The Structure of a 19 -Hydroxy-14,15-oxido Steroid, $C_{23}H_{34}O_6$*

By George I. Birnbaum
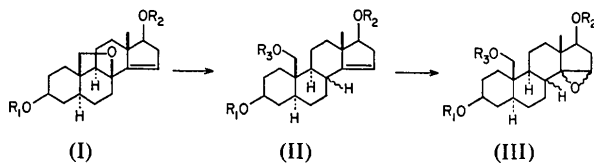
Division of Biological Sciences, National Research Council of Canada, Ottawa, Canada K1A 0R6

$3\beta,17\beta$-Diacetoxy-$14\alpha,15\alpha$-oxido-19-hydroxy-$5\alpha,8\beta$-androstane, $C_{23}H_{34}O_6$, crystallizes in the orthorhombic space group $P2_12_12_1$ ($Z=4$) with cell dimensions $a=27\cdot241\pm0\cdot003$, $b=12\cdot171\pm0\cdot001$ and $c=6\cdot585\pm0\cdot002$ Å. Crystal densities are $D_x=1\cdot237$ and $D_m=1\cdot235$ g cm^{-3}. Data were collected at room temperature with an automatic four-circle diffractometer. The structure was solved by direct methods and refined by the least-squares procedure to a final value of $R=0\cdot056$ for 1803 observed reflexions. The steroid skeleton has a *trans-anti-trans* configuration at the $A/B/C$ junctions with the three six-membered rings in chair conformations. Ring D is a C(17) α-envelope, and the dihedral angle between its mean plane and the epoxide ring is $77\cdot0°$. All C–C bonds adjacent to the epoxide ring are $0\cdot03$–$0\cdot04$ Å shorter than normal.

Introduction

Until recently an all-chemical route from bulk steroids, such as androstenolone acetate, to 14-functionalized 19-hydroxy steroids was unknown. This was recently achieved by Kruger (1971), who succeeded in converting $3\beta,17\beta$-diacetoxy-8,19-oxido-5α-androst-14-ene (I: $R_1=R_2=Ac$) to the 19-hydroxy compound (II: $R_1=R_2=Ac$, $R_3=H$) by zinc-dust reduction of the 8,19-oxido bridge. However, the configuration at C(8) in the product was unknown. In order to determine it and to confirm the rest of the structure an X-ray analysis of the corresponding epoxide (III: $R_1=R_2=Ac$, $R_3=H$) was carried out. Its results showed that the hydrogen atom at C(8) was in the β-configuration, the molecule thus having the common *trans-anti-trans-anti-trans* stereochemistry. A preliminary report of this work has been published (Kruger & Birnbaum, 1973).

(I)   (II)   (III)

Experimental

Crystal data

$3\beta,17\beta$-Diacetoxy-$14\alpha,15\alpha$-oxido-19-hydroxy-$5\alpha,8\beta$-androstane, $C_{23}H_{34}O_6$;
M.W. 406·5; orthorhombic:
$a=27\cdot241\pm0\cdot003$, $b=12\cdot171\pm0\cdot001$,
$c=6\cdot585\pm0\cdot002$ Å, $V=2183\cdot3$ Å^3, $F(000)=880$
$D_x=1\cdot237$ g cm^{-3}
$D_m=1\cdot235$ g cm^{-3} (flotation in KI solution)
$Z=4$
$\mu=7\cdot27$ cm^{-1} (Cu $K\alpha$, $\lambda=1\cdot5418$ Å)

Absent reflexions: $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd. Space group: $P2_12_12_1$.

The material was obtained by reduction and subsequent epoxidation of the corresponding Δ^{14}-8,19-oxido-steroid. Colourless prismatic crystals (m.p. 174·5–175·0°C) were obtained from a mixture of methanol and ethyl ether. One of them was cut to a size of $0\cdot21\times0\cdot21\times0\cdot35$ mm and mounted along the prism c axis on an automated Picker four-circle diffractometer equipped with a Cu target tube and a scintillation counter. Monochromation was achieved by a nickel filter and a pulse-height analyser. The cell dimensions were measured at room temperature at a small take-off angle and with a narrow slit, using both Cu $K\alpha_1$ ($\lambda=1\cdot5405$ Å) and Cu $K\alpha_2$ ($\lambda=1\cdot5443$ Å) radiations. The moving-crystal, moving-counter method ($\theta/2\theta$ scan) was used to measure the intensity data (2° scans for $2\theta<100°$, 3° for $2\theta\geq100°$) and background counts were recorded for 20 sec at the beginning and end of each scan. When the count rate exceeded 20,000 c.p.s. the current was reduced and, if necessary, brass attenuators were used. A standard reflexion 19,4,0 was monitored at frequent intervals. Its intensity did not change while the first 60% of the data were being measured. After that the intensity decreased gradually until, at the end, it was off by 15%. The data were scaled accordingly. A net count of 70 or 5% of the background, whichever was higher, was accepted as threshold intensity below which reflexions were considered unobserved. Of 2163 reflexions accessible to the diffractometer ($2\theta\leq130°$) 1805 (83%) had intensities above threshold values. All reflexions were indexed with respect to a right-handed set of axes. In view of the low value of μR ($0\cdot15$) absorption effects are negligible and corrections were not applied.

