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The Conformation of Non-Aromatic Ring Compounds. LXXXV. The Crystal and Molecular Structure of Lumisterol$_3$ at −170°

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Lumisterol$_3$ in its orthorhombic modification forms a 1:1 complex with ethanol. The lattice constants at −170°C are $a=18\cdot79$ (1), $b=18\cdot85$ (1) and $c=7\cdot382$ (5) Å. The space group is $P2_12_12_1$ and $Z=4$. The structure was solved by direct methods and refined with the least-squares technique using graphite-monochromatized Mo $K\alpha$ diffractometer data. The main features of the structure are the stressed side chain, the boat conformation of ring C and an unusual loose packing with 10 lumisterol and 6 ethanol molecules surrounding the reference molecule, which results in a very low density (1·05 g cm^{-3}).

Introduction

Continuing our X-ray investigations into the structures of steroids belonging to the vitamin-D series [3,20-bis(ethylenedioxy) analogues of vitamin-D (Knobler, Romers, Braun & Hornstra, 1972) and ergosterol (Braun, Hornstra, Knobler, Rutten & Romers, 1973)], we now wish to report on lumisterol$_3$.

The title compound with the systematic name 9β,10α-cholesta-5,7-diene-3β-ol was obtained by ultraviolet radiation of ergosterol. The presuffix 9β,10α indicates that the configuration of the atomic centres 9 and 10 is reversed with respect to ergosterol. The numbering of the atoms is indicated in Fig. 1(*a*).

The nomenclature of lumisterol and its position in the scheme of photochemical and thermal conversions of previtamin D are discussed by Sanders, Pot & Havinga (1969).

Experimental

Orthorhombic crystals of lumisterol$_3$ were obtained by recrystallization from ethanol. The lattice dimensions at 20°C and at −170°C (Table 1) were measured manually with a three-circle diffractometer using Cu $K\alpha$ radiation ($\lambda=1\cdot54178$ Å). The reflexions $h00$, $0k0$ and $00l$, being absent when h, k or l is odd, point to the space group $P2_12_12_1$. The low density (1·05 g cm^{-3}) determined by the flotation method results in 4·5 steroid molecules per unit cell. The n.m.r. spectrum of the crystals dissolved in $CDCl_3$ indicates, however, the presence of a 1:1 complex of lumisterol and ethanol molecules. Accepting this 1:1 ratio we calculated a density of 1·057 g cm^{-3} for four molecules of the complex per unit cell. We then verified (see *Solution of the structure*) that the crystals indeed contain ethanol, forming a 1:1 complex with lumisterol. A second form without molecules of solvent (Bernal, Crowfoot & Fankuchen, 1940) is monoclinic (space group $P2_1$) with four molecules per unit cell.

Table 1. *Crystal data of lumisterol–ethanol* (9β,10α-*cholesta*-5,7-*diene*-3β-*ol*)

Molecular composition $C_{27}H_{44}O.C_2H_5OH$, $M=430\cdot7$
4 molecules per unit cell, space group $P2_12_12_1$

20°	−170°
$a=19\cdot17$ (1) Å	$a=18\cdot79$ (1) Å
$b=18\cdot89$ (1)	$b=18\cdot85$ (1)
$c=$ 7·48 (1)	$c=$ 7·382 (5)

$d_{obs}=1\cdot05$ g cm^{-3}
$d_{calc}=1\cdot057$ g cm^{-3}
$F(000)=960$ e
μ(Mo $K\alpha$) $=0\cdot68$ cm^{-1}
Observed significant reflexions: 3163
Reflexions less than twice the background: 693
Non-observed reflexions within $\theta=30°$: 234

A crystal with dimensions 0·4 × 0·6 × 0·3 mm was mounted about its longest dimension on the φ axis of a three-circle diffractometer. The crystal was kept at a temperature of −170°C by means of a cooling system (van Bolhuis, 1971) and exposed to Mo $K\alpha$ radiation, which was monochromatized by graphite. By means of standard reflexions (131 and 411) measured after each series of 19 reflexions a polynomial function of the time was calculated in order to correct for loss of scattering by the crystal during exposure. Because the linear absorption coefficient for Mo $K\alpha$ radiation is very small no absorption correction was applied. The reflexion intensities were reduced to structure factor moduli in the usual way.

A preliminary overall scale and temperature factor were estimated by means of a Wilson plot.

Solution of the structure

The structure was solved by direct methods using a program developed by Motherwell & Isaacs (1971) and described by Kennard, Isaacs, Motherwell, Coppola, Wampler, Larson & Watson (1971).

In order to convert the structure factors into their normalized form, the scale and temperature factor were adjusted so as best to fulfil the statistical criteria listed in Table 2.

