 (3)	5443 (2)	42 (1)
C(2)	8940 (3)	2206 (4)	5603 (3)	58 (1)
C(3)	9586 (2)	2635 (4)	6307 (3)	55 (1)
C(4)	9252 (2)	3475 (4)	6991 (3)	55 (1)
C(5)	8409 (2)	3860 (3)	7042 (2)	46 (1)
C(6)	8069 (2)	4532 (4)	7871 (2)	55 (1)
C(7)	7465 (2)	5634 (3)	7668 (2)	51 (1)
C(8)	6746 (2)	5336 (3)	6955 (2)	35 (1)
C(9)	7192 (2)	4761 (3)	6112 (2)	31 (1)
C(10)	7731 (2)	3545 (3)	6317 (2)	36 (1)
C(11)	6582 (2)	4669 (3)	5283 (2)	36 (1)
C(12)	6053 (2)	5876 (3)	5099 (2)	36 (1)
C(13)	5579 (2)	6369 (3)	5950 (2)	36 (1)
C(14)	6269 (2)	6538 (3)	6701 (2)	37 (1)
C(15)	5768 (2)	7270 (4)	7425 (3)	54 (1)
C(16)	5169 (3)	8160 (3)	6876 (3)	55 (1)
C(17)	5217 (2)	7737 (3)	5890 (3)	45 (1)
O(31)	10345 (2)	2243 (3)	6331 (2)	76 (1)
C(19)	7160 (2)	2463 (3)	6691 (3)	53 (1)
O(111)	6015 (2)	3608 (2)	5355 (2)	53 (1)
C(18)	4822 (2)	5495 (4)	6232 (3)	50 (1)
C(20)	4340 (2)	7823 (4)	5361 (3)	55 (1)
O(201)	3641 (2)	7834 (3)	5761 (2)	83 (1)
C(21)	4367 (3)	7796 (4)	4321 (3)	62 (1)
C(211)	3764 (3)	6834 (5)	3928 (4)	90 (2)
O(171)	5897 (2)	8455 (2)	5411 (2)	48 (1)
C(172)	5728 (3)	9664 (3)	5211 (3)	59 (1)
O(173)	5037 (2)	10167 (3)	5379 (2)	81 (1)
C(174)	6513 (3)	10252 (4)	4741 (3)	72 (1)
C(175)	6663 (4)	9764 (5)	3808 (4)	96 (2)
C(176)	7382 (4)	10473 (5)	3323 (4)	100 (2)