Determination and refinement of the structure

Several attempts to solve the structure by an application of the Σ_2 formula followed by tangent refinement

(Karle, 1970) were unsuccessful. This approach was abandoned in favour of a multi-solution method (Germain & Woolfson, 1968). In addition to the four fixed phases required to define the origin and the enantiomorph in this space group, two more reflexions were chosen on the basis of their high $|E|$ values and numerous triplet interactions and all combinations of the phases $\pm \pi/4$ and $\pm 3\pi/4$ were successively assigned to them. Tangent refinement of other phases proceeded in three stages with 64 reflexions ($|E| \geq 1.97$), 98 reflexions ($|E| \geq 1.80$) and 219 reflexions ($|E| \geq 1.55$). The following input yielded $R_E (= \sum ||E_o| - |E_c||/\sum |E_o|) = 0.24$, the lowest value of all:

h	k	l	$|E|$	φ	
23	0	2	3.89	0	
21	0	5	3.51	$\pi/2$	origin defining
0	1	4	2.96	$\pi/2$	
20	3	0	2.56	0	enantiomorph defining
2	9	2	2.71	$\pi/4$	
15	7	1	2.19	$-3\pi/4$	

The phases thus obtained were used to extend the tangent refinement by including 316 reflexions with $|E| \geq 1.40$. At the end of this final refinement, during which only the first four phases were kept constant, the R_E value was reduced to 0.22; the phase of 292 changed from 45 to $-33°$ and that of 15,7,1 from 225 to 198°. An E map calculated with these phases revealed all but three of the non-hydrogen atoms. The missing three atoms, which were easily located in a subsequent difference Fourier map, were in the CH_3CO-group attached to O(3). It will be seen later that they are subject to strong thermal vibration.

The block-diagonal approximation of the least-squares method was used to refine the atomic parameters. The scattering factors for C and O were those given by Hanson, Herman, Lea & Skillman (1964) and those for bonded H were taken from Stewart, Davidson & Simpson (1965). The oxygen curve was corrected for anomalous dispersion with $\Delta f'' = 0.1$ (*International Tables for X-ray Crystallography*, 1962). After

Table 1. *Final parameters (and their e.s.d.'s) of the nonhydrogen atoms*

All coordinates are $\times 10^4$. The U^{ij} values (in Å^2) are $\times 10^3$ and are defined by
$$\exp\left[-2\pi^2(U^{11}h^2a^{*2} + U^{22}k^2b^{*2} + U^{33}l^2c^{*2} + 2U^{23}klb^*c^* + 2U^{13}hla^*c^* + 2U^{12}hka^*b^*)\right].$$

