$CH_3(18) + 14\text{-}CH_3$; 2.07, *s* $CH_3(4)$ ($CDCl_3$); – not yet crystallized][3]. Finally, **8** was converted by catalytic hydrogenation [5%-Pd/C in ethanol/triethylamine; → **11**[3]] and cyclisation [HCl in acetic acid] into 3-oxo-17β-acetoxy-14α-methyl-Δ^4-8α,9β,10α,13α-estrene (**12**) [m.p. 86–88°; – $[\alpha]_D = +1°$ ($CHCl_3$). – IR.: 1729, 1665, 1620, 1255 ($CHCl_3$); – UV.: 245 nm ($\varepsilon = 14500$ in ethanol). – NMR.: 0.98 + 0.99, 2*s*, $CH_3(18) + 14\text{-}CH_3$; 1.98, *s*, 17-$OCOCH_3$; 5.05, b*m*, CH(17); 5.70, b*s*, CH(4) ($CDCl_3$). – MS.: $M^+ = 330$ ($C_{21}H_{30}O_3$). – CD.: 320 nm ($\Delta\varepsilon = 1.37$ in ethanol)]. The structure of **12** was subsequently confirmed by three-dimensional X-ray diffraction; in addition the 8α,9β,10α,13α,14α-configuration of this steroid like derivative **12** was also established by the X-ray results[8].

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[8] We wish to express our sincerest thanks to Dr. *G. Koyama* for the structure determination by X-ray analysis [2].

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40. The Crystal and Molecular Structure of 3-Oxo-17β-acetoxy-Δ^4-14α-methyl-8α,9β,10α,13α-estrene

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(8. I. 73)

Summary. The crystal and molecular structure of 3-oxo-17β-acetoxy-Δ^4-14α-methyl-8α,9β,10α,13α-estrene, $C_{21}H_{30}O_3$, has been determined by X-ray diffraction analysis. The crystals belong to the orthorhombic space group $P2_12_12_1$, with the cell dimensions $a = 12.093$ Å, $b = 19.667$ Å, $c = 7.746$ Å; Z = 4. Intensity data were collected at room temperature with an automatic four-circle diffractometer. The structure was solved by direct methods and the parameters were refined by least-squares analysis. All the hydrogen atoms were included in the refinement. The final R value was 0.038 for 1413 observed reflections. The conformation of ring A is intermediate between a half-chair and a 1,2-diplanar form. The hydrogens at C(9) and C(10) are *anti*, the B/C ring junction is *trans*, and rings B and C adopt chair conformations. Ring D is *cis* fused and is halfway between C_2 and C_s forms.

The transformation of dehydroabietic acid into a 14α-methyl steroid product is described in the preceding communications [1]. Since the configurations at C(8),

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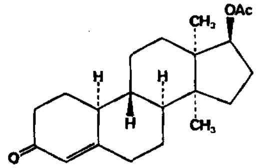
C(9), C(10), C(13) and C(17) in the product molecule were unknown, an X-ray analysis has been carried out in order to obtain this information. The resulting stereochemical formula is:



Crystal data. – 3-Oxo-17β-acetoxy-Δ^4-14α-methyl-8α,9β,10α,13α-estrene, $C_{21}H_{30}O_3$, M.W. 330.5, m.p. 86–88°, orthorhombic, $a = 12.093$, $b = 19.667$, $c = 7.746$ Å, V = 1842 Å^3, space group $P2_12_12_1$, Z = 4, $D_x = 1.192$, $D_m = 1.195$.

Experimental. – Crystals were obtained from ether/pentane. The specimen for the present work had dimensions 0.40×0.20×0.25 mm. Cell constants were determined from (h0l) and (0kl) precession photographs. Intensity data were collected on the Y-290 four-circle diffractometer (*Hilger & Watts Co.*) by the $2\theta/\omega$ scanning technique using MoKα (λ = 0.71069 Å) radiation. Backgrounds were measured on both sides of the peak for $^1/_4$ of the total scanning time for the reflection. A total of 1883 independent reflections ($\theta \leq 25°$) were measured. *Lorentz* and polarization corrections were applied in converting these intensities into F- and E-values. Absorption corrections were not applied.

