

Crystal and Molecular Structures of the 2 β -Carbomethoxy-5 α ,6 α -dihydroxy and 2 α -Carbomethoxy-5 β -chloroacetoxy-6 β -hydroxy Derivatives of 7,7-Dimethyltricyclo[6,2,1,0^{1,6}]undecane, C₁₅H₂₄O₄ and C₁₇H₂₅O₅Cl

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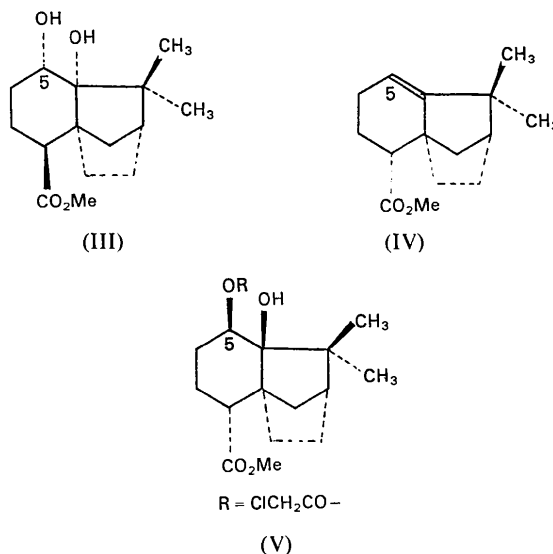
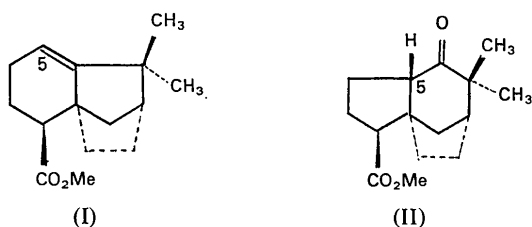
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The structures of the title compounds, the 6-monomesylates of which are used respectively in the stereospecific syntheses of the naturally occurring epimers zizanoic acid and epizizanoic acid, have been determined by single-crystal X-ray analyses from diffractometer data, and have been refined by least-squares calculation to final *R* values of 0.066 (for the dihydroxy compound) and 0.058 (for the chloroacetoxy derivative). The absolute stereochemistries of both compounds have been inferred by comparison of unchanging centres with the known absolute stereochemistries of the natural zizanoic and epizizanoic acids. The analyses reveal that the osmylation of the tricyclic olefin precursors of the two compounds has proceeded by different stereochemical routes controlled, at least in part, by the 2 β - and 2 α -orientations of the carbomethoxy groups. There are also small, but significant differences in the detailed geometries of the two molecules which probably result from the different spatial arrangements of substituents. Both bicyclo[2,2,1]heptyl residues exhibit twisting of the *Synchro*(-) type.

Introduction

In the course of a successful synthetic route to the tricyclovetivane sesquiterpene zizanoic acid (MacSweeney & Ramage, 1971), a key step involved rearrangement of the 6-monomesylate of the 5,6-diol produced by osmylation of the tricyclic olefin (I). The stereochemistry of the rearrangement product (II) was known by direct comparison with authentic material produced by degradation of methyl zizanoate. However, in order to elucidate the factors which influence addition reactions of the olefin (I), and also to understand the stereochemical consequences of the rearrangement process leading to (II), it was necessary to determine unambiguously the stereochemistry of the intermediate 5,6-diol. We therefore undertook a single-crystal X-ray analysis of the 5,6-diol produced by osmylation of (I), and proved it to be the 5 α ,6 α -isomer (III). Hence by comparison of the stereochemistries at C(5) in (3) and (2), it may be inferred that the rearrangement occurs with inversion at the site of solvolytic cleavage of the mesylate ion. This would indicate a concerted process analogous to an *S_N2* reaction.