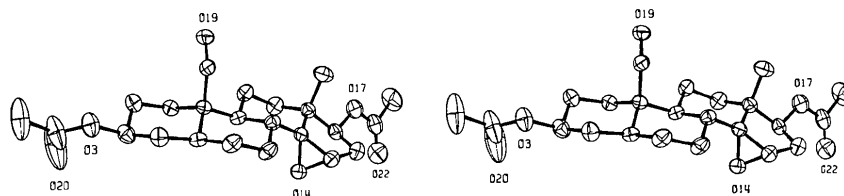|	x/a	y/b	z/c	U^{11}	U^{22}	U^{33}	$2U^{23}$	$2U^{13}$	$2U^{12}$
C(1)	4500 (1)	6660 (3)	700 (6)	32 (2)	34 (2)	33 (2)	-5 (3)	10 (3)	-6 (3)
C(2)	3951 (1)	6774 (4)	206 (6)	40 (2)	43 (2)	35 (2)	-3 (4)	-5 (4)	-8 (4)
C(3)	3676 (1)	5728 (4)	669 (7)	34 (2)	48 (2)	43 (2)	-13 (4)	5 (4)	-14 (4)
C(4)	3763 (1)	5355 (3)	2827 (7)	33 (2)	43 (2)	42 (2)	10 (4)	12 (3)	-17 (3)
C(5)	4304 (1)	5287 (3)	3386 (6)	34 (2)	27 (2)	40 (2)	-1 (3)	17 (3)	1 (3)
C(6)	4377 (1)	4894 (3)	5550 (7)	40 (2)	35 (2)	48 (2)	26 (4)	16 (4)	-8 (3)
C(7)	4914 (1)	4682 (3)	6018 (7)	40 (2)	32 (2)	52 (3)	32 (4)	9 (4)	-1 (3)
C(8)	5243 (1)	5668 (3)	5465 (6)	36 (2)	31 (2)	32 (2)	2 (3)	6 (3)	5 (3)
C(9)	5150 (1)	6105 (3)	3285 (6)	34 (2)	25 (2)	35 (2)	3 (3)	11 (3)	7 (3)
C(10)	4594 (1)	6369 (3)	2942 (6)	34 (2)	28 (2)	29 (2)	-7 (3)	5 (3)	0 (3)
C(11)	5504 (1)	7049 (3)	2770 (7)	30 (2)	36 (2)	57 (3)	21 (4)	-1 (4)	-8 (3)
C(12)	6052 (2)	6714 (4)	3005 (7)	38 (2)	45 (2)	49 (2)	15 (4)	9 (4)	-6 (4)
C(13)	6156 (1)	6273 (3)	5143 (6)	34 (2)	36 (2)	40 (2)	-7 (3)	-4 (3)	-1 (3)
C(14)	5780 (1)	5376 (3)	5574 (6)	40 (2)	29 (2)	31 (2)	-2 (3)	-3 (3)	-5 (3)
C(15)	6019 (2)	4488 (3)	6693 (7)	42 (2)	37 (2)	51 (2)	4 (4)	-14 (4)	6 (4)
C(16)	6553 (2)	4756 (4)	6973 (8)	47 (2)	47 (2)	51 (3)	4 (5)	-22 (4)	12 (4)
C(17)	6646 (1)	5634 (3)	5351 (7)	36 (2)	42 (2)	50 (2)	-14 (4)	-22 (4)	-7 (4)
C(18)	6119 (2)	7177 (4)	6760 (8)	62 (3)	42 (2)	58 (3)	-31 (5)	-5 (5)	-2 (4)
C(19)	4410 (1)	7295 (3)	4350 (6)	43 (2)	33 (2)	35 (2)	-1 (4)	-6 (4)	13 (3)
C(20)	2951 (2)	5929 (7)	-1351 (8)	46 (3)	147 (6)	52 (3)	-22 (8)	-12 (5)	-52 (7)
C(21)	2423 (2)	6217 (9)	-1295 (11)	41 (3)	194 (9)	77 (4)	36 (11)	-29 (6)	-34 (8)
C(22)	7493 (2)	5950 (4)	5905 (7)	39 (2)	69 (3)	45 (2)	-2 (5)	-6 (4)	-20 (4)
C(23)	7865 (2)	6801 (6)	6502 (11)	48 (3)	94 (4)	100 (5)	-22 (8)	-23 (6)	-48 (6)
O(3)	3150 (1)	5934 (3)	475 (5)	36 (2)	70 (2)	47 (2)	-2 (4)	-6 (3)	-13 (3)
O(14)	5911 (1)	4359 (2)	4537 (5)	40 (2)	35 (1)	53 (2)	-15 (3)	-15 (3)	5 (2)
O(17)	7038 (1)	6381 (3)	5891 (5)	41 (2)	54 (2)	61 (2)	-4 (3)	-13 (3)	-12 (3)
O(19)	4574 (1)	8370 (2)	3814 (5)	58 (2)	29 (1)	47 (2)	-7 (3)	-11 (3)	4 (3)
O(20)	3181 (2)	5784 (8)	-2837 (7)	69 (3)	323 (10)	52 (2)	-92 (9)	-10 (4)	-10 (9)
O(22)	7581 (1)	5014 (3)	5513 (6)	41 (2)	81 (2)	73 (2)	-13 (4)	13 (3)	7 (3)

Fig. 1. Stereoscopic view of the structure; the ellipsoids include 50% probability.