The use of reflexion 580 (Table 2) in the origin-determining set requires its invariance with respect to introduction of the enantiomorphic structure. It can be seen that this demand is met by the conversion of coordinates x,y,z into $\frac{1}{2}-x,\bar{y},\bar{z}$, which implies the phases $\varphi(5,11,5)=\pi/4$ or $5\pi/4$ for the structure and $\varphi(5,11,5)=3\pi/4$ or $7\pi/4$ for the enantiomorph. The limitation $\varphi(5,11,5)=\pi/4$ or $5\pi/4$ (Table 2) therefore fixes the enantiomorph. According to the criteria of Karle & Karle (1966), Drew, Templeton & Zalkin (1969) and van Ingen Schenau, Verschoor & Romers (1974), solution No. 1 is the best, having (Table 2) the lowest R_{Karle}, highest α' and t values and consuming the highest number of triplet relations. According to the criteria $\langle\varphi\rangle \rightarrow 0$ and $\langle|\varphi|\rangle \rightarrow \pi/2$ solution No. 2 is somewhat better, but consultation of E maps confirmed that No. 1 is the correct solution.

Refinement

The refinement of the structure was quite straightforward and hardly needs comment. During the early

Table 2. *Direct-methods data of lumisterol*

	Experimental	Theory (non-centric distribution)
$\langle\lvert E^2-1\rvert\rangle$	0·784	0·736
$\langle\lvert E\rvert\rangle$	0·881	0·886

Origin-defining reflexions

h	k	l	E	φ
22	13	0	3·23	0
5	8	0	3·51	$\pi/2$
0	2	3	2·53	0

Trial reflexions

h	k	l	E	φ	φ
5	11	5	2·86	$\pi/4$	$5\pi/4$
20	16	0	2·59	0	π
6	21	0	2·79	0	π

Solution

No.	R_{Karle}	α'	t	φ	$\lvert\varphi\rvert$	Triplets
1	18·0	145	0·71	0·079π	0·462π	4256
2	25·3	125	0·65	0·024π	0·462π	4040
3	27·5	124	0·66	0·116π	0·470π	3881
4	28·6	115	0·61	0·064π	0·454π	3977
5	31·0	112	0·64	0·056π	0·424π	3593
6	32·2	115	0·61	0·092π	0·474π	3910
7	34·8	100	0·58	0·074π	0·414π	3536
8	36·0	97	0·57	0·112π	0·442π	3551

See Kennard *et al.* (1972) and Drew *et al.* (1969) for the definitions of R_{Karle}, α_{Karle} and t; $\alpha'=\alpha_{\text{Karle}}\sigma^{3/2}(2\sigma_3)^{-1}$.

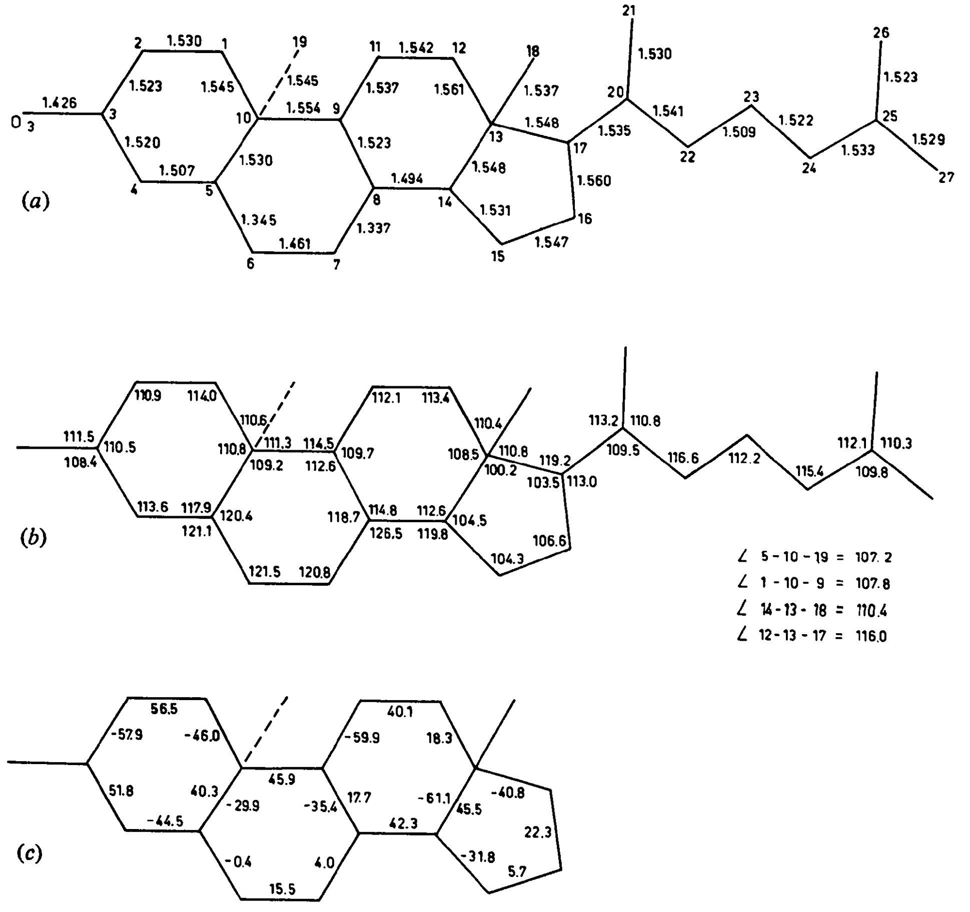

Fig. 1. (*a*) Bond distances and numbering of the atoms. (*b*) Valency angles. (*c*) Torsional angles.

stage an extra ethanol molecule was located in a difference Fourier map.

