The presence of the 2-methyl group appears to have little effect on the minor conformational differences among the series except that the acid groups adopt a position *trans* to the substituent methyl group of the ring. Distortion of the *exo*-C(1) angles, a feature of the majority of the phenoxy acid structures, is also observed (115·8, 123·0°). The angles about the carboxylic acid group are likewise distorted, C(8)—C(9)—O(10) [122·3 (3)°], C(8)—C(9)—O(11) [114·4 (3)°] and O(10)—C(9)—O(11) [123·5 (3)°].

Partial disorder in the cyclic carboxylic acid dimer unit is also evident, appearing as a contraction in the difference between the C—O(carbonyl) and C—O(hydroxyl) bond distances (1·238 and 1·277 Å). A similar degree of disorder is found for the symmetrically substituted 2-(3,5-dichlorophenoxy)propionic acid (3,5-DP) (1·237, 1·276 Å) and 2,4,6-trichlorophenoxyacetic acid (2,4,6-T) (1·234, 1·262 Å) (Smith & Kennard, 1979). The only example of complete disorder is phenoxyacetic acid where both bonds are equal and the acid proton is delocalized. In considering the packing environment of the dimer unit (Fig. 2) there appears to be no good reason for the disorder phcnomcnon. The closest intermolecular contact to either O(10) or O(11) (outside the dimer unit) is 3·163 Å [O(10)···O(11)] although there is an intramolecular contact between O(11) and C(12) (2·91 Å).

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Methyl 3β-Acetoxy-17α-methyl-18-nor-5α-androstane-17β-carboxylate*

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Abstract. $C_{23}H_{36}O_4$, $M_r = 376\cdot5$, triclinic, $P\overline{1}$, $a = 7\cdot813\,(2)$, $b = 11\cdot360\,(2)$, $c = 6\cdot860\,(2)$ Å, $\alpha = 101\cdot44\,(3)$, $\beta = 112\cdot11\,(3)$, $\gamma = 71\cdot99\,(3)°$, $V = 534\cdot12$ Å^3, $Z = 1$, $D_m = 1\cdot167$ (flotation in KI solution at 294 K), $D_x = 1\cdot171$ Mg m^{-3}, $\mu(\text{Cu }K\alpha) = 0\cdot586$ mm^{-1}; $R = 0\cdot042$ and $R_w = 0\cdot040$ for 1753 observed reflexions. The 17 angular methyl group adopts an α-axial orientation as predicted by studies on Favorsky rearrangement of 17-halogenated 20-keto steroids devoid of the 18-methyl group.

Introduction. A unifying explanation of the complex results in Favorsky rearrangements of α-halogenated acetylcycloalkanes was advanced by Engel, Roy, Capitaine, Bilodeau, McPherson-Foucar & Lachance (1970). Their basic assumptions concerning the multiplicity of mechanisms and the influence of the 18-methyl group on the stereochemical course of the

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reaction have been supported by recent studies with new material (Engel, Lachance, Capitaine & Merand, 1980). The title compound which was obtained by partial synthesis from epidihydroandrosterone (3β-acetoxyandrost-5-en-17-one) has been examined in this recent work. Its stereochemistry at position 17, with the angular methyl group in the α configuration, has been predicted partly on the basis of mechanistic considerations, and its crystal structure has been examined in order to check the validity of this preliminary assignment.

Crystal data were measured on an automatic Picker diffractometer with Ni-filtered Cu radiation and a prismatic crystal $0.2 \times 0.3 \times 0.4$ mm. The cell parameters were derived from the angular settings of six high-order axial reflexions ($2\theta = 70$ to $101°$) and their equivalents measured at 2θ and -2θ for $K\alpha_1$ and $K\alpha_2$ [$\lambda(K\alpha_1) = 1.54050$, $\lambda(K\alpha_2) = 1.54434$ Å]. The intensities were obtained by $\theta-2\theta$ scans at $2°$ min^{-1} in 2θ, and the backgrounds were recorded for 20 s with a stationary counter at the start and end of each scan. Two standard reflexions were scanned at regular intervals for scaling but showed very small variations. Of the 1809 non-equivalent reflexions with $2\theta < 130°$, 1756 (97%) had significant net counts and were considered observed. The net intensities were corrected for Lorentz and polarization effects, but not for absorption ($\mu = 0.586$ mm^{-1}).