five cycles of refinement with isotropic temperature parameters the value of R decreased to 0·126. Three more cycles with anisotropic parameters ($R=0·096$) were followed by a low-angle difference Fourier synthesis which revealed 31 hydrogen atoms on peaks ranging from 0·23 to 0·42 e Å^{-3}. The positions of the H atoms attached to C(23) were not obtainable owing to poor peak resolution. The contributions of the 31 H atoms were included in subsequent structure-factor calculations, but their parameters were not refined. The following weighting scheme was introduced at this stage and kept until the end of the refinement:

$$w = w_1 w_2$$

where $w_1 = 1$ for $|F_o| \le 10$

$$= \frac{10}{|F_o|} \quad \text{for } |F_o| > 10$$

and $w_2 = \frac{\sin^2 \theta}{0·2}$ for $\sin^2 \theta \le 0·2$

$$= 1 \quad \text{for } \sin^2 \theta > 0·2.$$

This weighting scheme was fairly successful in eliminating the dependence of $w\Delta F^2$ on $|F_o|$ and $\sin^2 \theta$. Throughout the refinement the function $\sum w(|F_o| - |F_c|)^2$ was minimized and a factor of 0·8 was applied to all shifts. Two reflexions, 200 and 091, were excluded from the final stages of the refinement since their uneven backgrounds indicated mis-setting of the crystal. During the scan of 20,3,4 the shutter had accidentally remained closed; this reflexion was therefore classified as unobserved.

The refinement converged after the 14th cycle with the average parameter shift equalling $0·1\sigma$ and the largest one $0·3\sigma$. The agreement index $R = (\sum|\Delta F|/\sum|F_o|)$ for 1803 observed reflexions was 0·056 and the weighted index $R' = (\sum w\Delta F^2/\sum wF_o^2)$ was 0·072. Inclusion of 358 unobserved reflexions, of which only 26 had $|F_{th}| < |F_c| \le 1·5|F_{th}|$, gave $R = 0·078$. A final difference Fourier map was featureless except for the unresolved H peaks (up to 0·31 e Å^{-3}) in the vicinity of C(23). The final coordinates and temperature parameters of the non-hydrogen atoms are shown in Table 1. The estimated standard deviations (shown everywhere in parentheses and referring always to the last digits) were derived from the inverse of the least-squares matrix. Table 2 gives the approximate coordinates of the hydrogen atoms which were obtained from the difference Fourier map and the temperature parameters assigned to them. Observed and calculated structure factors are listed in Table 3.

Discussion of the structure

The structure analysis revealed an androstane skeleton with the normal *trans-anti-trans* configuration at the $A/B/C$ junctions. An epoxide ring is fused to ring D at C(14) and C(15) and, being on the α-side, the C/D junction is also *trans*. An ORTEP drawing (Johnson,

Table 2. *Final parameters of hydrogen atoms*

Positional parameters are $\times 10^3$.

	x/a	y/b	z/c	B
H(11)	470	745	35	3·1 Å^2
H(12)	463	600	−20	3·1
H(21)	395	685	−147	3·9
H(22)	382	756	111	3·9
H(31)	375	512	−66	3·7
H(41)	359	471	329	3·3
H(42)	361	578	380	3·3
H(51)	449	471	263	3·3
H(61)	421	556	668	3·6
H(62)	416	425	582	3·6
H(71)	499	438	769	3·3
H(72)	506	394	526	3·3
H(81)	519	635	673	2·8
H(91)	528	548	223	3·2
H(111)	542	770	380	3·5
H(112)	541	750	121	3·5
(H121)	628	750	273	4·1
H(122)	614	614	177	4·1
H(151)	573	403	774	3·9
H(161)	655	512	840	4·3
H(162)	673	422	673	4·3
H(171)	670	531	380	3·6
H(181)	621	690	795	4·5
H(182)	639	781	633	4·5
H(183)	572	759	668	4·5
H(191)	459	715	552	3·1
H(192)	399	715	425	3·1
H(211)	239	712	−71	6·8
H(212)	222	567	−25	6·8
H(213)	228	635	−248	6·8
H(O19)	437	871	228	3·9

1965) is shown in Fig. 1. The three six-membered rings are in the chair conformation while the conformation of the D-ring, imposed by the fusion with the epoxide ring, corresponds to an α-envelope. An unusual feature of the latter is the fact that it is C(17), rather than C(13) or C(14), which is displaced below the mean plane through the other four atoms. Details of the conformation can best be seen from the torsional angles which are shown, together with bond lengths and bond angles, in Fig. 2. Their values, particularly those in ring D, are quite unusual, undoubtedly due to the presence of the epoxide ring. The angle strain in this small ring necessitates a re-hybridization of C(14) and C(15), and consequently the orbitals used by these atoms for bonding to neighboring carbon atoms may be regarded as sp^2 hybridized. The presence of one or two trigonal carbon atoms in the D-ring is expected to cause a flattening of that ring as well as its pseudo-rotation toward one of the envelope forms (Altona, Geise & Romers, 1968). Both of these effects are observed in the present structure. The flattening is manifested by a decrease of the geometrical parameter φ_m (maximum possible torsional angle) from the usual value of 47 to 33·8°, and by the decreased displacement of C(17) from the least-squares plane through the other four atoms (0·516 Å). The other effect is shown by the value of the phase angle of pseudorotation ($\Delta = 103·3°$) which deviates only slightly from $\Delta = 108°$ in an ideal envelope.

