

The Crystal and Molecular Structure of the Diterpene 6-Acetyldolatriol

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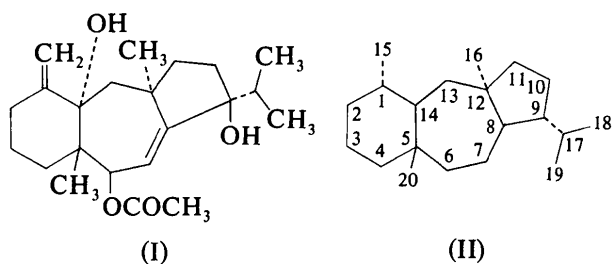
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A crystal-structure analysis of the diterpene 6-acetyldolatriol, $C_{22}H_{34}O_4$, has revealed an unusual molecular-packing scheme consistent with the space group $R\bar{3}$. The molecules are bound together by hydrogen bonds to form three-fold helical columns which close pack in a hexagonal array. The molecular structure of 6-acetyldolatriol consists of a 6–7–5 set of fused rings, all with *cis*-equatorial ring junctions. The structure was solved by direct methods of analysis of data from a crystal with $a = 14.297(8) \text{ \AA}$, $\alpha = 115.20(1)^\circ$, $Z = 3$ and $\rho_{\text{calc.}} = 1.124$, $\rho_{\text{obs.}} = 1.125 \text{ g cm}^{-3}$. Anisotropic least-squares refinement converged to a conventional $R = 0.130$ ($R_w = 0.086$) for 1897 independent observed reflections, recorded with $\text{Mo } K\alpha$ radiation on an automatic four-circle diffractometer.

Introduction

During the course of an evaluation of ethanol extracts of an Indian Ocean sea hare (*Dolabella* sp), obtained off the coast of East Africa, for antineoplastic activity, the unique diterpene 6-acetyldolatriol (I) had been isolated (Pettit, Ode, Herald, Von Dreele & Michel, 1976), and an X-ray crystal structure analysis was performed to unequivocally establish its structure. During the course of this work it became evident that 6-acetyldolatriol crystallizes in a highly unusual fashion which follows the space group $R\bar{3}$. We wish to report the details of this molecular-packing scheme and the molecular-bonding parameters for this unique diterpene.



Experimental

Data collection

6-Acetyldolatriol, $C_{22}H_{34}O_4$, crystallized as large hexagonal needles from acetone–heptane, and a suitable crystal for X-ray diffraction ($0.70 \times 0.20 \times 0.20 \text{ mm}$) was cleaved from one of these needles. From the symmetry and lack of systematic extinctions evident in the X-ray diffraction photographs, it was con-

cluded that the space group is the very unusual $R\bar{3}$. A set of 74 reflections within the angular range $4.7 \leq 2\theta \leq 23.0^\circ$ for $\text{Mo } K\alpha$ radiation were automatically centered on a Syntex $P\bar{1}$ auto-diffractometer; a least-squares refinement of the angular settings gave the lattice parameters $a = 14.297(8) \text{ \AA}$ and $\alpha = 115.20(1)^\circ$, which for $Z = 3$ gives $\rho_{\text{calc.}} = 1.124$ ($\rho_{\text{obs.}} = 1.125 \text{ g cm}^{-3}$). For the hexagonal description, $a = 24.142(13)$ and $c = 9.552(5) \text{ \AA}$.

The diffraction intensities were measured with graphite-monochromated $\text{Mo } K\alpha$ radiation and the diffractometer operating in the variable-speed θ – 2θ scan mode. For each reflection, the scan speed (between 1 and 8° min^{-1}) was determined from the intensity found in a rapid sampling scan. The scans were taken over the range $2\theta \text{ } K\alpha_1 - 1.0^\circ$ to $2\theta \text{ } K\alpha_2 + 1.0^\circ$, with background counts for 0.25 of the scan time taken at each end of the scan. The 2646 reflections with $2\theta \leq 55^\circ$ were investigated and 1897 were retained as objectively observed with $|F_o| \geq 0.675\sigma_F$; $\sigma_F = 0.025 |F_o| + (C + k^2B)^{1/2}R/(2|F_o|Lp)$, where C is the total count in a scan taken at the rate R , and k ($= 2$) is the ratio of scanning time to the time for the total background count B . The intensity of three reflections periodically monitored showed a maximum 2% random variation during the time of data collection. Corrections were applied for Lorentz and polarization effects for monochromated radiation (Azaroff, 1955), but absorption ($\mu = 5.69 \text{ cm}^{-1}$) and extinction effects were ignored.