Precession photographs indicated a triclinic system; the crystal density and the lack of a centre of symmetry in the molecule uniquely determined the space group as $P1$ with $Z = 1$, a rather uncommon space group for steroids. The distribution statistics of the E magnitudes were found to be closer to those for a centrosymmetric structure, but this anomaly was attributed to the fact that 20 of the 27 nonhydrogen atoms could be related by a pseudo centre of symmetry at the mid-point of C(9)–C(10).

Direct phasing by the tangent procedure on 16 starting phase sets produced 11 sets with $R_{Karle} \simeq 0.19$ (for the 292 reflexions with $|E| > 1.30$) and no obvious indication in favour of a particular set. An E map computed for one of these phase sets yielded a composite centrosymmetric structure of the molecule and its enantiomorph. The correct structure was then determined from this map, in stages by trial and error, with the aid of Fourier and difference maps.

Refinement was by block-diagonal least-squares calculations, minimizing $\sum w(|F_o| - |F_c|)^2$, with $w = \{1 + [(|F_o| - 10)/18]^2\}^{-1}$. The parameters in the weighting function were selected to make $\langle w(\Delta F)^2 \rangle$ independent of $|F_o|$. All H atoms were located on a difference map and refined isotropically. Scattering factors were those of Hanson, Herman, Lea & Skillman (1964) for C and O, and of Stewart, Davidson & Simpson (1965) for H. The unobserved reflexions and three strong reflexions showing extinction effects

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2$) *for the* C *and* O *atoms*

|	x	y	z	B_{eq}
C(1)	−2045 (5)	−221 (4)	−1164 (6)	4.8
C(2)	−3685 (5)	901 (4)	−955 (5)	4.9
C(3)	−3423 (5)	1345 (3)	1354 (5)	3.4
O(3)	−4961 (3)	2470 (2)	1338 (4)	3.7
C(4)	−1506 (5)	1594 (3)	2525 (5)	3.0
C(5)	116 (4)	451 (3)	2309 (5)	2.8
C(6)	2045 (5)	643 (3)	3674 (6)	4.0
C(7)	3624 (5)	−552 (4)	3616 (6)	4.7
C(8)	3557 (4)	−1085 (3)	1378 (5)	2.9
C(9)	1542 (4)	−1224 (3)	−34 (5)	3.3
C(10)	0 (0)	0 (0)	0 (0)	3.0
C(11)	1547 (5)	−1801 (4)	−2233 (6)	5.7
C(12)	3007 (6)	−3052 (4)	−2218 (6)	5.5
C(13)	4984 (4)	−2886 (3)	−837 (5)	3.1
C(14)	5005 (4)	−2335 (3)	1391 (5)	3.2
C(15)	7104 (5)	−2365 (4)	2608 (6)	4.2
C(16)	8253 (5)	−3491 (4)	1523 (6)	5.0
C(17)	6766 (5)	−4020 (3)	−445 (6)	3.6
C(19)	179 (6)	990 (4)	−1097 (7)	4.3
C(20)	−5314 (5)	2876 (4)	3145 (6)	3.9
O(20)	−4515 (4)	2381 (3)	4734 (4)	5.4
C(21)	−6892 (6)	4076 (4)	2891 (8)	5.8
C(22)	7474 (5)	−4390 (3)	−2289 (6)	3.6
O(22A)	6670 (5)	−4047 (4)	−4005 (5)	7.3
O(22B)	9166 (4)	−5220 (3)	−1802 (5)	5.5
C(23)	10026 (7)	−5682 (5)	−3415 (8)	5.9
C(24)	6409 (7)	−5146 (4)	51 (8)	4.9
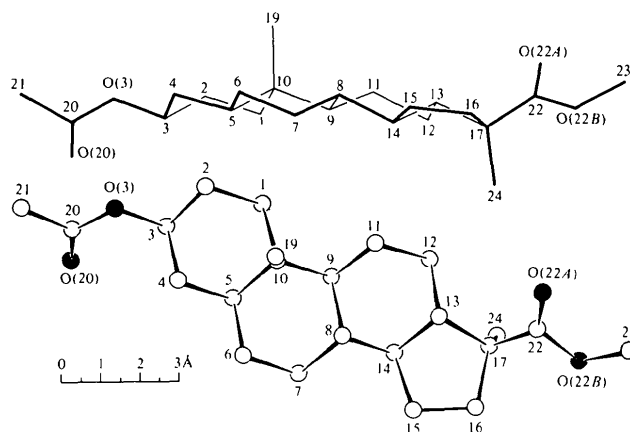
Fig. 1. Two orthogonal projections showing the molecular structure and atom numbering.