The iteration started with $R=32{\cdot}4\%$ (model derived from E map) and converged to $R=5{\cdot}4\%$. During the final stage all heavy atoms were refined anisotropically, while the hydrogen atoms (located in difference Fourier maps) were refined with isotropic B values. Since the strongest reflexions suffered from extinction, a correction for secondary extinction was made. The final weighted value R_w was also 5·4%.*

The positional coordinates and thermal parameters of heavy atoms and hydrogen atoms (including B values) are listed in Table 3.

The average estimated standard deviations are 0·0025, 0·0035 and 0·025 Å for oxygen, carbon and hydrogen atoms respectively. Since the heavy and light atoms were refined separately in diagonal blocks we have added 50% to these values to give e.s.d.'s of 0·0065, 0·007 and 0·04 Å for carbon–oxygen, carbon–carbon, and carbon–hydrogen bond lengths and e.s.d.'s of 0·3° and 0·5° for bond angle and torsion angles involving the heavy atoms. Inspection of Table 3 and Fig. 2 shows that there is no prominent thermal motion of the heavy atoms, the largest motions being observed for the tail atoms C(28) and C(29). This result is quite regular and in sharp contrast with the anisotropy found for the low-temperature structure of 5α,17α-pregnane-3β,20α-diol (Romers, de Graaff, Hoogenboom & Rutten, 1974).

Discussion of the structure

The overall shape of the molecule is illustrated in Fig. 2. The bond lengths, valency and endocyclic torsion angles are listed in Fig. 1. The mean value of the $C(sp^3)$–$C(sp^3)$ bond distances amounts to 1·536 (15) Å, in good agreement with the commonly observed value of 1·533 Å (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1965) and the same value stated for standard C–C bonds in n-alkanes (Bonham, Bartell & Kohl, 1959). The lengths of C(22)–C(23) and C(12)–C(13) (1·509 and 1·561 Å, respectively) deviate significantly, however, from both the quoted standard value and the observed average value. In a survey of 140 steroids by Romers, Altona, Jacobs & de Graaff (1974) average $C(sp^3)$–$C(sp^3)$ values were calculated for 22 steroids having e.s.d.'s in bond distances smaller than 0·007 Å. For bond C(12)–C(13) the value

Table 3. *Fractional coordinates and thermal parameters*

Fractional coordinates are × 10^4 for non-hydrogen atoms. C(28), C(29) and O(2) refer to the ethanol molecule. Estimated standard deviations in the least significant digits are given in parentheses. Thermal parameters and their standard deviations are × 10^3 Å^2 for non-hydrogen atoms. The temperature factor is defined as $\exp\,[-2\pi^2 \sum_{ij} h_i h_j a_i^* a_j^* U(ij)]$ $i,j=1,2,3$.