A conformation of ring *D* similar to the one in this structure was found in $\Delta^{8,14}$-anhydrodigitoxigenin (Gilardi & Karle, 1970) in which *one* atom in that ring,

C(14), is sp^2 hybridized. In that structure C(17) is displaced 0·637 Å below the plane through atoms C(13) to C(16). From the published torsional angles one can

Table 3. *Observed and calculated structure factors* ($\times 10$)

An asterisk indicates an unobserved reflexion to which the estimated threshold value was assigned.

calculate $\varphi_m = 43\cdot6°$ and $\varDelta = 104\cdot8°$. In batrachotoxinin A (Karle & Karle, 1969) there are *two* trigonal carbon atoms in ring *D*, C(16) and C(17), and the ring is a flattened α-envelope with C(14) only 0·30 Å out of the plane through the other four atoms. While the presence of two sp^2 hybridized atoms in ring *D* necessarily imposes an envelope conformation, the effect of one such atom is less clear cut. A list of seven steroids with sp^2 hybridization at C(17) (Weeks, Cooper, Norton, Hauptman & Fisher, 1971) reveals that $\varDelta$ varies between $-7\cdot8$ and $-38\cdot9°$. For another such steroid, in which a cyclohexadiene ring is fused to ring *D* (Pollard & Ahmed, 1971), $\varDelta = +12\cdot4°$ can be calculated.

The effect of the deformation of ring *D* on the conformations of the other rings can be assessed by considering, at first, the torsional angles at the *C/D* junction. Since the *D*-ring is almost exactly envelope-shaped one would expect the torsional angle C(17)–C(13)–C(14)–C(15) to be approximately $+27°$ (Altona *et al.*, 1968). The corresponding angle in $\varDelta^{8,14}$-anhydrodigitoxigenin was found to be 26·6°. The closing of this angle by 6° observed in this structure is a concomitant of the ring flattening and should result, in view of the *C/D* trans-junction, in a corresponding opening of the angle C(12)–C(13)–C(14)–C(8) in ring *C*. Using force-field calculations, Allinger & Wu (1971) derived a value of $-62\cdot0°$ for the latter angle in 5α,14α-androstane. A comparison with this theoretical result indicates that the observed torsional angle is 10° smaller than expected. Presumably, this can be attributed to the re-hybridization of C(14). Other deviations of the torsional angles from calculated values are shown in Fig. 3.

All four substituents on the ring skeleton are on the β-side. As the Newman projections (Fig. 4) show, the conformations of the two acetoxy groups differ substantially from what has been suggested (Mathieson, 1965) as the preferred conformation, in which the group H–C–O–C=O is coplanar. The torsional angle H(31)–C(3)–O(3)–C(20) deviates by 33° from that con-

formation while in the case of the 17β-acetoxy group the rotation amounts to 61°. The substituents of the C(10)–C(19) bond are completely staggered, with the

(a)

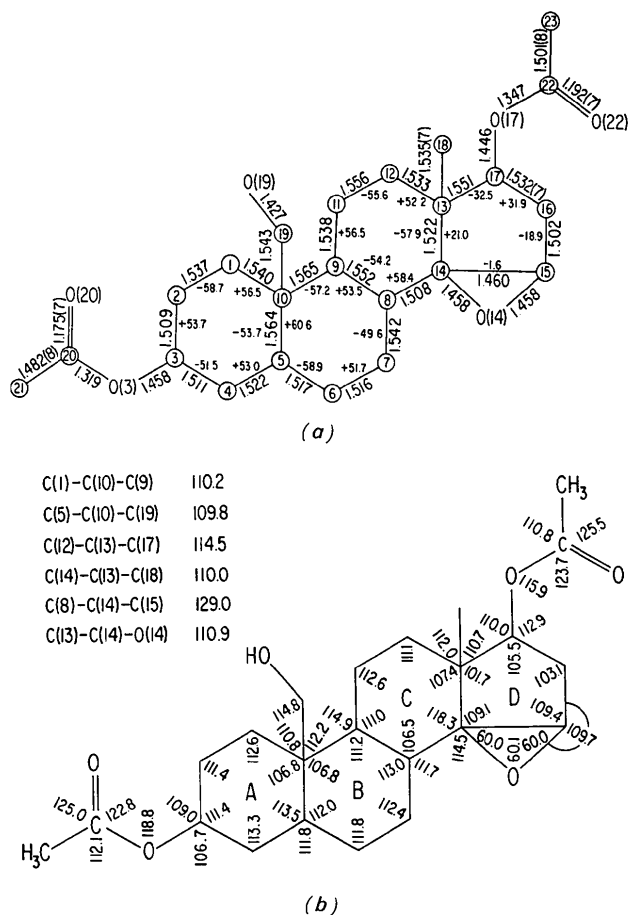|	
C(1)–C(10)–C(9)	110.2
C(5)–C(10)–C(19)	109.8
C(12)–C(13)–C(17)	114.5
C(14)–C(13)–C(18)	110.0
C(8)–C(14)–C(15)	129.0
C(13)–C(14)–O(14)	110.9