Two features which would be expected to influence the direction of reagent-approach to the tricyclic system of (I), are the known preference of the bicyclo[2,2,1]heptyl system for reaction from the *exo* face (Sauers, How & Feilich, 1965), and the stereochemistry of the bulky carbomethoxy group at C(2). The subtle interplay of these effects is evidenced by the high degree of stereospecificity in reactions of (I), in contrast to the markedly less selective reactions of the epimeric ester (IV). Since the 5,6-diol resulting from (IV) is used in an analogous synthetic route to epizizanoic acid (Kido,

Uda & Yoshikoshi, 1972), we also undertook a single-crystal X-ray analysis of the 5-monochloroacetate of the major 5,6-diol* resulting from osmylation of (IV), and have shown that it possesses the structure and absolute stereochemistry (V). By comparing the stereochemistries of (III) and (V), it is apparent that the osmium tetroxide has preferentially approached the *endo*-face of (I) to produce (III), but has approached the *exo*-face of (IV) to produce (V).

In the present paper we present details of the analyses of (III) and (V), and compare their molecular geometries. Application of the chemical and stereochemical principles emergent from these studies will be discussed more fully elsewhere.

Experimental

Crystal data

2 β -Carbomethoxy-5 α ,6 α -dihydroxy-7,7-dimethyltricyclo[6,2,1,0^{1,6}]undecane (III), C₁₅H₂₄O₄,
M = 268.4.

Monoclinic, $a = 10.886$ (3), $b = 7.766$ (4), $c = 8.591$ (2) Å, $\beta = 100.93$ (2)°, $U = 713.1$ Å³.

$D_m = 1.24$ g cm⁻³ (by flotation in aqueous KI),
 $Z = 2$,

$D_c = 1.25$ g cm⁻³, $F(000) = 292$.

Space group $P2_1$ (C_2^2 , No. 4).

Linear absorption coefficient for X-rays ($\lambda = 0.7107$ Å),
 $\mu = 0.96$ cm⁻¹.

2 α -Carbomethoxy-5 β -chloroacetoxy-7,7-dimethyltricyclo[6,2,1,0^{1,6}]undecan-6 β -ol (V), C₁₇H₂₅O₅Cl,
M = 344.8.

Orthorhombic, $a = 14.270$ (6), $b = 7.541$ (5),
 $c = 15.824$ (8) Å, $U = 1702.8$ Å³.

$D_m = 1.33$ g cm⁻³ (by flotation in aqueous KI),
 $Z = 4$,

$D_c = 1.34$ g cm⁻³, $F(000) = 736$.

Space group $P2_12_12_1$ (D_2^2 , No. 19).

Linear absorption coefficient for X-rays ($\lambda = 0.7107$ Å),
 $\mu = 2.50$ cm⁻¹.

Crystallographic measurements

The cell parameters of both compounds were initially determined from oscillation and Weissenberg photographs taken with Cu $K\alpha$ ($\lambda = 1.5418$ Å) radiation, and from precession photographs taken with Mo $K\alpha$ ($\lambda = 0.7107$ Å) radiation, and were later refined by least-squares techniques immediately prior to the diffractometer data collections. Both the systematic absences in the X-ray spectra, and the known optical activity of the two molecules, uniquely defined the space groups as $P2_1$ [for (III)], and $P2_12_12_1$ [for (V)].

Intensity measurements were made on a Hilger and Watts Y290 computer-controlled diffractometer with Zr-filtered Mo radiation, and the 2θ -scan technique

in the range 2θ 0 \rightarrow 56°. For (III), a flat plate (0.6 \times 0.2 \times 0.1 mm) mounted about **b**, produced 1240 independent reflexions ($I > 2\sigma_I$; $\sigma_I = \sqrt{I + B_1 + B_2}$), while for (V), a plate (0.8 \times 0.4 \times 0.3 mm) also mounted about **b**, resulted in 2057 independent reflexions ($I > 2\sigma_I$). Both sets of intensities were corrected for Lorentz and polarization factors, but absorption effects were considered negligible and ignored.