	x/a	y/b	z/c	$U(11)$	$U(22)$	$U(33)$	$2U(21)$	$2U(23)$	$2U(31)$
C(1)	4125 (1)	3881 (2)	372 (4)	20 (1)	22 (1)	16 (1)	−2 (2)	−3 (2)	−3 (2)
C(2)	3468 (2)	3402 (2)	390 (4)	24 (1)	22 (1)	23 (1)	−4 (2)	−4 (2)	−5 (2)
C(3)	2934 (1)	3650 (2)	1807 (4)	20 (1)	24 (1)	26 (1)	−11 (2)	4 (2)	1 (2)
C(4)	3274 (2)	3661 (2)	3675 (4)	24 (1)	30 (2)	21 (1)	−11 (2)	4 (3)	5 (2)
C(5)	3966 (1)	4065 (2)	3744 (4)	21 (1)	21 (1)	17 (1)	−1 (2)	12 (2)	2 (2)
C(6)	4147 (1)	4447 (2)	5211 (4)	22 (1)	25 (1)	16 (1)	0 (2)	3 (2)	7 (2)
C(7)	4858 (2)	4751 (2)	5410 (3)	28 (1)	20 (1)	12 (1)	3 (2)	2 (2)	−2 (2)
C(8)	5297 (1)	4801 (1)	3990 (3)	19 (1)	14 (1)	14 (1)	6 (2)	0 (2)	−1 (2)
C(9)	5024 (1)	4580 (1)	2131 (3)	18 (1)	16 (1)	13 (1)	1 (2)	2 (2)	4 (2)
C(10)	4504 (1)	3940 (1)	2223 (4)	20 (1)	16 (1)	17 (1)	−3 (2)	1 (2)	0 (2)
C(11)	5655 (1)	4478 (2)	831 (3)	22 (1)	20 (1)	13 (1)	0 (2)	−8 (2)	2 (2)
C(12)	6094 (1)	5163 (2)	602 (3)	19 (1)	21 (1)	13 (1)	1 (2)	0 (2)	3 (2)
C(13)	6197 (1)	5583 (1)	2406 (3)	17 (1)	14 (1)	12 (1)	2 (2)	1 (2)	0 (2)
C(14)	6041 (1)	5078 (1)	4010 (3)	18 (1)	15 (1)	12 (1)	9 (2)	0 (2)	0 (2)
C(15)	6317 (1)	5475 (2)	5677 (3)	24 (1)	20 (1)	13 (1)	3 (2)	−1 (2)	0 (2)
C(16)	6955 (1)	5911 (2)	4957 (3)	23 (1)	20 (1)	14 (1)	−1 (2)	−2 (2)	−2 (2)
C(17)	6969 (1)	5804 (1)	2862 (3)	17 (1)	14 (1)	14 (1)	5 (2)	2 (2)	−2 (2)
C(18)	5695 (1)	6227 (1)	2465 (4)	21 (1)	20 (1)	19 (1)	7 (2)	4 (2)	0 (2)
C(19)	4903 (2)	3245 (1)	2667 (4)	27 (1)	18 (1)	28 (1)	1 (2)	4 (2)	0 (3)
C(20)	7305 (1)	6432 (1)	1850 (3)	20 (1)	16 (1)	19 (1)	4 (2)	0 (2)	0 (2)
C(21)	7273 (1)	6355 (2)	−212 (4)	19 (1)	30 (1)	16 (1)	−2 (2)	8 (2)	−2 (2)
C(22)	8079 (1)	6534 (1)	2491 (4)	21 (1)	21 (1)	22 (1)	−5 (2)	4 (2)	−4 (2)
C(23)	8494 (2)	7126 (2)	1611 (4)	21 (1)	21 (1)	19 (1)	−1 (2)	3 (2)	2 (2)
C(24)	9230 (2)	7215 (1)	2443 (4)	24 (1)	21 (1)	20 (1)	−8 (2)	2 (2)	−1 (2)
C(25)	9669 (2)	7836 (2)	1699 (4)	28 (1)	22 (1)	16 (1)	−14 (2)	−2 (2)	3 (2)
C(26)	9382 (2)	8553 (2)	2331 (4)	38 (2)	22 (1)	34 (2)	−15 (2)	−9 (3)	6 (3)
C(27)	10447 (2)	7752 (2)	2263 (4)	27 (1)	33 (2)	25 (1)	−21 (2)	5 (3)	1 (3)
C(28)	3435 (2)	5978 (2)	2482 (4)	35 (2)	33 (2)	34 (2)	−2 (3)	1 (3)	20 (3)
C(29)	3377 (2)	6762 (2)	2873 (5)	39 (2)	33 (2)	43 (2)	−6 (3)	12 (3)	12 (3)
O(2)	2773 (1)	5648 (1)	2913 (3)	32 (1)	26 (1)	28 (1)	0 (2)	−4 (2)	9 (2)
O(3)	2675 (1)	4345 (1)	1413 (3)	29 (1)	28 (1)	27 (1)	7 (2)	−5 (2)	−10 (2)

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* The list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30411 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3 (*cont.*)

Fractional coordinates for hydrogen atoms are $\times 10^3$ units, isotropic B values $\times 10$ Å^2. The hydrogen atoms have numbers corresponding to those of their parent carbon atoms. H(30) and H(31) refer to the hydrogen atoms bonded to O(3) and O(2) respectively.