Table 1 *Final parameters (and e.s.d.'s) of non-hydrogen atoms* (× 10^4)
The temperature factors take the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	12153(3)	966(3)	5162(5)	133(4)	102(2)	241(9)	−134(5)	−105(11)	109(8)
O(2)	10592(2)	378(1)	4983(4)	54(2)	34(1)	196(6)	5(2)	−14(7)	41(4)
O(3)	2613(2)	1559(2)	709(5)	48(2)	69(2)	294(9)	−19(3)	−28(8)	−12(7)
C(1)	5036(3)	1552(2)	3391(6)	52(3)	37(1)	160(9)	5(4)	32(9)	2(6)
C(2)	3918(3)	1862(2)	2881(6)	51(3)	43(2)	207(10)	9(4)	57(10)	−5(8)
C(3)	3586(3)	1645(2)	1093(6)	48(3)	31(1)	246(11)	3(3)	1(11)	18(7)
C(4)	4466(3)	1591(2)	−170(6)	61(3)	28(1)	177(9)	4(3)	25(9)	12(6)
C(5)	5534(3)	1670(2)	228(5)	54(3)	21(1)	165(8)	10(3)	−5(8)	−3(5)
C(6)	6395(3)	1745(2)	−1143(5)	60(3)	36(1)	131(8)	12(4)	−9(9)	1(6)
C(7)	7421(3)	1310(2)	−796(5)	53(3)	34(1)	132(8)	13(3)	18(9)	−8(6)
C(8)	7894(3)	1457(2)	1000(5)	45(3)	22(1)	134(8)	2(3)	17(8)	−3(5)
C(9)	6998(3)	1289(2)	2360(5)	48(3)	23(1)	134(8)	3(3)	19(8)	−3(5)
C(10)	5944(3)	1730(2)	2071(5)	46(3)	26(1)	148(8)	2(3)	19(8)	−14(6)
C(11)	7451(3)	1374(2)	4187(5)	55(3)	35(1)	135(8)	12(4)	21(9)	−4(6)
C(12)	8513(3)	963(2)	4457(5)	57(3)	34(1)	122(8)	10(4)	8(8)	−14(6)
C(13)	9437(3)	1166(2)	3210(5)	51(3)	22(1)	145(8)	7(3)	6(8)	4(5)
C(14)	9028(3)	1103(2)	1295(5)	46(2)	21(1)	143(8)	3(3)	10(8)	−6(5)
C(15)	9000(3)	320(2)	1021(6)	62(3)	23(1)	177(9)	2(3)	−1(9)	−15(6)
C(16)	9939(4)	31(2)	2128(7)	72(3)	25(1)	246(11)	26(4)	−7(11)	−8(6)
C(17)	10364(3)	622(2)	3236(6)	51(3)	28(1)	165(8)	9(3)	6(8)	22(6)
C(18)	9899(4)	1870(2)	3677(6)	79(4)	27(1)	197(9)	−5(4)	−21(10)	−12(6)
C(19)	9862(3)	1423(2)	33(6)	48(3)	34(1)	167(8)	4(3)	20(9)	5(6)
C(20)	11520(4)	569(2)	5759(6)	70(3)	38(2)	179(9)	2(4)	5(11)	−1(7)
C(21)	11687(4)	239(3)	7467(7)	102(5)	41(2)	197(11)	32(5)	−30(12)	9(8)