Structure determinations

Both structures were solved by application of non-centrosymmetric direct methods with programs developed by Stewart (1967), and incorporated into the X-RAY 70 suite programs. Table 1 lists the initial assignment of phase values to several reflexions with high $|E|$ values. Trial sets of phases were then derived for those 201 reflexions of (III) and 262 reflexions of (V) with $|E| > 1.50$ with the phase-refinement techniques of the tangent-formula reiteration procedure. E maps, computed with those trial sets of phases with lowest Karle R index (Karle & Karle, 1966) [0.17 for (III), 0.19 for (V)], completely revealed both structures. Improved coordinates for use in the least-squares refinements were in each case obtained by two rounds of structure-factor and electron-density calculations. After each structure-factor calculation, in which overall isotropic thermal parameters $U_{iso} = 0.05$ Å² were assumed. The two sets of data were placed on approximate absolute scales by equating $k \sum |F_o|$ and $\sum |F_c|$.

Table 1. Origin-defining and variable reflexions

(a) For (III)

h	k	l	Phase	$ E $
1	0	-4 O.D.	0	3.31
2	0	-1 O.D.	0	2.21
7	5	-1 O.D.	0	2.86
1	4	-6 Enantiomorph	$(\pi/4, \pi/2, 3\pi/4)$	2.82
2	6	1 Variable	$(\pi/4, 3\pi/4, 5\pi/4, 7\pi/4)$	2.91

Correct solution: ($E = 3\pi/4$; $V = \pi/4$), $R = 0.17$.

(b) For (V)

h	k	l	Phase	$ E $
0	3	12 O.D.	$\pi/2$	3.56
3	0	14 O.D.	π	3.06
17	0	7 O.D.	$\pi/2$	2.80
1	4	0 Enantiomorph	$\pi/2$	2.17
9	3	5 Variable	$(\pi/4, 3\pi/4, 5\pi/4, 7\pi/4)$	3.19

Correct solution: ($E = \pi/2$; $V = 3\pi/4$), $R = 0.19$.

Structure refinements

The positional, vibrational and overall-scale parameters for both structures were refined initially by full-matrix least-squares calculations and subsequently by the block-diagonal approximation (on introduction of anisotropic thermal parameters). For (III) the calculations converged after 12 cycles when R was 0.066 and R' ($= \sum w\Delta^2 / \sum w|F_o|^2$) was 0.006, while for (V) convergence was reached after 15 cycles when R was 0.058 and R' was 0.005.

* This material was kindly shown by Professor Yoshikoshi to be identical with the intermediate used in his synthesis of epizanoic acid.

Table 2 (cont.)

(e) H-atom fractional coordinates for (V)

H(O1)	0.2201 (40)	-0.2194 (81)	0.4971 (34)
H(2)	0.4263 (39)	-0.2690 (81)	0.4424 (34)
H(31)	0.4207 (38)	-0.1411 (77)	0.2673 (35)
H(32)	0.4279 (38)	-0.3326 (77)	0.2899 (34)
H(41)	0.2721 (39)	-0.2594 (79)	0.2584 (33)
H(42)	0.2767 (37)	-0.3211 (80)	0.3482 (35)
H(5)	0.2602 (38)	0.0557 (78)	0.3123 (34)
H(8)	0.3556 (38)	0.2931 (82)	0.5800 (34)
H(91)	0.4761 (40)	0.3724 (78)	0.4589 (35)
H(92)	0.3718 (39)	0.4054 (75)	0.4136 (36)
H(101)	0.4998 (35)	0.1526 (79)	0.3659 (36)
H(102)	0.3946 (37)	0.1758 (81)	0.3298 (35)
H(111)	0.3996 (35)	-0.0149 (80)	0.5659 (34)
H(112)	0.4953 (38)	0.0909 (78)	0.5390 (35)
H(121)	0.1387 (38)	0.2453 (80)	0.4255 (35)
H(122)	0.2404 (39)	0.3027 (82)	0.3861 (33)
H(123)	0.2041 (40)	0.4113 (74)	0.4733 (34)
H(131)	0.2408 (39)	0.0500 (78)	0.6099 (34)
H(132)	0.1416 (37)	0.0563 (78)	0.5529 (34)
H(133)	0.1842 (38)	0.2479 (79)	0.5944 (33)
H(151)	0.7057 (39)	-0.1056 (76)	0.2765 (35)
H(152)	0.7188 (38)	-0.2674 (79)	0.3556 (34)
H(153)	0.7091 (38)	-0.0990 (73)	0.3769 (34)
H(171)	-0.0141 (36)	-0.2515 (80)	0.3326 (37)
H(172)	-0.0219 (36)	-0.0071 (81)	0.3790 (34)