	x/a	y/b	z/c	B (iso)
H(1*A*)	394 (1)	437 (1)	−3 (4)	41 (7)
H(1*B*)	444 (1)	371 (1)	−55 (4)	52 (8)
H(2*A*)	326 (1)	341 (1)	−83 (3)	53 (8)
H(2*B*)	364 (1)	291 (1)	74 (4)	46 (7)
H(3)	253 (1)	335 (1)	189 (3)	36 (6)
H(4*A*)	339 (1)	317 (1)	408 (4)	32 (6)
H(4*B*)	296 (1)	390 (1)	453 (4)	27 (6)
H(6)	382 (1)	450 (1)	628 (4)	28 (6)
H(7)	499 (1)	490 (1)	654 (3)	20 (5)
H(9)	473 (1)	499 (1)	165 (3)	45 (7)
H(11*A*)	598 (1)	406 (1)	134 (4)	21 (5)
H(11*B*)	547 (1)	433 (1)	−39 (4)	31 (6)
H(12*A*)	657 (1)	503 (1)	5 (4)	38 (7)
H(12*B*)	588 (1)	547 (1)	−25 (3)	2 (3)
H(14)	639 (1)	468 (1)	390 (3)	18 (5)
H(15*A*)	650 (1)	514 (1)	660 (4)	30 (6)
H(15*B*)	595 (1)	578 (1)	614 (3)	16 (5)
H(16*A*)	741 (1)	576 (1)	555 (3)	21 (5)
H(16*B*)	686 (1)	644 (1)	523 (4)	11 (4)
H(17)	728 (1)	539 (1)	269 (3)	32 (6)
H(18*A*)	577 (1)	653 (1)	356 (3)	33 (6)
H(18*B*)	580 (1)	653 (1)	141 (3)	8 (4)
H(18*C*)	519 (1)	610 (1)	238 (4)	9 (4)
H(19*A*)	523 (1)	311 (1)	176 (4)	14 (4)
H(19*B*)	520 (1)	327 (1)	370 (4)	27 (6)
H(19*C*)	458 (1)	284 (1)	300 (4)	28 (6)
H(20)	709 (1)	686 (1)	221 (3)	20 (5)
H(21*A*)	759 (1)	595 (1)	−56 (3)	19 (5)
H(21*B*)	682 (1)	631 (1)	−61 (3)	17 (5)
H(21*C*)	746 (1)	674 (1)	−86 (4)	17 (5)
H(22*A*)	806 (1)	659 (1)	388 (4)	12 (4)
H(22*B*)	832 (1)	613 (1)	227 (3)	25 (5)
H(23*A*)	820 (1)	758 (1)	181 (4)	11 (4)
H(23*B*)	855 (1)	706 (1)	33 (3)	17 (5)
H(24*A*)	920 (1)	726 (1)	375 (4)	17 (5)
H(24*B*)	951 (1)	680 (1)	225 (4)	9 (4)
H(25)	964 (1)	781 (1)	34 (3)	10 (4)
H(26*A*)	944 (1)	857 (1)	364 (4)	18 (5)
H(26*B*)	966 (1)	895 (1)	166 (4)	20 (5)
H(26*C*)	890 (1)	862 (1)	206 (4)	17 (5)
H(27*A*)	1049 (1)	776 (2)	369 (5)	13 (4)
H(27*B*)	1066 (1)	730 (1)	173 (4)	18 (5)
H(27*C*)	1074 (1)	813 (1)	175 (4)	21 (5)
H(28*A*)	383 (1)	579 (1)	334 (4)	25 (5)
H(28*B*)	351 (1)	590 (1)	128 (4)	34 (6)
H(29*A*)	384 (1)	697 (1)	252 (4)	20 (5)
H(29*B*)	299 (2)	701 (1)	216 (4)	26 (6)
H(29*C*)	328 (2)	684 (2)	419 (5)	15 (4)
H(30)	253 (2)	436 (2)	48 (5)	17 (5)
H(31)	278 (1)	525 (1)	237 (5)	25 (5)

1·529 (1) Å was found. Attempts to reproduce our observed value by means of a valence force-field calculation of $9\beta,10\alpha$-androsta-5,7-diene-3β-ol [Romers, Altona, Jacobs & de Graaff (1974), see Table 5] gave no definite results. Although the overall agreement between experimental and calculated values is rather good, the largest deviation is observed for the bond C(12)–C(13). It must be pointed out, however, that the calculated structure did not contain the 17β-side-chain atoms. Without additional evidence it is hard to say whether the observed enlargement of bond C(12)–C(13) is a real effect.

Taking into account the double bonds and the quaternary carbon atoms C(10) and C(13), the distribution of valency angle values in the molecule is quite regular and in agreement with the calculated values (Table 5). Note, however, that the bond angles 20–22–23 and 23–24–25 are quite large (116·6° and 115·4°).

Inspection of Fig. 1(*c*) shows that the chair conformation of ring *A* is distorted, the torsion angles about bonds 1–2, 2–3 being larger and about bonds 3–4, 4–5, 5–10 and 1–10 being smaller than the standard value (55·9°; Geise, Buys & Mijlhoff, 1971). This kind of deformation is regularly observed for compounds having a small torsion angle 9–10–5–6 in ring *B*. Note that deformation destroys the D_{3d} symmetry but approximately retains the C_s symmetry with mirror plane perpendicular to the bonds 2–3 and 5–10.

Ring *B* has a 1–3 diplanar conformation (Bucourt, 1964) with C_2 symmetry, its dyad running through the midpoints of bonds 9–10 and 6–7. Note that the atoms 10,5,6 and 7 are in a quite planar configuration, while the atoms 6, 7, 8 and 9 are slightly displaced (0·009, 0·018, 0·017 and 0·008 Å, respectively) from their least-squares plane.

Ring *C* is boat-shaped. Its conformation is neither an ideal boat with symmetry C_{2v} nor a twist-boat with symmetry D_2.

Buys & Geise (1968) have pointed out that six-membered rings with boat conformation, just like five-membered rings (Altona, Geise, Romers, 1968), can be described by means of a phase angle of pseudorotation Δ and a maximum puckering angle φ_m. Designating the torsion angles about the bonds 8–14, 8–9, ...13–14 as φ_0, $\varphi_1 \ldots \varphi_5$ we find $\Delta = -4{\cdot}7°$ and $\varphi_m = 61°$, the conformation being intermediate between a boat (B) and a twist-boat (TB). Ring *C* retains a

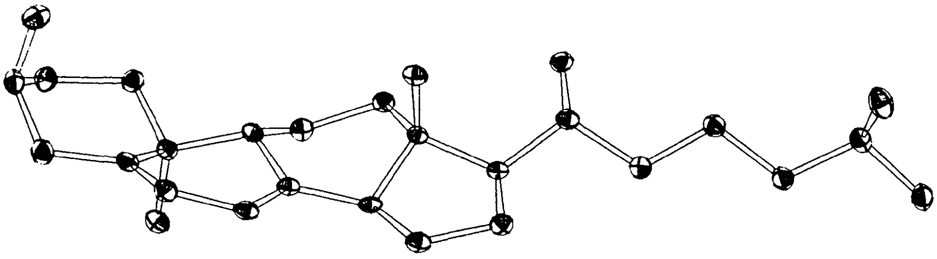

Fig. 2. An *ORTEP* projection of the molecule (Johnson, 1967).

twofold symmetry axis perpendicular to its average ring plane.