Structure analysis. – The structure was solved by direct methods. The program MULTAN [2] was utilized for obtaining the starting set, while the symbolic addition procedure for phase determination in non-centrosymmetric space groups [3] was worked out at the same time. The MULTAN program could not afford a suitable starting set but it gave two important pieces of information: 1) The phase of the reflection (2 0 6) seemed to be assigned as $\varphi = 0°$ from the Σ_1 relations with probability 0.864. 2) Judging from the convergence map output by the program, the reflection (6 15 2) seemed to play an important role in the whole phase determination process. This reflection was completely overlooked in the symbolic addition procedure which had been done prior to the MULTAN computation. Thus the following starting set was built up: the reflections (019; $\varphi = 90°$), (1 4 0: $\varphi = 90°$) and (6 15 2: $\varphi = 45°$) specify the origin, (2 0 6: $\varphi = 0°$) was introduced as of known phase, (7 1 5: $\varphi = 45°, 135°$) fixes the enantiomorph and (2 1 3) was assigned a variable phase of $\varphi = 45°, 135°, 225°, 315°$. Tangent refinement was carried out for each of eight phase combinations using the 202 reflections with $/E/ > 1.5$. The lowest value (0.29) of $R_E = \Sigma(/E_o/ - /E_c)/\Sigma/E_o/$ was obtained for the run with ϕ (7 1 5) $= 45°$, ϕ (2 1 3) $= 45°$. An E-map computed on the basis of the 204 refined phases in this run revealed the positions of 20 out of the 24 non-hydrogen atoms. The coordinates obtained from the E-map were refined by least-squares analysis. Two cycles of full-matrix refinement with isotropic thermal parameters on the 1413 reflections with $F > 3\,\sigma(F)$ were carried out. A difference *Fourier*-synthesis based on the refined atomic parameters for these atoms showed peaks corresponding to the four missing atoms, C(16), C(18), C(21) and O(1). Two cycles of full-matrix least-squares analysis with isotropic thermal parameters reduced the R-factor to 13.7%. At this stage, the coordinates of all 30 hydrogen atoms were calculated and included in the subsequent refinement using the block-diagonal approximation. Two cycles with anisotropic thermal parameters for non-hydrogen atoms and a constant isotropic thermal parameter (B = 4.5 Å²) for hydrogens reduced R to 6.0%. In order to confirm the positions of the hydrogen atoms, a $(F_o - F_c)$-synthesis was computed using the 575 reflections with $\sin \theta/\lambda < 0.4$ and $F > 2\sigma(F)$. In six subsequent cycles, the hydrogen positions thus obtained were also refined with isotropic thermal parameters. The final R factor was 3.8% for 1413 reflections. No electron density greater than 0.1/Å³ was found in a final difference synthesis (R = 3.2%) calculated as above. The final atomic coordinates and thermal parameters are tabulated in Tables 1 and 2 with their estimated standard deviations in parentheses. A list of observed F-values is obtainable on request from the author.

Table 2 *Final parameters (and their e.s.d.'s) of hydrogen atoms*

(Coordinates are × 10³)

	x	y	z	B		x	y	z	B
H(1α)	531(3)	171(2)	467(5)	5.3 Å²	H(12β)	835(3)	44(2)	430(5)	5.3
H(1β)	495(3)	102(2)	344(5)	4.6	H(15α)	910(3)	21(2)	– 20(5)	4.6
H(2α)	399(3)	247(2)	281(6)	5.3	H(15β)	828(3)	11(2)	132(4)	3.2
H(2β)	334(3)	182(2)	366(5)	5.0	H(16α)	1054(3)	– 15(2)	163(5)	5.7
H(4)	423(3)	153(2)	–138(5)	5.6	H(16β)	973(3)	– 37(2)	285(5)	4.0
H(6α)	662(3)	228(2)	–114(5)	4.2	H(17α)	1108(3)	82(2)	275(5)	4.6
H(6β)	609(3)	165(2)	–214(5)	3.9	H(18α)	1054(3)	202(2)	301(5)	5.1
H(7α)	787(3)	141(2)	–163(5)	4.6	H(18b)	995(3)	191(2)	490(5)	5.7
H(7β)	724(3)	79(2)	– 93(4)	3.2	H(18c)	936(3)	224(2)	347(5)	5.5
H(8α)	807(3)	199(2)	103(4)	2.6	H(19a)	1054(3)	132(2)	20(6)	5.8
H(9β)	674(3)	75(2)	217(5)	4.1	H(19b)	988(3)	197(2)	11(5)	5.5
H(10α)	617(3)	230(2)	231(5)	4.8	H(19c)	967(3)	126(2)	–108(6)	6.4
H(11α)	763(3)	190(2)	440(5)	3.9	H(21a)	1101(4)	10(2)	790(6)	6.9
H(11β)	695(3)	120(2)	510(5)	4.5	H(21b)	1198(4)	53(2)	810(6)	8.3
H(12α)	875(3)	99(2)	567(5)	4.8	H(21c)	1202(4)	– 14(2)	719(6)	7.5