(b)

Fig. 2. (a) Bond lengths and torsional angles. Unless otherwise indicated the e.s.d.'s are 0·005–0·006 Å and 0·4°, respectively. (b) Bond angles. All e.s.d.'s are 0·3–0·4° except at C(20) and C(22) where they are in the range 0·4–0·7°.

Table 4. *Weighted least-squares planes*

The e.s.d.'s of $\varDelta$ are 0·003–0·010 Å for non-hydrogen atoms

Plane 1			Plane 2			Plane 3			Plane 4	
Atom	$\varDelta$		Atom	$\varDelta$		Atom	$\varDelta$		Atom	$\varDelta$
C(13)	$-0\cdot004$ Å		C(14)	0·0 Å		O(17)	0·000 Å		O(3)	$+0\cdot001$ Å
C(14)	$+0\cdot007$		C(15)	0·0		C(22)	$+0\cdot004$		C(20)	$-0\cdot025$
C(15)	$-0\cdot009$		O(14)	0·0		O(22)	$-0\cdot001$		O(20)	$+0\cdot010$
C(16)	$+0\cdot006$					C(23)	$-0\cdot002$		C(21)	$+0\cdot010$
C(17)*	$+0\cdot516$					C(17)*	$-0\cdot005$		C(3)*	$+0\cdot049$
O(14)*	$+1\cdot228$					H(171)*	$+0\cdot90$		H(31)*	$-0\cdot56$
O(17)*	$+0\cdot040$									

$\chi^2 = 10\cdot8$ $\chi^2 = 0$ $\chi^2 = 0\cdot9$ $\chi^2 = 11\cdot5$

Dihedral angles: $\angle 1,2 = 77\cdot0°$; $\angle 1,3 = 41\cdot3°$

Plane 1: $0\cdot2212X - 0\cdot4438Y - 0\cdot8684Z = -2\cdot6154$
Plane 2: $0\cdot8955X + 0\cdot3829Y - 0\cdot2267Z = 15\cdot7751$
Plane 3: $0\cdot1152X + 0\cdot2465Y - 0\cdot9623Z = 0\cdot3899$
Plane 4: $0\cdot2107X + 0\cdot9744Y - 0\cdot0779Z = 8\cdot8201$

* Not included in the calculation of the plane.

two H atoms at C(19) lying above rings *A* and *B*. Details of some least-squares planes and dihedral angles are shown in Table 4.

Most bond lengths and angles (Fig. 2) are normal for steroids and require few comments. The foreshortened distances in the acetoxy groups, particularly the one attached to C(3), can be ascribed to thermal motion. However, in view of recent theoretical studies of strained heterocyclic rings (*e.g.* Bonaccorsi, Scrocco & Tomasi, 1970), the geometry and surroundings of the epoxide ring may be of particular interest. The C(14)–C(15) distance of 1·460 (6) Å is in good agreement with the corresponding C–C bond length of 1·460(5) Å in 1,6:2,3-dianhydro-β-D-gulopyranose (Berking & Seeman, 1971). On the other hand, the C–O bonds are quite long in comparison with the average of 1·437 (3) Å in that pyranose. This may be attributable, at least in part, to a participation of the oxygen atom in a hydrogen bond. One would expect the delocalization of the oxygen electrons towards the approaching proton to result in a weaker C–O bond. In the structure of scopolamine *N*-oxide (Huber, Fodor & Mandava, 1971) the C–O bonds in an epoxide ring were found to be 1·458 (10) Å long. There, too, the oxygen atom is involved in a hydrogen bond. The three C–C bonds adjacent to the epoxide ring are 0·03–0·04 Å shorter than normal, their lengths thus corresponding to C(sp^2)–C(sp^3) bonds. This is in agreement with the

re-hybridization of C(14) and C(15) mentioned above. The large angles C(13)–C(14)–C(8) and C(8)–C(14)–C(15), 118·3 and 129·0° respectively, reflect the same phenomenon. The final difference Fourier map was searched for the presence of peaks and troughs which could appear in the vicinity of the epoxide ring as a result of bent bonds (Hartman & Hirshfeld, 1966; Fritchie, 1966). However, no such features were evident, presumably because they were compensated by increased thermal parameters (Coppens, Sabine, Delaplane & Ibers, 1969).