For ring *D* we calculate a phase angle $\Delta = 21·2°$ and $\varphi_m = 45·9°$. Its conformation is intermediate between a $C_s(13)$ envelope and $C_2(16)$ half-chair. The dihedral angles characterizing the side chain are listed in Table 4. It can be seen that the chain is stressed (see also Fig. 2).

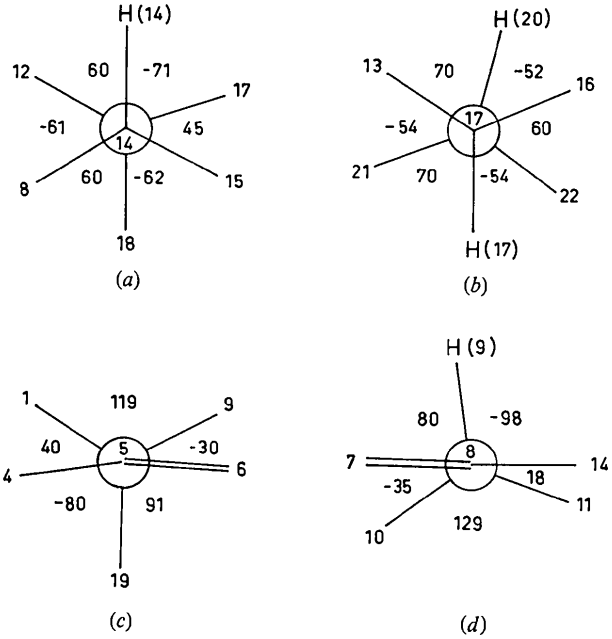

Fig. 3. Newman projections along (*a*) C(14)–C(13), (*b*) C(17)–C(20), (*c*) C(5)–C(10) and (*d*) C(8)–C(9).

Table 4. *Dihedral angles (decimal degrees) defining the side-chain and geometrical entities of the alcohol molecule*

13–17–20–21	−54°	Bond distances	
13–17–20–22	182	C(28)–C(29)	1·510 Å
16–17–20–22	184	C(28)–O(2)	1·426
17–20–22–23	−179	Bond angle	
20–22–23–24	−176	C(29)–C(28)–O(2)	108·7°
22–23–24–25	−184		
23–24–25–26	72		
23–24–25–27	195		

A number of salient Newman projections about the bonds 14–13, 17–20, 5–10 and 8–9 are illustrated in Fig. 3(*a*), (*b*), (*c*) and (*d*). The antiplanar configuration of C(18) and H(14) is nearly ideal, the hydrogen atoms H(17) and H(20) [Fig. 3(*b*)] deviating by 14° from this ideal configuration. This deviation is significant on a 99% confidence level (assuming e.s.d.'s of 4° in dihedral angles involving hydrogen atoms).

Packing

The packing of molecules is illustrated in Fig. 4 in a projection along [010]. Only molecules involving the screw axis operation parallel to [001] are shown. The involved symmetry and translational operations are presented in Table 6.

Table 5. *Experimental and calculated geometric entities of lumisterol*

The calculated values (Romers, Altona, Jacobs & de Graaff, 1974) are derived from 9β,10α-androsta-5,7-diene-3-ol.

Bond distances (Å)			Bond angles (°)			Torsion angles (°)		
	exp.	calc.		exp.	calc.		exp.	calc.
1– 2	1·530	1·531	10– 1– 2	114·0	115·8	*A*		
1–10	1·545	1·543	1– 2– 3	110·9	109·8	1–10	−46·0	−43·6
2– 3	1·523	1·521	2– 3– 4	110·5	108·8	1– 2	56·5	55·9
3– 4	1·520	1·523	3– 4– 5	113·6	112·2	2– 3	−57·9	−60·7
4– 5	1·507	1·508	4– 5–10	117·9	117·5	3– 4	51·8	57·9
5–10	1·530	1·535	5–10– 1	110·8	109·8	4– 5	−44·5	−49·4
5– 6	1·345	1·344	4– 5– 6	121·1	121·4	5–10	40·3	40·3
6– 7	1·461	1·450	1–10– 9	107·8	109·5	*B*		
7– 8	1·337	1·341	1–10–19	110·6	110·6	5–10	−29·9	−33·1
8– 9	1·523	1·512	9–10–19	111·3	110·2	5– 6	−0·4	−0·8
9–10	1·554	1·561	9–10– 5	109·2	107·8	6– 7	15·5	18·5
9–11	1·537	1·538	10– 5– 6	120·4	119·8	7– 8	4·0	3·1
11–12	1·542	1·544	5– 6– 7	121·5	121·3	8– 9	−35·4	−38·3
12–13	1·561	1·539	6– 7– 8	120·8	120·4	9–10	45·9	50·6
13–14	1·548	1·531	7– 8– 9	118·7	118·6	*C*		
8–14	1·494	1·496	8– 9–10	112·6	111·1	8– 9	17·7	3·7
14–15	1·531	1·534	7– 8–14	126·5	124·8	9–11	−59·9	−49·4
15–16	1·547	1·547	10– 9–11	114·5	118·3	11–12	40·1	41·4
16–17	1·560	1·545	8–14–13	112·6	111·1	12–13	18·3	11·9
13–17	1·548	1·532	14– 8– 9	114·8	116·3	13–14	−61·1	−57·7
13–18	1·537	1·547	8– 9–11	109·7	111·2	8–14	42·3	50·8
10–19	1·545	1·539	9–11–12	112·1	112·9			
			11–12–13	113·4	115·3			
			12–13–14	108·5	109·9			
			15–14–18	119·8	123·3			
			12–13–17	116·0	116·0			
			12–13–18	110·4	109·6			
			14–13–18	110·4	111·2			