Structure determination and refinement

The structure of 6-acetyldolatriol was readily solved with the *MULTAN-74* system of computer programs (Germain, Main & Woolfson, 1971; Declercq, Germain, Main & Woolfson, 1973; Koch, 1974). A set of normalized structure factors, E_{hkl} , was obtained from a

Wilson (1942) analysis of 2020 reflections ($|F_o| > 0$). The 250 reflections with $E_{hkl} \geq 1.41$ were expanded over 2000 Σ_2 interactions in the rhombohedral description of R_3 and were then subjected to a convergence analysis to give the starting set $6\bar{5}2(0)$, $11\bar{1}(\pm\pi/4)$, $7\bar{2}3(\pm\pi/4 \text{ or } \pm 3\pi/4)$ and $5\bar{4}2(\pm\pi/4 \text{ or } \pm 3\pi/4)$. The first phase fixes the origin (Hauptman & Karle, 1956) and the remaining three are variable with the $11\bar{1}$ determining the enantiomorph. A multiple-solution tangent refinement of the 32 possible starting sets gave the lowest $\psi(0) = 194$ (Cochran & Douglas, 1955) for the best solution. As is usually the case with polar space groups, the other figures of merit given by *MULTAN* did not indicate the correct solution. A Fourier synthesis of this set of phases revealed the positions of 21 possible atoms of which 19 were ultimately correct. These positions were used to phase ($R = 41\%$) a difference Fourier synthesis* which revealed four additional atoms. A subsequent difference synthesis indicated the complete set of positions and a refinement of occupancy factors permitted the identification of the atoms. At this point the reflection set and atom posi-

tions were transformed to the hexagonal form of $R3$ to avoid the difficulty of having to fix the molecular position along the body diagonal of the rhombohedral cell. In the hexagonal cell a single atomic z coordinate is fixed.

The model was refined with isotropic thermal parameters by full-matrix least-squares analysis of the 1897 strongest reflections (each assigned a weight $w = 1/\sigma_F^2$), and with atomic scattering factors for C^0 , O^0 and H^0 (*International Tables for X-ray Crystallography*, 1974). At convergence the standard residual was $R = 0.179$ and the weighted residual, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, was 0.146. The model with anisotropic temperature factors was refined by large-block least squares (234 parameters in two blocks, one containing atomic coordinates and the other a scale factor and thermal parameters) to yield $R = 0.160$ and $R_w = 0.119$ at convergence. A difference Fourier synthesis based on these results gave the positions of some of the H atoms, including the hydroxyl H atoms. All of the carbon H atoms were placed in idealized positions 1.0 Å from their respective C atoms, and the two oxygen H atoms were placed as found. The positions and thermal parameters for the nonhydrogen atoms were again refined in the same manner as before to give the residuals $R = 0.130$ and

* From this point on, all calculations were performed with the *CRYSTALS* system of computer programs adapted for the Univac 1110 (Rollett & Carruthers, 1974).

Table 1. Fractional coordinates ($\times 10^4$) and thermal parameters ($\times 10^3$) for 6-acetyldolatriol in the hexagonal description of $R3$