The crystal structure consists of chains of molecules related by the screw axes parallel to *y*. In each chain the molecules are linked *via* hydrogen bonds, H(O19) being donated to O(14) in another molecule. The O(19)···O(14) distance of 2·839 (4) Å indicates that the hydrogen bond is of medium strength. In addition, there are several fairly short intermolecular distances, *viz.* O(20)···C(4) 3·307 (6), O(20)···H(42) 2·50, O(14)···C(2) 3·172 (5) and O(14)···H(22) 2·35 Å. Since the C(4)–H(42) bond length obtained from this analysis is 0·92 Å instead of the normal length of 1·08 Å the actual O(20)···H(42) distance could be as low as 2·34 Å. This repulsion could account for the excessive vibration of O(20). Conversely, the O(14)··· H(22) contact may be longer than it appears to be, the observed C(2)–H(22) bond length being 1·18 Å. The contents of a unit cell are shown in Fig. 5.

All calculations were carried out with the help of programs written by Ahmed, Hall, Pippy & Huber (1966). I am grateful to Dr G. Kruger for supplying the crystals and to Dr M. Przybylska for her continued encouragement and interest in this work.
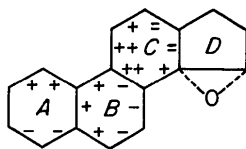

Fig. 3. Distortions from normal conformation in rings *A*, *B* and *C*: + and − denote opening and closing, respectively, of torsional angles.

References

AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. IUCr *World List of Crystallographic Computer Programs*. 2nd edition. Appendix, p. 52.

ALLINGER, N. L. & WU, F. (1971). *Tetrahedron*, **27**, 5093–5113.

ALTONA, C., GEISE, H. J. & ROMERS, C. (1968). *Tetrahedron*, **24**, 13–32.

BERKING, B. & SEEMAN, N. C. (1971). *Acta Cryst.* B**27**, 1752–1760.

BONACCORSI, R., SCROCCO, E. & TOMASI, J. (1970). *J. Chem. Phys.* **52**, 5270–5284.

COPPENS, P., SABINE, T. M., DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* B**25**, 2451–2458.
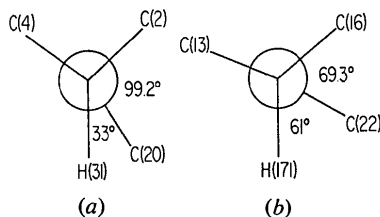
Fig. 4. Newman projections (*a*) along the C(3)–O(3) bond and (*b*) along the C(17)–O(17) bond.
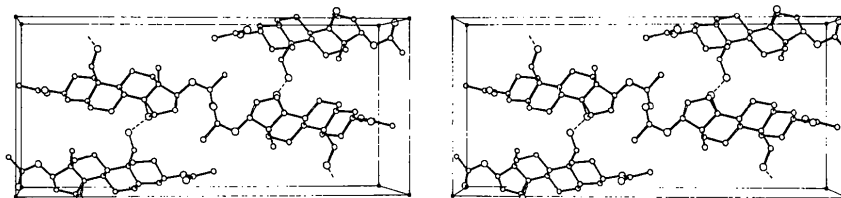

Fig. 5. Stereoscopic view along *z* of the contents of a unit cell. The directions of axes are *x* → (from 0·25 to 1·25), *y* ↑ (0 to 1·0) and *z* ⊙.

FRITCHIE, C. J. JR (1966). *Acta Cryst.* **20**, 107–118.

GERMAIN, G. & WOOLFSON, M. M. (1968). *Acta Cryst.* B**24**, 91–96.

GILARDI, R. D. & KARLE, I. L. (1970). *Acta Cryst.* B**26**, 207–218.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.

HARTMAN, A. & HIRSHFELD, F. L. (1966). *Acta Cryst.* **20**, 80–82.

HUBER, C. S., FODOR, G. & MANDAVA, N. (1971). *Canad. J. Chem.* **49**, 3258–3271.