Discussion. – A stereoscopic view of the molecule is shown in Fig. 1. The absolute configuration was assigned by chemical considerations: in the starting material for

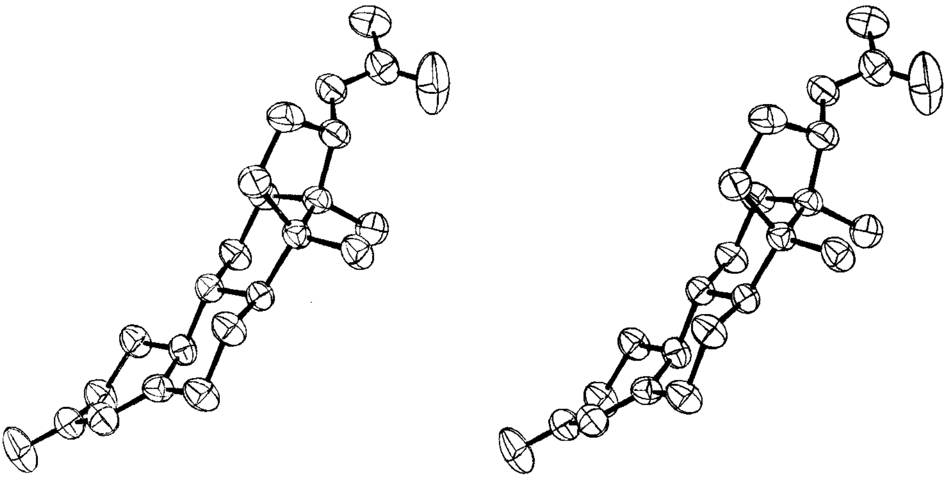


Fig. 1. *A stereoscopic view of the molecule* (hydrogen atoms are omitted for the sake of clarity)

the synthesis of this compound the configuration at C(14) is known to be S(α-methyl group). Bond distances, bond angles and torsion angles in the rings are shown in Fig. 2 and 3. The conformation of ring A is intermediate between a half-chair and a 1,2-diplanar (sofa) form. A similar conformation of ring A in another Δ^4-3-keto steroid occurs in 14α,17α-etheno-15,16-di(trifluoromethyl)-4,15-pregnadiene-3,20-dione [4]. Ring B has a chair conformation, slightly flattened by the presence of the double bond