The thermal parameters are expressed in the form $T = \exp[-2\pi^2(U_{11}h^2a^2 + \dots + 2U_{23}klb^*c^*)]$, where the U_{ij} values are in Å². The estimated standard deviations are listed in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	-122 (4)	-1878 (4)	5329 (10)	60 (6)	66 (6)	41 (5)	36 (5)	8 (4)	8 (4)
C(2)	-222 (4)	-1325 (4)	4994 (12)	37 (5)	86 (7)	81 (7)	26 (5)	-12 (5)	-2 (6)
C(3)	292 (4)	-849 (4)	4028 (11)	82 (7)	56 (6)	88 (7)	42 (5)	-17 (6)	-2 (5)
C(4)	954 (3)	-651 (3)	4619 (10)	41 (4)	47 (5)	56 (5)	19 (4)	4 (4)	4 (4)
C(5)	1062 (3)	-1215 (3)	4913*	38 (4)	31 (4)	46 (4)	16 (3)	-8 (3)	-7 (3)
C(6)	1728 (3)	-937 (3)	5638 (9)	44 (4)	36 (4)	38 (4)	18 (4)	15 (4)	6 (3)
C(7)	1999 (3)	-1380 (3)	5689 (9)	35 (4)	43 (4)	46 (4)	19 (4)	3 (3)	7 (4)
C(8)	1752 (3)	-1918 (3)	6386 (9)	46 (4)	44 (5)	45 (5)	22 (4)	-18 (4)	-14 (4)
C(9)	2024 (4)	-2368 (3)	6394 (10)	60 (5)	40 (5)	56 (5)	26 (4)	-17 (4)	-12 (4)
C(10)	1672 (4)	-2832 (4)	7572 (10)	95 (7)	51 (5)	61 (6)	43 (6)	-18 (5)	3 (5)
C(11)	1015 (4)	-2876 (4)	7590 (10)	75 (6)	54 (5)	63 (6)	30 (5)	-3 (5)	13 (4)
C(12)	1145 (3)	-2198 (3)	7264 (10)	44 (5)	42 (5)	49 (5)	17 (4)	-3 (4)	1 (4)
C(13)	564 (4)	-2256 (3)	6462 (9)	56 (5)	44 (6)	32 (4)	16 (4)	-3 (4)	-8 (3)
C(14)	540 (3)	-1655 (3)	5992 (9)	20 (3)	51 (5)	48 (5)	14 (3)	1 (3)	5 (4)
C(15)	-568 (4)	-2474 (4)	5028 (11)	33 (4)	63 (5)	72 (6)	3 (4)	-18 (4)	-7 (5)
C(16)	1285 (4)	-1834 (4)	8660 (10)	84 (7)	70 (6)	39 (5)	37 (5)	2 (5)	7 (4)
C(17)	2748 (4)	-2064 (4)	6398 (12)	58 (6)	63 (6)	94 (7)	38 (5)	-7 (5)	7 (5)
C(18)	3054 (5)	-1629 (5)	7623 (15)	88 (8)	79 (8)	147 (11)	39 (7)	-41 (8)	-19 (8)
C(19)	2961 (6)	-2544 (6)	6285 (14)	132 (10)	108 (9)	134 (10)	90 (9)	-19 (8)	-11 (8)
C(20)	1042 (3)	-1549 (3)	3561 (9)	43 (4)	54 (5)	31 (4)	21 (4)	-5 (3)	4 (4)
C(21)	2642 (5)	78 (5)	5457 (12)	77 (7)	73 (7)	64 (7)	10 (6)	-7 (6)	-3 (6)
C(22)	3106 (4)	593 (4)	4573 (13)	53 (6)	30 (5)	147 (10)	-4 (4)	11 (6)	13 (5)
O(6)	2178 (2)	-389 (5)	4813 (8)	41 (3)	37 (3)	59 (3)	10 (2)	-1 (3)	5 (3)
O(9)	1783 (3)	-2746 (3)	5108 (8)	106 (5)	60 (4)	65 (4)	52 (4)	-20 (4)	-27 (3)
O(14)	601 (2)	-1275 (2)	7180 (8)	45 (3)	53 (3)	43 (3)	20 (3)	4 (3)	-10 (3)
O(21)	2718 (4)	45 (4)	6721 (12)	117 (6)	126 (7)	119 (7)	-26 (6)	-4 (6)	-28 (6)

* z coordinate fixed.