were excluded from the refinement. After the final cycle, $R = 0.042$ and $R_w = 0.040$ for the observed reflexions, and the mean and maximum parameter shifts were 0.12 and 0.56 of their e.s.d.'s. The final difference map showed random residual density within -0.17 to 0.15 e Å^{-3}. All calculations were carried out with the NRC system of programs (Ahmed, Hall,

$C_{23}H_{36}O_4$

Table 2. *Fractional coordinates* $(\times 10^3)$ *and temperature factors* $(Å^2)$ *of the* H *atoms*

	x	y	z	B
H(1,1)	−196 (7)	−98 (4)	−21 (7)	8·6 (1·3)
H(1,2)	−225 (5)	−32 (3)	−271 (6)	5·8 (0·9)
H(2,1)	−369 (5)	169 (4)	−158 (6)	6·8 (1·0)
H(2,2)	−498 (6)	75 (4)	−165 (6)	6·6 (1·0)
H(3)	−344 (5)	81 (3)	241 (5)	4·6 (0·8)
H(4,1)	−141 (4)	227 (3)	208 (5)	3·9 (0·7)
H(4,2)	−127 (5)	184 (3)	406 (5)	4·8 (0·8)
H(5)	7 (4)	−24 (3)	304 (5)	3·9 (0·7)
H(6,1)	225 (5)	127 (3)	317 (5)	4·5 (0·8)
H(6,2)	217 (5)	101 (3)	528 (5)	4·8 (0·8)
H(7,1)	347 (5)	−123 (3)	436 (5)	5·1 (0·8)
H(7,2)	474 (5)	−31 (3)	434 (5)	5·5 (0·9)
H(8)	392 (4)	−52 (3)	76 (5)	3·3 (0·7)
H(9)	129 (4)	−178 (3)	78 (5)	3·1 (0·6)
H(11,1)	190 (6)	−116 (4)	−291 (7)	7·4 (1·2)
H(11,2)	35 (5)	−175 (3)	−312 (5)	4·7 (0·8)
H(12,1)	272 (5)	−372 (4)	−151 (6)	6·0 (0·9)
H(12,2)	306 (7)	−330 (4)	−371 (7)	8·5 (1·2)
H(13)	527 (5)	−224 (3)	−150 (5)	4·0 (0·8)
H(14)	466 (4)	−294 (3)	208 (5)	3·5 (0·7)
H(15,1)	738 (5)	−152 (4)	242 (6)	6·4 (1·0)
H(15,2)	746 (5)	−246 (3)	434 (6)	5·8 (0·9)
H(16,1)	895 (6)	−298 (4)	87 (6)	7·4 (1·1)
H(16,2)	898 (6)	−405 (4)	272 (7)	8·2 (1·2)
H(19,1)	−57 (7)	171 (4)	−86 (8)	9·2 (1·4)
H(19,2)	144 (6)	109 (4)	−50 (7)	8·1 (1·2)
H(19,3)	−3 (6)	68 (4)	−244 (6)	6·6 (1·0)
H(21,1)	−679 (9)	465 (6)	238 (9)	14·6 (1·9)
H(21,2)	−727 (8)	463 (5)	421 (9)	12·0 (1·7)
H(21,3)	−786 (9)	388 (5)	206 (9)	13·1 (1·9)
H(23,1)	1027 (7)	−478 (5)	−367 (8)	11·9 (1·4)
H(23,2)	1130 (8)	−601 (5)	−280 (9)	11·8 (1·7)
H(23,3)	918 (7)	−598 (4)	−452 (8)	9·2 (1·4)
H(24,1)	615 (8)	−498 (5)	150 (8)	10·6 (1·5)
H(24,2)	763 (7)	−560 (5)	51 (8)	9·5 (1·4)
H(24,3)	551 (5)	−545 (3)	−127 (6)	5·0 (0·9)
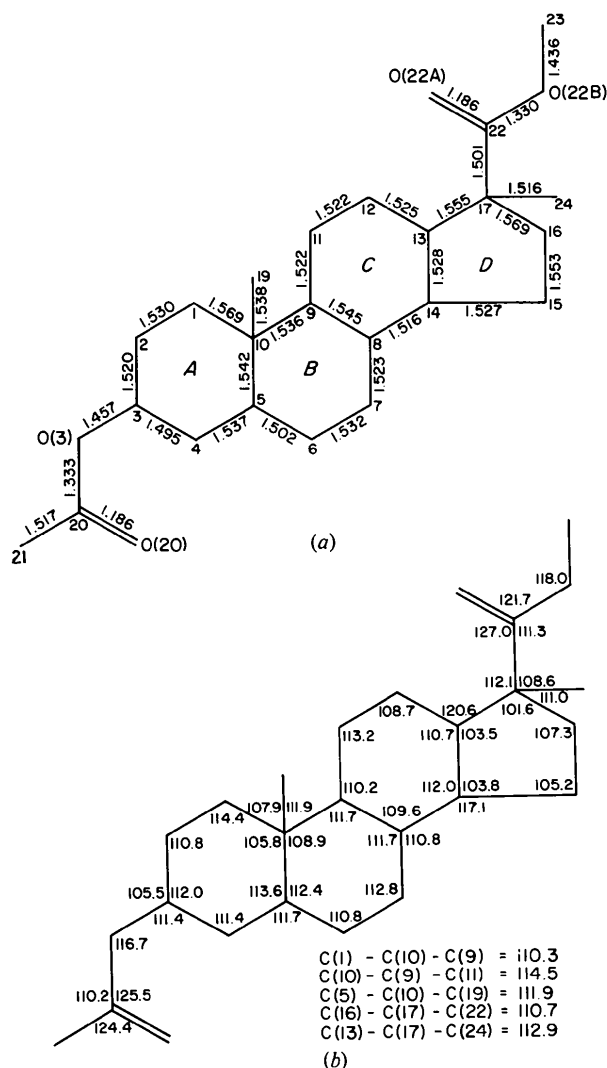
Pippy & Huber, 1973). The refined atomic parameters are listed in Tables 1 and 2.*