Table 6. *Intermolecular interactions within* 3·0 Å

Involved are ten lumisterol and six ethanol molecules.

Molecule	Operation			Number of inter-actions	Average distance	Minimum distance
(*a*) Hydrophobic H···H interactions						
IV	$1\frac{1}{2}-x$,	$1-y$,	$-\frac{1}{2}+z$	23	2·71	2·29
V	$1\frac{1}{2}-x$,	$1-y$,	$\frac{1}{2}+z$	23	2·71	2·29
VI	x,	y,	$1+z$	6	2·71	2·56
XIII	x,	y,	$-1-z$	6	2·71	2·56
VIII	$1-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$	8	2·74	2·22
X	$1-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$	8	2·74	2·22
VII	$\frac{1}{2}+x$,	$1\frac{1}{2}-y$,	$-z$	5	2·67	2·42
XII	$-\frac{1}{2}+x$,	$1\frac{1}{2}-y$,	$-z$	5	2·67	2·42
IX	$-\frac{1}{2}+x$,	$1\frac{1}{2}-y$,	$1-z$	5	2·71	2·48
XI	$\frac{1}{2}+x$,	$1\frac{1}{2}-y$,	$1-z$	5	2·71	2·48
EI	x,	y,	z	4	2·52	2·22
EII	$\frac{1}{2}+x$,	$1-y$,	$\frac{1}{2}+z$	1	2·98	—
EIII	$\frac{1}{2}-x$,	$1-y$,	$-\frac{1}{2}+z$	5	2·75	2·48
EVII	$\frac{1}{2}+x$,	$1\frac{1}{2}-y$,	$-z$	5	2·74	2·63
EX	$1-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$	1	2·82	—
EXI	$\frac{1}{2}+x$,	$1\frac{1}{2}-y$,	$1-z$	3	2·82	2·78
(*b*) Hydrophobic C···H interactions						
IV	$1\frac{1}{2}-x$,	$1-y$,	$-\frac{1}{2}+z$	1	2·93	—
V	$1\frac{1}{2}-x$,	$1-y$,	$\frac{1}{2}+z$	1	2·93	—
EI	x,	y,	z	1	2·94	—
EIII	$\frac{1}{2}-x$,	$1-y$,	$-\frac{1}{2}+z$	1	2·94	—
(*c*) Hydrophilic O···O interactions						
EI	x,	y,	z	1	2·700	—
EIII	$\frac{1}{2}-x$,	$1-y$,	$-\frac{1}{2}+z$	1	2·717	—
(*d*) O···H interactions (non-hydrogen bonding)						
EII	$\frac{1}{2}-x$,	$1-y$,	$\frac{1}{2}+z$	1	2·98	—
EIII	$\frac{1}{2}-x$,	$1-y$,	$-\frac{1}{2}+z$	1	2·78	—
(*e*) Hydrophilic O···H interactions (hydrogen bonding)						
EI	x,	y,	z	1	1·86	—
EIII	$\frac{1}{2}-x$,	$1-y$,	$-\frac{1}{2}+z$	1	1·98	—

The main features of the structure are hydrogen bonds, running in the direction [001]. The scheme of hydrogen bonds, with lengths of 2·700 and 2·717 Å, is:

$$\mathrm{O(3,III)}\cdots\mathrm{H{-}O(2,EIII)}\cdots$$
$$\mathrm{H{-}O(3,I)}\cdots\mathrm{H{-}O(2,EI)}\cdots\mathrm{H{-}O(3,II)}\cdots$$

in which each oxygen atom donates and accepts a hydrogen atom.

All intermolecular H–H, C–H, O–H and O–O contacts less than 3·0 Å are listed in Table 6. It can be deduced that one lumisterol molecule is surrounded by 10 neighbouring steroid molecules. According to the rules of Kitaigorodsky (1961) this type of stacking, lacking two molecules in the first sphere of contacts, is not close-packed. The experimental density (1·05 g cm^{-3} at 20°C) is, indeed, conspicuously low, the density values usually being in the range 1·15 to 1·29 g cm^{-3} for steroids not containing heavy atoms. On the other hand, the gap is partially filled by six additional ethanol molecules, having hydrophobic as well as hydrophilic contacts with the steroid molecule.