$R_w = 0.086$ at convergence, with an estimated standard deviation of 1.20 for a reflection of unit weight. A difference Fourier synthesis based on these results showed only scattered peaks, all less than $0.38 \text{ e } \text{Å}^{-3}$ high.*

Results

Final atomic coordinates and thermal parameters for 6-acetyldolatriol in the hexagonal setting of $R3$ are

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32162 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Fractional coordinates ($\times 10^3$) for the hydrogen atoms given in the hexagonal description of $R3$

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
H(2a)	-21	-109	594	H(16b)	92	-204	933
H(2b)	-66	-148	461	H(16c)	137	-137	849
H(3a)	26	-106	308	H(17a)	293	-176	554
H(3b)	26	-46	385	H(18a)	352	-140	768
H(4a)	99	-42	555	H(18b)	287	-188	856
H(4b)	129	-34	398	H(18c)	291	-128	770
H(6a)	166	-85	669	H(19a)	345	-235	630
H(7a)	242	-123	514	H(19b)	280	-285	713
H(10a)	163	-327	743	H(19c)	280	-282	543
H(10b)	190	-267	852	H(20a)	113	-192	375
H(11a)	80	-304	852	H(20b)	139	-125	289
H(11b)	74	-319	685	H(20c)	62	-173	310
H(13a)	18	-253	707	H(22a)	295	52	359
H(13b)	52	-252	559	H(22b)	352	60	461
H(15a)	-49	-284	525	H(22c)	317	101	492
H(15b)	-99	-258	460	H(9)*	171	-244	462
H(16a)	168	-178	913	H(14)*	20	-146	776

* As found in the difference Fourier synthesis; all other H atoms are at idealized positions 1.00 Å from their respective heavy atoms.

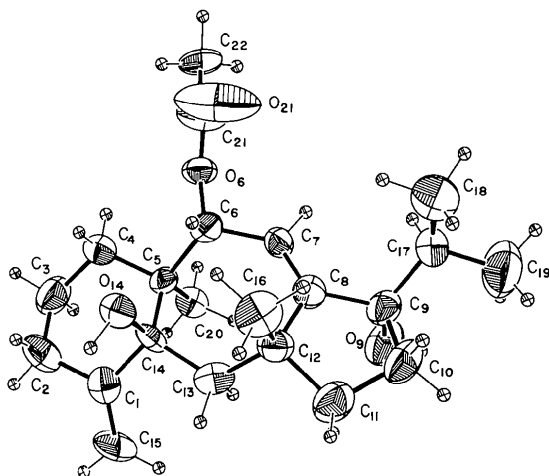


Fig. 1. A perspective representation of the structure of 6-acetyldolatriol.

Table 3. Bond distances (Å) and angles (°) for 6-acetyldolatriol

Values in parentheses are the estimated standard deviations in the last figure.