$$\dagger U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

Table 3. *Interatomic distances* (\AA) *and angles* ($^\circ$) *for ORG 6216*

C(2)-C(1)	1.329 (10)	C(12)-C(11)	1.529 (10)
C(10)-C(1)	1.476 (9)	O(111)-C(11)	1.439 (11)
C(3)-C(2)	1.464 (12)	C(13)-C(12)	1.534 (9)
C(4)-C(3)	1.464 (10)	C(14)-C(13)	1.515 (10)
O(31)-C(3)	1.229 (11)	C(17)-C(13)	1.576 (10)
C(5)-C(4)	1.316 (11)	C(18)-C(13)	1.553 (12)
C(6)-C(5)	1.498 (9)	C(15)-C(14)	1.526 (8)
C(10)-C(5)	1.535 (11)	C(16)-C(15)	1.531 (10)
C(7)-C(6)	1.521 (9)	C(17)-C(16)	1.558 (10)
C(8)-C(7)	1.538 (11)	C(161)-C(16)	1.538 (14)
C(9)-C(8)	1.539 (8)	C(171)-C(17)	1.549 (14)
C(14)-C(8)	1.535 (9)	C(20)-C(17)	1.512 (11)
C(10)-C(9)	1.574 (9)	C(21)-C(20)	1.516 (12)
C(11)-C(9)	1.539 (10)	O(201)-C(20)	1.223 (10)
C(19)-C(10)	1.539 (12)	C(211)-C(21)	1.459 (19)
C(10)-C(1)-C(2)	125.9 (6)	C(13)-C(12)-C(11)	115.1 (6)
C(3)-C(2)-C(1)	120.5 (6)	C(14)-C(13)-C(12)	106.8 (6)
C(4)-C(3)-C(2)	116.3 (8)	C(17)-C(13)-C(12)	119.7 (6)
O(31)-C(3)-C(2)	122.3 (7)	C(17)-C(13)-C(14)	100.4 (6)
O(31)-C(3)-C(4)	121.4 (8)	C(18)-C(13)-C(12)	110.2 (6)
C(5)-C(4)-C(3)	123.2 (8)	C(18)-C(13)-C(14)	111.5 (6)
C(6)-C(5)-C(4)	122.2 (7)	C(18)-C(13)-C(17)	107.6 (6)
C(10)-C(5)-C(4)	122.4 (6)	C(13)-C(14)-C(8)	115.4 (6)
C(10)-C(5)-C(6)	115.3 (6)	C(15)-C(14)-C(8)	118.3 (6)
C(7)-C(6)-C(5)	108.7 (5)	C(15)-C(14)-C(13)	104.8 (6)
C(8)-C(7)-C(6)	114.3 (6)	C(16)-C(15)-C(14)	105.5 (6)
C(9)-C(8)-C(7)	110.5 (6)	C(17)-C(16)-C(15)	106.3 (5)
C(14)-C(8)-C(7)	110.2 (6)	C(161)-C(16)-C(15)	113.8 (8)
C(14)-C(8)-C(9)	108.0 (5)	C(161)-C(16)-C(17)	116.3 (8)
C(10)-C(9)-C(8)	113.4 (5)	C(16)-C(17)-C(13)	102.3 (6)
C(11)-C(9)-C(8)	113.2 (6)	C(171)-C(17)-C(13)	113.1 (6)
C(11)-C(9)-C(10)	114.8 (5)	C(171)-C(17)-C(16)	111.7 (7)
C(9)-C(10)-C(1)	110.6 (5)	C(20)-C(17)-C(13)	112.2 (7)
C(9)-C(10)-C(5)	104.3 (5)	C(20)-C(17)-C(16)	110.9 (6)
C(19)-C(10)-C(1)	107.6 (5)	C(20)-C(17)-C(171)	106.8 (7)
C(19)-C(10)-C(5)	108.2 (6)	C(21)-C(20)-C(17)	120.6 (7)
C(19)-C(10)-C(9)	114.8 (6)	O(201)-C(20)-C(17)	123.6 (7)
C(12)-C(11)-C(9)	111.3 (6)	O(201)-C(20)-C(21)	115.7 (8)
O(111)-C(11)-C(9)	112.3 (6)	C(211)-C(21)-C(20)	116.7 (9)
O(111)-C(11)-C(12)	108.8 (6)		

in (II) the corresponding atoms are much closer to a staggered relationship. The torsion angles are 11.8 (3) (I) and 45.9 (4)° (II). Since this observation was unexpected, an explanation was sought from consideration of possible steric interactions, either with the relatively bulky 17-butyrate group, or with an adjacent