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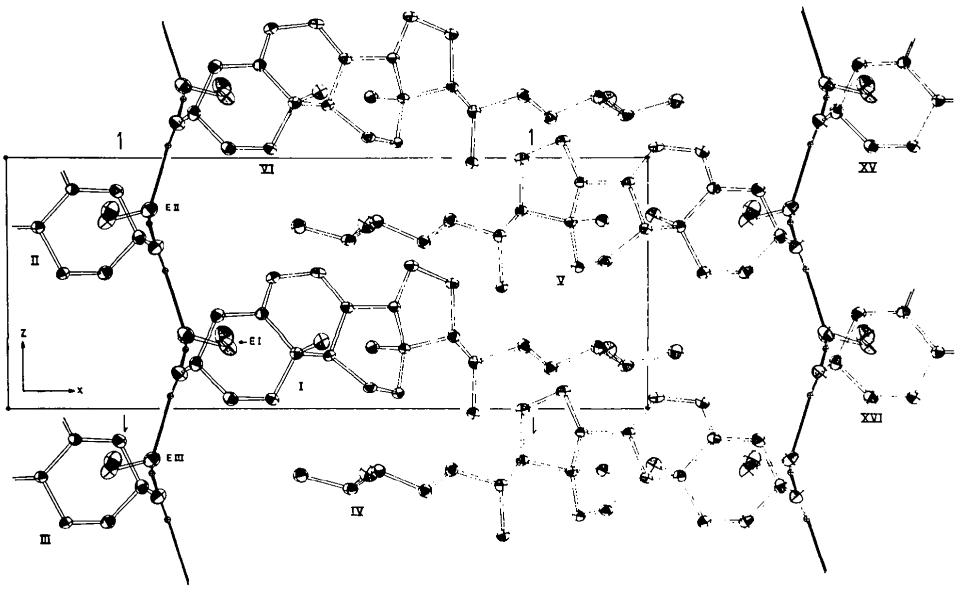

Fig. 4. A projection of a part of the unit cell along [010]. Heavy lines indicate the hydrogen bonds. The numbers XV and XVI refer to steroid molecules at positions $1+x,y,1+z$ and $1+x,y,z$ respectively. The remaining numbers are explained in Table 6.

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The Structures of Fluorides. VIII. The Crystal Structure of β-Uranium Oxide Tetrafluoride

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UOF_4 is the first actinide oxide tetrahalide to be characterized. β-UOF_4, formed by slow crystallization from HF solution, is tetragonal, with $a = 11{\cdot}4743$ (11) and $c = 5{\cdot}2043$ (5) Å, and the space group $I\bar{4}2d$ (D_{2d}^{12}), and is of the β-UF_5 structure type. The structure was refined by a least-squares analysis with 272 independent $F(hkl)$ values collected on an automatic single-crystal X-ray diffractometer, and the final weighted and unweighted R values were 0·089 and 0·110. The U and O atoms are in positions 8(d) with $x_{\rm U} = 0{\cdot}0861$ (2) and $x_{\rm O} = 0{\cdot}249$ (12). The fluorine atoms F(1) and F(2) are at [0·142 (2), 0·077 (2), 0·003 (7)] and [0·036 (4), 0·181 (3), 0·442 (11)], in positions 16(e). The configuration around the uranium is a pentagonal bipyramid, the oxygen atom being in the pentagonal ring; this is the first example of this type of coordination polyhedron for uranium. The four F(1) atoms in the ring form asymmetric bridges to neighbouring uranium atoms. The F(2) and O atoms are terminal, and there is possible O, F disorder in the terminal positions.

Introduction

Recently, the preparation of the important compound UOF_4 was described (Wilson, 1973). Although transition metal oxide tetrafluorides of the second and third transition series such as $MoOF_4$, WOF_4 and $ReOF_4$ have been prepared and their structures determined, UOF_4 is the first actinide oxide tetrahalide to be discovered. Because of the uniqueness of this compound, it was felt that a study of its structure would be interesting and could possibly reveal new bonding patterns for uranium.

Preparation

The crystals of UOF_4 were grown from solution in anhydrous HF and took several months to grow sufficiently large for analysis. The starting UOF_4 powder was prepared as described previously (Wilson, 1973).

The crystals grown were orange-yellow and were very hygroscopic. Some of these crystals were ground, and a Debye–Scherrer powder photograph was taken with Cu $K\alpha$ radiation. The pattern was similar to that of β-UF_5 reported by Zachariasen (1949), but differed from the powder pattern of the initial UOF_4 precipitate. Thus the larger crystals appeared to be a second polymorphic form of UOF_4. Because of their structural similarity to β-UF_5, the larger UOF_4 crystals, grown slowly from HF solution, were designated β-UOF_4, while the UOF_4 as prepared in the original way (Wilson, 1973) was designated α-UOF_4.

In view of the above difference between the powder patterns of the starting material and the large crystals, there was initially some doubt if the crystals were actually UOF_4. It was clearly demonstrated that the compound was UOF_4 by the subsequent crystal study, and the similarity of the infrared spectra of the crystals