(f) Anisotropic temperature factors (\AA^2) for (V)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Cl(1)	0.0334	0.1055	0.1092	0.0396	-0.0575	-0.0043
O(1)	0.0270	0.0394	0.0333	0.0136	0.0033	-0.0071
O(2)	0.0230	0.0506	0.0354	0.0072	-0.0055	-0.0071
O(3)	0.0344	0.1065	0.0440	0.0270	-0.0078	0.0416
O(4)	0.0303	0.0571	0.0445	0.0115	0.0069	-0.0008
O(5)	0.0413	0.1006	0.0411	0.0331	-0.0176	0.0005
C(1)	0.0207	0.0331	0.0302	0.0025	-0.0035	-0.0014
C(2)	0.0270	0.0388	0.0320	0.0006	0.0017	-0.0019
C(3)	0.0313	0.0510	0.0333	-0.0197	0.0059	0.0025
C(4)	0.0319	0.0447	0.0369	-0.0226	-0.0056	-0.0037
C(5)	0.0207	0.0394	0.0336	0.0009	-0.0059	0.0018
C(6)	0.0245	0.0353	0.0292	0.0023	-0.0027	0.0017
C(7)	0.0320	0.0353	0.0406	-0.0137	-0.0028	0.0084
C(8)	0.0329	0.0445	0.0576	-0.0356	-0.0027	-0.0053
C(9)	0.0422	0.0332	0.0882	-0.0094	0.0077	-0.0105
C(10)	0.0330	0.0345	0.0558	0.0229	0.0063	-0.0081
C(11)	0.0300	0.0480	0.0409	-0.0168	-0.0120	0.0001
C(12)	0.0466	0.0414	0.0657	-0.0061	-0.0056	0.0320
C(13)	0.0436	0.0543	0.0476	-0.0227	0.0167	0.0144
C(14)	0.0302	0.0401	0.0424	-0.0011	0.0017	0.0117
C(15)	0.0308	0.0528	0.0541	0.0091	0.0071	0.0016
C(16)	0.0376	0.0492	0.0380	-0.0146	-0.0138	0.0106
C(17)	0.0237	0.0761	0.0584	-0.0062	-0.0141	0.0052

Average estimated standard deviations (\AA^2)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Cl	0.0004	0.0011	0.0011	0.0021	0.0012	0.0014
O	0.0012	0.0020	0.0013	0.0029	0.0022	0.0028
C	0.0016	0.0021	0.0020	0.0036	0.0031	0.0033

Details of least-squares planes calculated for various portions of the molecular frameworks are given in Table 4. The atomic numbering schemes are shown in Figs. 1 and 2, while Figs. 3 and 4 show projected views of both molecular packings. The absolute stereochemistries [with the exception of the stereochemistries at C(5) and C(6)] of both molecules were known prior to the X-ray analyses, and all formulae and diagrams refer to the correct stereochemistries.