C(1)C(2)	1.506 (11)	C(2)C(1)C(14)	112.0 (14)
C(1)C(14)	1.544 (10)	C(2)C(1)C(15)	120.9 (13)
C(1)C(15)	1.327 (10)	C(14)C(1)C(15)	127.2 (13)
C(2)C(3)	1.510 (13)	C(1)C(2)C(3)	111.7 (15)
C(3)C(4)	1.530 (11)	C(2)C(3)C(4)	110.2 (17)
C(4)C(5)	1.535 (9)	C(3)C(4)C(5)	113.9 (12)
C(5)C(6)	1.560 (9)	C(4)C(5)C(6)	107.1 (12)
C(5)C(14)	1.563 (9)	C(4)C(5)C(14)	106.7 (12)
C(5)C(20)	1.510 (9)	C(4)C(5)C(20)	110.1 (11)
		C(6)C(5)C(14)	108.0 (12)
		C(6)C(5)C(20)	111.1 (12)
		C(14)C(5)C(20)	113.6 (11)
C(6)C(7)	1.509 (9)	C(5)C(6)C(7)	115.3 (11)
C(6)O(6)	1.453 (8)	C(5)C(6)O(6)	107.0 (12)
		O(6)C(6)C(7)	105.7 (12)
C(7)C(8)	1.309 (9)	C(6)C(7)C(8)	125.3 (11)
C(8)C(9)	1.525 (10)	C(7)C(8)C(9)	124.6 (12)
C(8)C(12)	1.523 (10)	C(7)C(8)C(12)	125.4 (12)
		C(9)C(8)C(12)	110.0 (14)
C(9)C(10)	1.513 (11)	C(8)C(9)C(10)	104.4 (16)
C(9)O(9)	1.464 (8)	C(8)C(9)O(9)	105.2 (13)
C(9)C(17)	1.523 (11)	C(8)C(9)C(17)	117.1 (13)
		O(9)C(9)C(10)	105.1 (15)
		O(9)C(9)C(17)	107.8 (13)
		C(10)C(9)C(17)	116.2 (13)
C(10)C(11)	1.537 (11)	C(9)C(10)C(11)	103.8 (16)
C(11)C(12)	1.535 (10)	C(10)C(11)C(12)	105.6 (16)
C(12)C(13)	1.542 (10)	C(8)C(12)C(11)	103.0 (15)
C(12)C(16)	1.539 (10)	C(8)C(12)C(13)	113.4 (13)
		C(8)C(12)C(16)	109.6 (14)
		C(11)C(12)C(13)	108.1 (14)
		C(11)C(12)C(16)	107.7 (14)
		C(13)C(12)C(16)	114.3 (13)
C(13)C(14)	1.549 (10)	C(12)C(13)C(14)	121.2 (11)
C(14)O(14)	1.418 (8)	C(1)C(14)C(5)	108.1 (12)
		C(1)C(14)C(13)	108.1 (13)
		C(1)C(14)O(14)	108.0 (12)
		C(5)C(14)C(13)	115.6 (10)
		C(5)C(14)O(14)	107.4 (13)
		C(13)C(14)O(14)	109.6 (12)
C(17)C(18)	1.496 (13)	C(9)C(17)C(18)	112.7 (18)
C(17)C(19)	1.487 (13)	C(9)C(17)C(19)	112.6 (17)
		C(18)C(17)C(19)	111.2 (16)
C(21)O(6)	1.282 (9)	O(6)C(21)O(21)	120.5 (17)
C(21)O(21)	1.229 (11)	O(6)C(21)C(22)	115.8 (17)
C(21)C(22)	1.456 (12)	O(21)C(21)C(22)	123.2 (15)
		C(6)O(6)C(21)	117.9 (12)

Table 4. Selected torsion angles (°) for 6-acetyldolatriol

C(1)C(2)C(3)C(4)	-52.2	C(8)C(12)C(13)C(14)	-67.4
C(2)C(3)C(4)C(5)	55.4	C(12)C(13)C(14)C(5)	63.3
C(3)C(4)C(5)C(14)	-59.2	C(13)C(14)C(5)C(6)	-64.3
C(4)C(5)C(14)C(1)	59.7	C(14)C(5)C(6)C(7)	80.2
C(5)C(14)C(1)C(2)	-61.0	C(8)C(9)C(10)C(11)	30.9
C(14)C(1)C(2)C(3)	57.2	C(9)C(10)C(11)C(12)	-37.3
C(5)C(6)C(7)C(8)	-65.3	C(10)C(11)C(12)C(8)	27.9
C(6)C(7)C(8)C(12)	0.5	C(11)C(12)C(8)C(9)	-8.7
C(7)C(8)C(12)C(13)	52.8	C(12)C(8)C(9)C(10)	-14.0