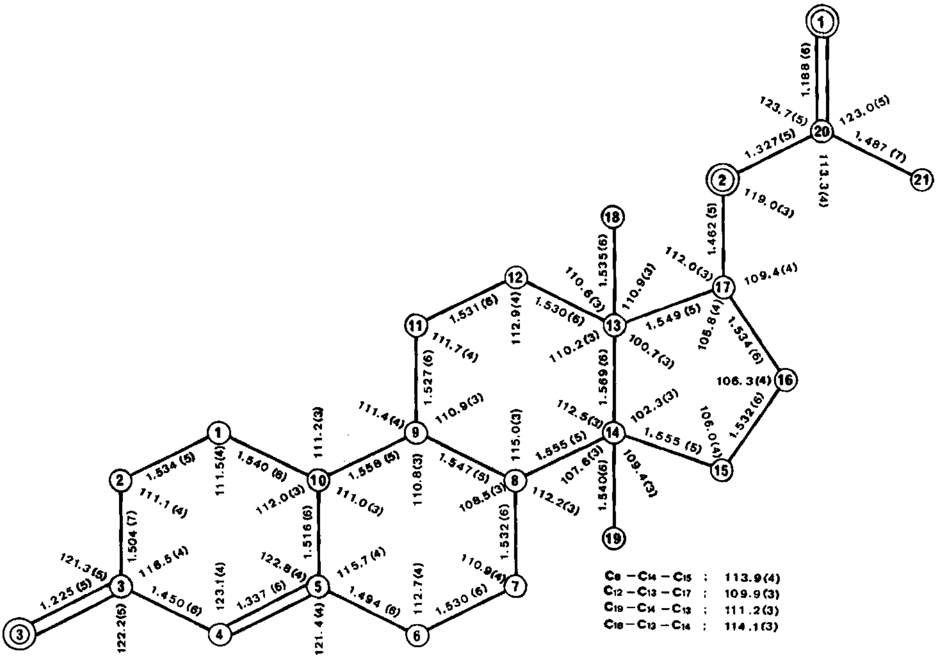


Fig. 2. *Bond distances and angles not involving hydrogen atoms*

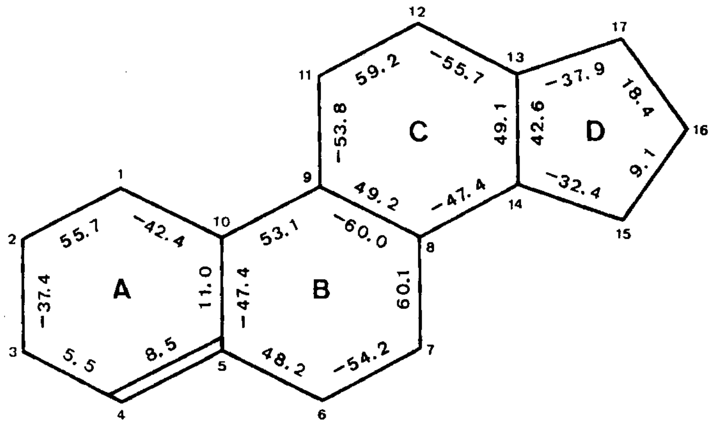


Fig. 3. *Torsion angles in the rings*

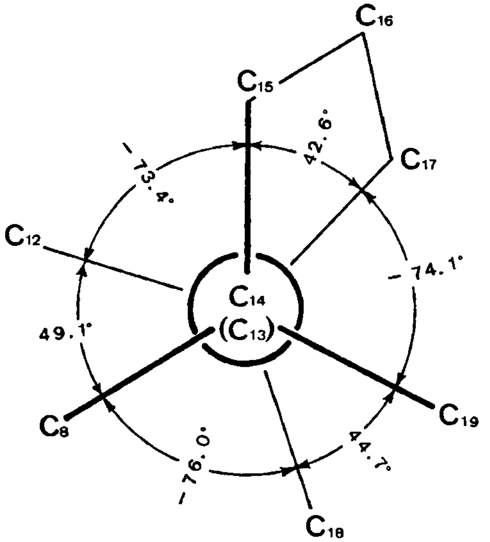


Fig. 4. Newman *projection along the C(14) – C(13) bond*

which leads to a decrease in the absolute values of the torsion angles about C(5)–C(6) and C(5)–C(10), as found in other Δ^4-3-keto steroids [4] [5]. Ring C also has a chair conformation, slightly flattened at C(14), which has the additional methyl substituent group C(19). At the unusual C/D *cis* fusion the relationship between the two torsion angles $\phi_C(12, 13, 14, 8)$ and $\phi_D(17, 13, 14, 16)$ is just the reverse of that in the C/D *trans* case. For the usual *trans* junction, when the torsion angle φ_D decreases, φ_C tends to increase, while in the present structure, when φ_D decreases, φ_C is also expected to decrease [6]. Consequently, the sum of φ_C and φ_D has the markedly small value of 