Table 4. Interatomic distances (Å) and angles (°) for ORG 7417

C(2)—C(1)	1.513 (5)	C(13)—C(12)	1.535 (4)
C(10)—C(1)	1.534 (4)	C(14)—C(13)	1.531 (4)
C(3)—C(2)	1.496 (5)	C(17)—C(13)	1.562 (5)
C(4)—C(3)	1.441 (6)	C(18)—C(13)	1.533 (5)
O(31)—C(3)	1.221 (5)	C(15)—C(14)	1.524 (5)
C(5)—C(4)	1.341 (5)	C(16)—C(15)	1.541 (5)
C(6)—C(5)	1.507 (5)	C(17)—C(16)	1.523 (5)
C(10)—C(5)	1.518 (5)	C(20)—C(17)	1.541 (5)
C(7)—C(6)	1.517 (5)	O(171)—C(17)	1.462 (4)
C(8)—C(7)	1.545 (5)	O(201)—C(20)	1.209 (5)
C(9)—C(8)	1.540 (4)	C(21)—C(20)	1.533 (6)
C(14)—C(8)	1.518 (5)	C(21)—C(21)	1.490 (7)
C(10)—C(9)	1.561 (4)	C(172)—O(171)	1.347 (4)
C(11)—C(9)	1.534 (4)	O(173)—C(172)	1.199 (5)
C(19)—C(10)	1.542 (5)	C(174)—C(172)	1.511 (6)
C(12)—C(11)	1.540 (4)	C(175)—C(174)	1.488 (8)
O(111)—C(11)	1.424 (4)	C(176)—C(175)	1.504 (8)
C(10)—C(1)—C(2)	113.3 (3)	C(14)—C(13)—C(12)	108.3 (2)
C(3)—C(2)—C(1)	112.7 (3)	C(17)—C(13)—C(12)	116.0 (3)
C(4)—C(3)—C(2)	116.6 (3)	C(17)—C(13)—C(14)	99.7 (3)
O(31)—C(3)—C(2)	121.9 (4)	C(18)—C(13)—C(12)	111.2 (3)
O(31)—C(3)—C(4)	121.4 (4)	C(18)—C(13)—C(14)	112.5 (3)
C(5)—C(4)—C(3)	124.2 (3)	C(18)—C(13)—C(17)	108.8 (3)
C(6)—C(5)—C(4)	121.0 (3)	C(13)—C(14)—C(8)	113.7 (3)
C(10)—C(5)—C(4)	122.3 (3)	C(15)—C(14)—C(8)	119.7 (3)
C(10)—C(5)—C(6)	116.5 (3)	C(15)—C(14)—C(13)	103.2 (3)
C(7)—C(6)—C(5)	114.5 (3)	C(16)—C(15)—C(14)	103.9 (3)
C(8)—C(7)—C(6)	113.4 (3)	C(17)—C(16)—C(15)	106.9 (3)
C(9)—C(8)—C(7)	108.9 (2)	C(16)—C(17)—C(13)	103.9 (3)
C(14)—C(8)—C(7)	109.2 (3)	C(20)—C(17)—C(13)	112.7 (3)
C(14)—C(8)—C(9)	110.2 (2)	C(20)—C(17)—C(16)	115.1 (3)
C(10)—C(9)—C(8)	113.8 (2)	O(171)—C(17)—C(13)	105.7 (2)
C(11)—C(9)—C(8)	113.9 (2)	O(171)—C(17)—C(16)	109.8 (3)
C(11)—C(9)—C(10)	114.4 (2)	O(171)—C(17)—C(20)	109.2 (3)
C(5)—C(10)—C(1)	109.8 (3)	O(201)—C(20)—C(17)	120.3 (4)
C(9)—C(10)—C(1)	108.3 (2)	C(21)—C(20)—C(17)	118.8 (3)
C(9)—C(10)—C(5)	107.7 (3)	C(21)—C(20)—O(201)	120.8 (4)
C(19)—C(10)—C(1)	110.5 (3)	C(21)—C(21)—C(22)	112.7 (4)
C(19)—C(10)—C(5)	106.9 (3)	C(172)—O(171)—C(17)	118.3 (3)
C(19)—C(10)—C(9)	113.6 (3)	O(173)—C(172)—O(171)	123.3 (4)
C(12)—C(11)—C(9)	113.4 (2)	C(174)—C(172)—O(171)	110.4 (3)
O(111)—C(11)—C(9)	110.7 (2)	C(174)—C(172)—O(173)	126.3 (4)
O(111)—C(11)—C(12)	111.4 (2)	C(175)—C(174)—C(172)	113.5 (4)
C(13)—C(12)—C(11)	112.6 (3)	C(176)—C(175)—C(174)	111.9 (5)

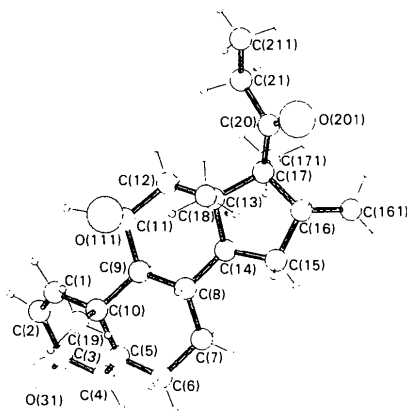


Fig. 1. 11 β -Hydroxy-16 α ,17 α ,21-trimethyl-5 α -pregna-1,4-diene-3,20-dione viewed perpendicular to the plane C(5),C(12),C(13).

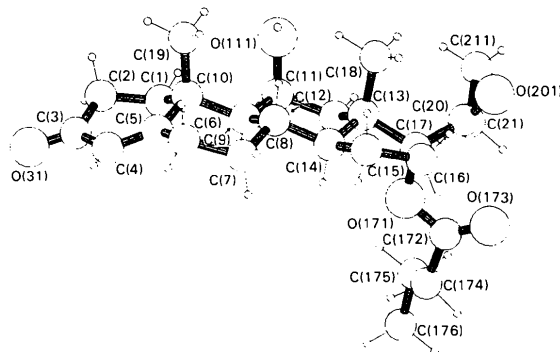


Fig. 2. 11 β ,17 α -Dihydroxy-21-methyl-5 α -pregna-4-en-3,20-dione 17-butyrate perspective view to show the C(17) side chains.

molecule in the crystal structure. There are, however, no contacts under 3.8 Å to C(211) in (I) or (II). The shortest intermolecular contacts in (II) apart from the hydrogen bond are from C(1), C(2) and C(3) to O(111) and O(173) of the adjacent molecule, related by the a -axis screw [3.48 (1)–3.56 (1) Å]. Within the molecule the O(201) to O(173) distance is 3.31 (1) Å. Steric interaction alone therefore is unlikely to be an explanation for the deviation from the expected conformation, and a long-range electronic effect, involving the butyrate carbonyl group, may be an influencing factor.

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