Table 5. *Non-bonded intermolecular contacts in 6-acetyldolatriol*

	<i>d</i> (Å)	Symmetry—translation operators
H(18c)···H(22b)	2.39	(i), (vi)
H(15b)···H(16a)	2.50	(ii), (vii)
H(15b)···H(22c)	2.47	(iii), (viii)
H(20b)···H(22c)	2.51	(i), (vi)
H(16b)···H(11b)	2.39	(v), (ix)
H(14)···O(9)	1.90*	(v)
H(13a)···O(9)	2.78	(v)
H(7a)···O(21)	2.49	(i)
H(22b)···O(21)	3.03	(i)
H(14)···C(9)	3.13	(v)
H(3a)···C(10)	3.15	(ii)
H(2b)···C(4)	3.12	(iii)
H(20a)···C(15)	3.18	(ix)
H(20c)···C(10)	3.16	(ii)
H(15b)···C(16)	3.21	(ii)
H(15b)···C(22)	3.24	(iii)
H(16a)···C(15)	3.25	(vii)
H(16a)···C(22)	3.18	(iv)
H(10b)···C(15)	3.20	(vii)
C(1)···O(9)	3.127	(v), (ix)
C(13)···O(9)	3.492	(v), (ix)
C(7)···O(21)	3.483	(i), (vi)
C(14)···O(9)	3.325	(v), (ix)
O(14)···O(9)	2.837*	(v), (ix)
C(15)···O(9)	3.364	(v), (ix)
O(6)···O(21)	3.350	(i), (vi)
C(22)···O(21)	3.483	(i), (vi)

Key for the symmetry—translation operators

(i) $\frac{1}{3} - y, -\frac{1}{3} + x - y, -\frac{1}{3} + z$	(vi) $\frac{2}{3} + y - x, \frac{1}{3} - x, \frac{1}{3} + z$
(ii) $-\frac{1}{3} - y, -\frac{2}{3} + x - y, -\frac{2}{3} + z$	(vii) $\frac{1}{3} + y - x, -\frac{1}{3} - x, \frac{2}{3} + z$
(iii) $y - x, x, z$	(viii) $y, x - y, z$
(iv) $\frac{1}{3} - y, -\frac{1}{3} + x - y, \frac{2}{3} + z$	(ix) $\frac{1}{3} + y - x, -\frac{1}{3} - x, -\frac{1}{3} + z$
(v) $-\frac{1}{3} - y, -\frac{2}{3} + x - y, \frac{1}{3} + z$	

* Hydrogen-bonding contact.

presented in Tables 1 and 2, with the estimated standard deviations derived from the least-squares analysis. The perspective view in Fig. 1 displays the essential relative configurational and conformational features of the molecule. Unfortunately, there is at present no chemical evidence which indicates the correct absolute configuration of 6-acetyldolatriol. Each nonhydrogen atom is represented by an ellipsoid consistent with the anisotropic thermal parameters in Table 1. Bond lengths and angles within the molecule are systematically recorded in Table 3. The set of torsion angles listed in Table 4 fully characterizes all the conformational features of the molecule. The set of closest intermolecular contacts is given in Table 5. A stereoscopic drawing of the hexagonal unit-cell contents is shown in Fig. 2. The H atoms have been omitted for clarity.

Discussion

In the crystal structure of 6-acetyldolatriol, the molecules are bound together by hydrogen bonds to

form threefold helical columns which close pack in a hexagonal array consistent with the space group $R\bar{3}$. As seen in the packing diagram in Fig. 2 and the list of intermolecular contacts (Table 5) each molecule forms hydrogen bonds to the two neighbouring molecules related by a threefold screw axis *via* the hydroxyl groups O(9)H(9) and O(14)H(14). The O—O distance (2.84 Å) is normal for a hydrogen bond (Donohue, 1968) and the apparent H positions as obtained from a difference Fourier synthesis indicate that O(14) is the proton donor and O(9) is the acceptor. The H on O(9) apparently does not participate in hydrogen bonding. In addition, the molecular orientations required to form these hydrogen bonds result in a large number of other non-bonded contacts between these molecules. Examination of the list of closest contacts shows that nearly 40% of the contacts are between the hydrogen-bonded molecules. As a result there are fewer contacts available for other molecules and therefore the molecular coordination number in this structure is only 9; a coordination number of 12 is more characteristic of closest-packed structures for organic compounds (Kitaigorodsky, 1973). The columns thus formed pack in a hexagonal array with only van der Waals attractive forces holding them together.