Discussion. The molecular structure and atom numbering are shown in Fig. 1. The substituents at C(17) are located in the orientation predicted from studies on Favorsky rearrangement of 17-halogenated 18-nor-20-keto steroids, with the methyl substituent in the axial 17α orientation. The bond lengths and angles, and endocyclic torsion angles are presented in Fig. 2. The C—H lengths are 0·84–1·15 Å (σ = 0·03 to 0·07 Å), and the shortest intermolecular contacts are 2·29 (7) Å for H···H and 3·443 (5) Å for C···O.

In general, the geometrical entities quoted in Fig. 2 are in good agreement with the corresponding mean

Fig. 2. (*a*) Bond lengths (Å) (σ = 0·003–0·007 Å), (*b*) bond angles (°) (σ = 0·2–0·4°), and (*c*) endocyclic torsion angles (°) (σ = 0·4–0·8°).

values for a sample of 24 5α steroids with all *trans* ring junctions (Duax & Norton, 1975). The largest discrepancies from the mean values occur in the bond lengths, particularly for C(1)—C(10) and C(9)—C(10) which are 1·569 (4) and 1·536 (4) Å in the present structure while the corresponding mean values are 1·536 (12) and 1·560 (18) Å, where the latter e.s.d.'s are calculated from the spread in the sample values. However, the present values actually fall within the corresponding spread in the sample.

The three six-membered rings have a highly symmetrical chair conformation. The maximum asymmetry parameters (Duax, Weeks & Rohrer, 1976) for the A, B and C rings are $\Delta C_2[\text{C}(3)-\text{C}(4)] = 3\cdot0$, $\Delta C_2[\text{C}(6)-\text{C}(7)] = 5\cdot3$ and $\Delta C_2[\text{C}(11)-\text{C}(12)] = 2\cdot8°$, respectively. The D ring has an envelope conformation with $\Delta C_s[\text{C}(13)] = 6\cdot9°$. O(3), C(20), O(20) and C(21) of the acetate substituent are coplanar ($\chi^2 = 0\cdot2$), and their mean plane makes an angle of 136·4° with the reference mean plane of C(5) to C(17). This planar group is antiperiplanar to C(2)—C(3), C(2)—C(3)—O(3)—C(20) = 164·8° (Duax & Norton, 1975), and its carbonyl group is synperiplanar to C(3), C(3)—O(3)—C(20)—O(20) = −1·9°. The 17β side chain has C(17), C(22), O(22A) and O(22B) almost coplanar ($\chi^2 = 8\cdot7$) with the mean plane at 139·3° from the reference mean plane of C(5) to C(17). The carbonyl O atom is

synperiplanar to C(13)—C(17), C(13)—C(17)—C(22)—O(22A) = −12·3°, and C(23) of the methyl group is synperiplanar to the carbonyl, O(22A)—C(22)—O(22B)—C(23) = 1·1°.

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