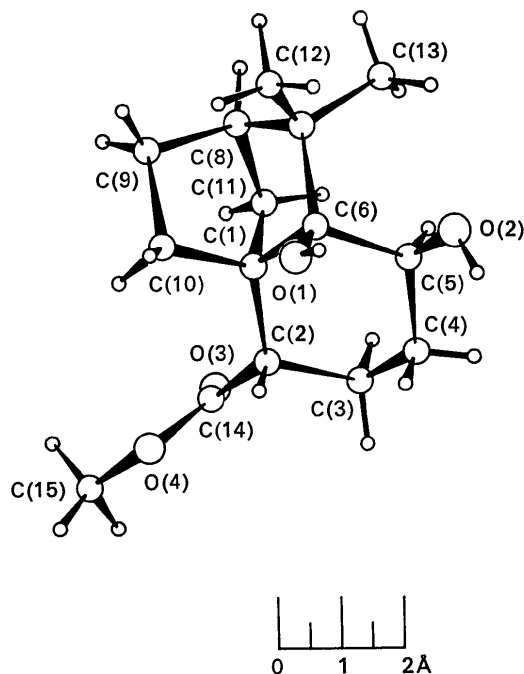


Fig. 1. A view of one molecule of (III), showing the atomic numbering. Hydrogen atoms are numbered as the carbon and oxygen atoms to which they are bonded.

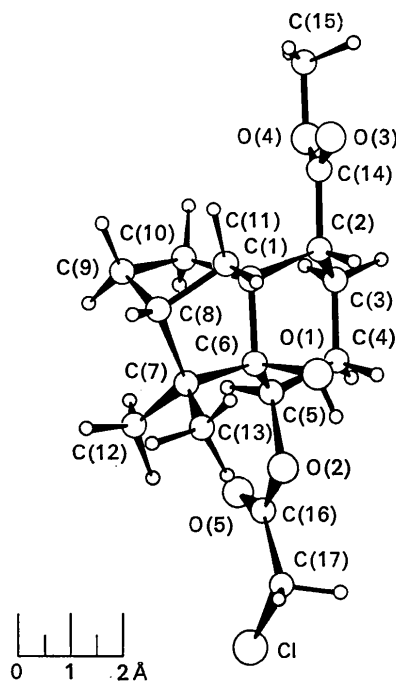


Fig. 2. A view of one molecule of (V), showing the atomic numbering. Hydrogen atoms are numbered as the carbon and oxygen atoms to which they are bonded.

Discussion

Although a mechanistic problem provided the original reason for undertaking both analyses, it is evident that, with the exception of the chloroacetoxy function, (III) and (V) differ only in stereochemistry. Comparison of their detailed molecular geometries thus affords an opportunity to examine the extent to which the dimen-

sions to the molecules may be influenced by the different spatial arrangements of virtually the same substituents.

The molecules (III) and (V) may be regarded as possessing similar bicyclo[2,2,1]heptyl skeletons fused in different ways to the cyclohexane rings, with corresponding reorientation of the other substituents. Although comparison of the mean C-C bond lengths