Apart from the normal hydrogen bonds, almost all of the apparent intermolecular contacts are equal to or greater than the sum of the van der Waals radii. The sole exception is the contact C(7)H(7a)···O(21) (2.49 Å), which is 0.1 Å less than the sum of the van der Waals radii for H and O (Donohue, 1968). As can be seen in Fig. 1 and Table 1 there is a very high degree of apparent anisotropic thermal motion (maximum r.m.s. displacement 0.55 Å) for O(21) perpendicular to the C(7)···O(21) interaction. It is possible that this atom is disordered over two sites on either side of the H atom and is in contact with it so that the true contact distance would be greater than the apparent distance obtained from the average position of O(21). A similar situation was noted by Donohue (1968) in the structure of glycyl-L-tyrosine hydrochloride (Smits & Wiebenga, 1953).

The molecular structure of 6-acetyldolatriol as shown in Fig. 1 consists of a 6–7–5 set of fused rings and the fifteen C atom diterpene skeleton has been designated as dolastane (II) (Pettit, Ode, Herald, Von Dreele & Michel, 1976). The six-membered ring is attached *cis*-equatorial to the seven-membered ring and is in the chair conformation. The seven-membered ring is also in the chair conformation made up of the planes C(5)C(14)C(13), C(5)C(6)C(12)C(13) and C(6)C(7)C(8)C(12). This conformation is a consequence of the steric requirements of the double bond at C(7)C(8) and the mode of attachment of the six-membered ring. The five-membered ring is also attached *cis*-equatorial to the seven-membered ring, and its conformation is fixed by the double bond at C(7)C(8) into a twist envelope with

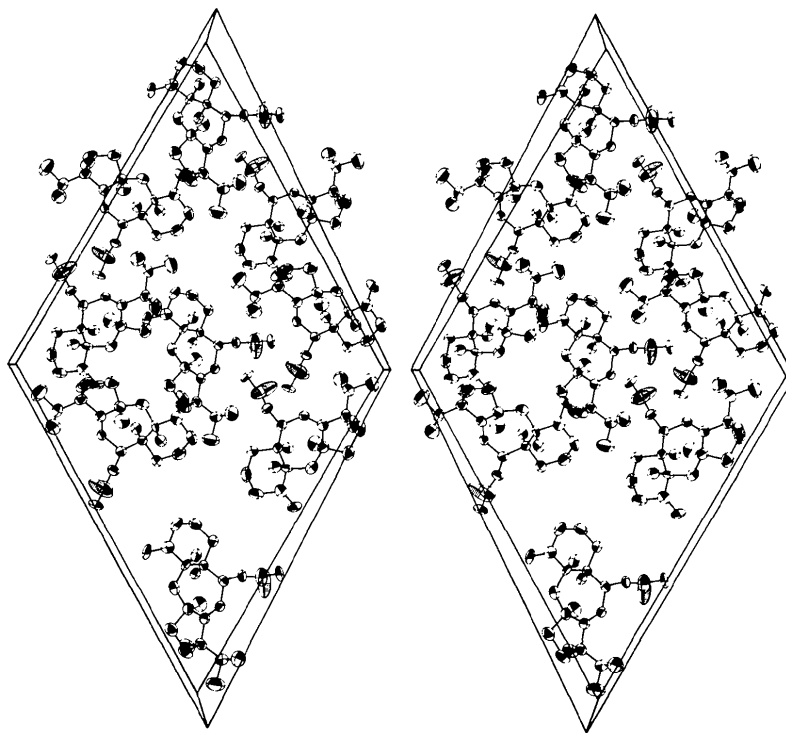


Fig. 2. A stereodiagram of the hexagonal unit cell and nine molecules of 6-acetyldolatriol. The H atoms have been omitted for clarity.

C(10) 0.330 above and C(11) 0.250 Å below the plane C(7)C(8)C(9)C(12). The isopropyl at C(9) is equatorial to the five-membered ring and the two methyl groups straddle the C(9)C(10) bond.

The bonding within the ring system is remarkably uniform; all C—C single-bond distances are normal with an average value of 1.532 (18) Å, as are the two double bonds C(1)C(15) and C(7)C(8) [average distance 1.318 (13) Å]. The bond angles within the rings show the usual pattern of being slightly greater than the tetrahedral angle for the six- and seven-membered rings and less for the five-membered ring.