International Tables for X-ray Crystallography (1962). Vol. III, p. 214. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

KARLE, I. L. (1970). In *Crystallographic Computing.* Edited by F. R. Ahmed, pp. 19–25, Copenhagen: Munksgaard.

KARLE, I. L. & KARLE, J. (1969). *Acta Cryst.* B**25**, 428–434.

KRUGER, G. (1971). Private communication.

KRUGER, G. & BIRNBAUM, G. I.(1973). *Tetrahedron Letters,* pp. 1501–1504.

MATHIESON, A. McL. (1965). *Tetrahedron Letters,* pp. 4137–4144.

POLLARD, D. R. & AHMED, F. R. (1971). *Acta Cryst.* B**27**, 1976–1982.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

WEEKS, C. M., COOPER, A., NORTON, D. A., HAUPTMAN, H. & FISHER, J. (1971). *Acta Cryst.* B**27**, 1562–1572.

Structure Cristalline du Nenadkevichite (Na,K)$_{2-x}$(Nb,Ti)(O,OH)Si$_2$O$_6$.2H$_2$O

PAR GUY PERRAULT, CHRISTIAN BOUCHER* ET JEAN VICAT†

Ecole Polytechnique, Casier Postal 501, Snowdon, Montréal 248, Canada

ET ELIO CANNILLO ET GIUSEPPE ROSSI

Istituto di Mineralogia del' Università di Pavia, Via Bassi 4, 27100 Pavia, Italie

Nenadkevichite from Saint-Hilaire, Quebec, Canada, corresponds to $(Na_{3.76}K_{0.24}Ca_{0.11}Mn_{0.03})$ $(Nb_{2.76}Ti_{1.18})$ $(O_{2.80}OH_{1.20})Si_8O_{24}.8H_2O$; it crystallizes in space group *Pbam*: $a=7.408$ (2), $b=14.198$ (3) and $c=7.148$ (2) Å. The structure was determined by the symbolic addition technique and refined by anisotropic full-matrix least-squares analysis, yielding an R value of 0.084 from 3264 independent observed X-ray reflexions. The structure consists of square rings of silica tetrahedra Si_4O_{12} in the (100) plane joined together by chains of NbO_6 octahedra in the [100] direction. The large cavities in this structure accommodate Na in two partially (0.53 and 0.54) occupied sites and H_2O in two fully occupied sites: some $Na–H_2O$ bonds are very short (2.20 to 2.28 Å). Hydrogen bonding is indicated between $H_2O(1)$ and $H_2O(2)$ by the bond length (2.979 Å). Other minerals in this series contain progressively more Ti^{4+} proxying for Nb^{5+} to the mineral labuntsovite which is essentially $(Na,K,Ba)_2Ti_2(O, OH)_2Si_4O_{12}.3H_2O)$; they crystallize in supercells of orthorhombic and monoclinic symmetry.

Introduction

Le nenadkevichite est une espèce minérale définie par Kouzmenko & Kazakova (1955) sur un matériau provenant du massif alcalin de Lovozero (U.R.S.S.) de formule chimique (Na,Ca) (Nb,Ti)Si$_2$O$_7$.2H$_2$O. Semenov (1959) fit le rapprochement entre cette espèce minérale et le labuntsovite de formule chimique (Na,K,Ba)TiSi$_2$O$_7$.1,5H$_2$O; il proposa que ces deux espèces appartenaient à une même série isomorphe où les remplacements principaux étaient Nb^{5+} par Ti^{4+}

et Na$^+$ par (K$^+$,Ba^{2+}). Une étude radiocristallographique récente (Perrault, 1972) a permis d'établir qu'il existe au moins cinq termes dans cette série (Tableau 1).

L'objet du présent mémoire est d'exposer la structure atomique du nenadkevichite de Saint-Hilaire (Specimen no. E.P. 12914); ce matériau est caractérisé par une maille cristalline qui est la plus petite qui nous soit connue dans cette série. Il est vraisemblable que le motif structural décrit ci après est fondamental à la structure des autres termes.

Partie expérimentale

La composition chimique du nenadkevichite du spécimen E. P. 12914 a été déterminée par une combinaison de mesures analytiques instrumentales (Perrault, 1972). Les résultats obtenus sont reportés au Tableau 2.

---

* Du Centre d'Etudes de Chimie Métallurgique, C.N.R.S., Vitry-sur-Seine (France), détaché au titre de la coopération technique.

† Du Laboratoire d'Electrostatique et de Physique du Métal, C.N.R.S., Grenoble (France), détaché au titre de la coopération technique.