91.7°. The *Newman* projection (Fig. 4) shows the situation. Ring D is intermediate between a half-chair and an envelope with the conformational parameters $\Delta = 13°$ and $\varphi_m = 43.0°$ [6]. The atoms of the acetoxy group, C(21), C(20), O(1) and O(2) are coplanar (maximum deviation 0.003 Å for C(20)), and C(17) is displaced from this

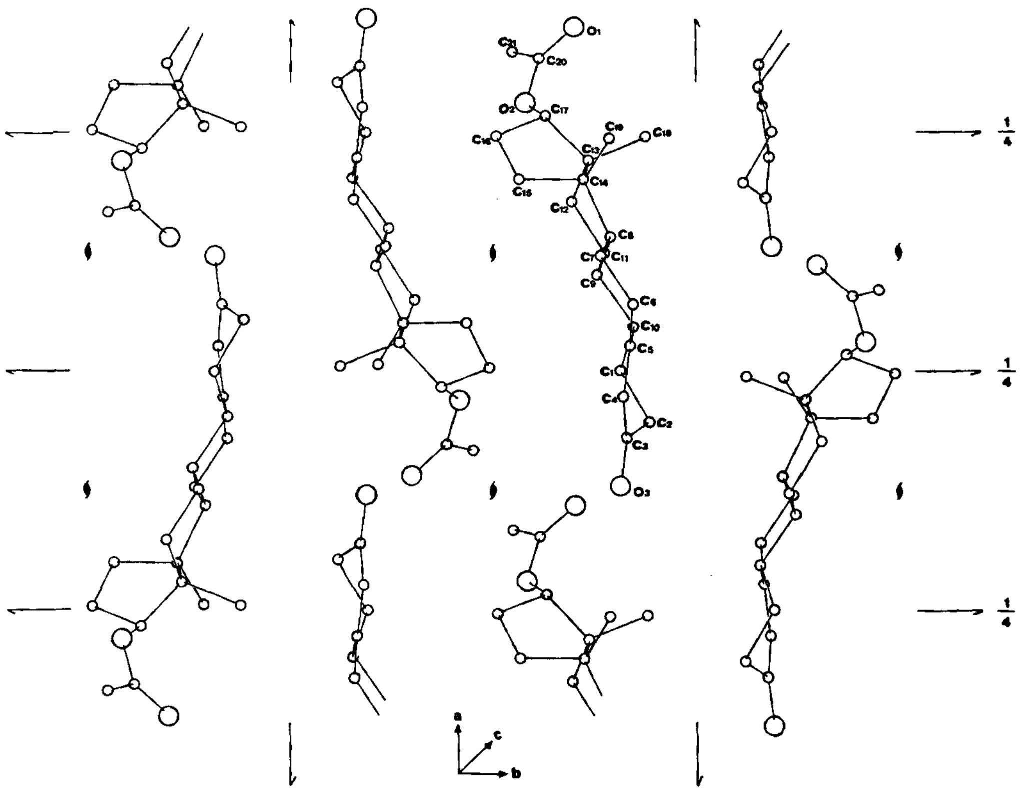


Fig. 5. *Crystal structure viewed along the c-axis*

plane by 0.1 Å. The atoms C(2), C(3), C(4), C(5), C(6), C(10) and O(3) involved in the conjugated Δ^4-3-keto system deviate markedly from coplanarity. The average deviation is 0.1 Å with C(2), C(6) and C(10) out of the best plane by more than 0.15 Å. The bond distances and angles, as a whole, do not involve significant discrepancies from expected values based on published data for similar molecules. The packing of the molecules in the crystal is shown in Fig. 5. There are no unduly short intermolecular contacts.

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