The acetate group attached at C(6) shows the effects of the possible disorder in the position of the carbonyl O. In particular, the bond O(6)C(12) (1.282 Å) is unusually short, a more typical value being 1.33 Å. Nor is the group flat, the average deviation from the plane O(6)C(21)O(21)C(22) being 0.021 Å.

The molecule displays some thermal motion, with the major-axis r.m.s. displacements in the range of 0.22–0.32 Å for the atoms in the ring system and somewhat larger for the substituent atoms. Especially noticeable are the apparent thermal motion of O(21) (maximum r.m.s. displacement of 0.55 Å) which is possibly a result of the disorder referred to earlier, and the motion of the isopropyl group [maximum r.m.s. displacements of 0.41 for C(18) and 0.40 Å for C(19)]. Because of this thermal motion, riding corrections (Bu-

sing & Levy, 1964) were applied to the bond lengths for the substituent atoms to give C(1)C(15) 1.368, C(5)C(20) 1.512, C(9)O(9) 1.478, C(12)C(16) 1.550, C(14)O(14) 1.436, C(17)C(18) 1.529, and C(17)C(19) 1.503 Å. The bond lengths in the acetate cannot be corrected in this way because they may be a consequence of disorder rather than thermal motion.

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Structure Cristalline de Complexes Moléculaires en Série Naphtoquinonique. I. Structure du Complexe 1 : 1 entre la Naphtoquinone-1,4 et l'Hydroquinone

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The crystal of the molecular complex between hydroquinone and 1,4-naphthoquinone is orthorhombic, space group $P2_12_12_1$, with $a = 6.145$ (2), $b = 26.820$ (4), $c = 7.768$ (2) Å, $Z = 4$. The structure has been determined by direct methods and refined to $R = 0.047$ for the 1376 reflexions recorded with an automatic single-crystal diffractometer. The molecular structure of each component shows no difference from that found in the pure complex product. The structure appears in the form of 'molecular sheets' parallel to the (010) plane and linked by van der Waals bonds. In a sheet along the [001] direction, there are alternate hydroquinone and naphthoquinone molecules bound to each other. The molecules are almost parallel. The C=O group of naphthoquinone is over the phenyl ring of hydroquinone and the OH group of hydroquinone is over the primary ring of naphthoquinone (distance of about 3.2 Å). There are very strong interactions between these two molecules and hydrogen bonds between these columns along the [201] direction. Each molecule of one species is bound to two molecules of the other species ($O \cdots O = 2.73$ Å).

Introduction

Les quinones forment des complexes moléculaires avec des espèces chimiques diverses comme les phénols. Si les nombreux complexes de la *para*-benzoquinone ont fait l'objet d'études approfondies, en revanche peu de complexes de la naphthoquinone-1,4 ont été préparés; quelques uns ont été obtenus à l'état solide, parmi ceux-ci le complexe naphthoquinone–hydroquinone connu depuis longtemps (Urban, 1907; Anderson, 1937).

Actuellement une attention particulière est prêtée à la complexation des naphthoquinones car elle intervient dans divers processus biologiques importants, par exemple l'antiactivité vitaminique K (Bravic, 1975). L'étude rapportée ici est la première d'une série dont l'objet est la caractérisation de l'interaction (sa géométrie, son énergie, sa nature) par des techniques

radiocristallographiques, calorimétriques, spectroscopiques. L'étude d'une semi-conduction est possible.

Partie expérimentale

Les cristaux utilisés dans cette étude ont été obtenus selon la méthode de Madinaveita (1929). Nous avons dissous la naphthoquinone et l'hydroquinone en quantité équimoléculaire dans la plus petite quantité possible d'éther sulfurique. Nous avons ajouté de l'éther de pétrole et la solution laissée au réfrigérateur a donné des cristaux à l'éclat métallique, de couleur vert foncé en réflexion et rouge en transmission.

La fusion de ces cristaux est observée à 123 °C par ATD et contrôlée au microscope polarisant équipé d'une platine chauffante.