Table 3. *Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses*

(a) Bonded distances for both molecules

	(III)	(V)		(III)	(V)
O(1)-C(6)	1.428 (6)	1.439 (4)	C(5)-C(6)	1.561 (8)	1.526 (5)
O(2)-C(5)	1.429 (7)	1.464 (4)	C(6)-C(7)	1.593 (7)	1.588 (5)
O(3)-C(14)	1.196 (8)	1.203 (5)	C(7)-C(8)	1.581 (9)	1.556 (5)
O(4)-C(14)	1.338 (8)	1.333 (5)	C(7)-C(12)	1.540 (9)	1.543 (6)
O(4)-C(15)	1.441 (10)	1.451 (5)	C(7)-C(13)	1.552 (10)	1.540 (6)
C(1)-C(2)	1.541 (7)	1.523 (5)	C(8)-C(9)	1.531 (10)	1.537 (7)
C(1)-C(6)	1.559 (7)	1.562 (4)	C(8)-C(11)	1.541 (9)	1.548 (6)
C(1)-C(10)	1.551 (8)	1.578 (5)	C(9)-C(10)	1.551 (10)	1.562 (6)
C(1)-C(11)	1.546 (8)	1.544 (5)	C(16)-C(17)	-	1.517 (5)
C(2)-C(3)	1.541 (9)	1.547 (5)	C(16)-O(2)	-	1.335 (4)
C(2)-C(14)	1.512 (8)	1.519 (5)	C(16)-O(5)	-	1.201 (5)
C(3)-C(4)	1.522 (8)	1.544 (5)	C(17)-Cl	-	1.773 (5)
C(4)-C(5)	1.513 (8)	1.526 (5)			
			(III)	(V)	
	Average O-H		0.78 (8)	0.89 (6)	
	Average C-H		0.98 (8)	1.01 (6)	

(b) Interbond angles for both molecules

	(III)	(V)		(III)	(V)
C(14)-O(4)-C(15)	116.7 (6)	117.5 (3)	C(6)-C(7)-C(8)	101.2 (4)	101.9 (3)
C(2)-C(1)-C(6)	112.6 (4)	109.3 (3)	C(6)-C(7)-C(12)	110.9 (4)	113.2 (3)
C(2)-C(1)-C(10)	112.7 (5)	113.9 (3)	C(6)-C(7)-C(13)	114.9 (5)	111.8 (3)
C(2)-C(1)-C(11)	119.7 (4)	121.3 (3)	C(8)-C(7)-C(12)	113.2 (6)	113.5 (3)
C(6)-C(1)-C(10)	108.9 (4)	110.3 (3)	C(8)-C(7)-C(13)	108.8 (5)	109.2 (3)
C(6)-C(1)-C(11)	99.7 (4)	99.2 (3)	C(12)-C(7)-C(13)	107.8 (5)	107.3 (3)
C(10)-C(1)-C(11)	102.0 (4)	101.6 (3)	C(7)-C(8)-C(9)	112.0 (5)	110.7 (3)
C(1)-C(2)-C(3)	111.2 (4)	110.4 (3)	C(9)-C(8)-C(11)	101.6 (5)	103.6 (3)
C(1)-C(2)-C(14)	112.1 (5)	111.1 (3)	C(6)-C(8)-C(11)	101.5 (5)	100.0 (3)
C(3)-C(2)-C(14)	110.4 (4)	113.8 (3)	C(8)-C(9)-C(10)	102.1 (5)	102.6 (3)
C(2)-C(3)-C(4)	108.2 (5)	110.8 (3)	C(1)-C(10)-C(9)	104.3 (5)	103.0 (3)
C(3)-C(4)-C(5)	111.7 (5)	112.2 (3)	C(1)-C(11)-C(8)	94.2 (4)	94.2 (3)
O(2)-C(5)-C(4)	112.1 (4)	108.0 (3)	O(3)-C(14)-O(4)	123.7 (7)	123.1 (3)
O(2)-C(5)-C(6)	106.3 (4)	106.5 (3)	O(3)-C(14)-C(2)	125.0 (6)	123.2 (3)
C(4)-C(5)-C(6)	113.0 (5)	111.3 (3)	O(4)-C(14)-C(2)	111.3 (5)	113.7 (3)
O(1)-C(6)-C(1)	108.8 (4)	104.8 (3)	C(5)-O(2)-C(16)	-	117.4 (3)
O(1)-C(6)-C(5)	104.9 (4)	107.3 (3)	O(2)-C(16)-O(5)	-	125.0 (3)
O(1)-C(6)-C(7)	113.6 (4)	111.5 (3)	O(2)-C(16)-C(17)	-	107.5 (3)
C(1)-C(6)-C(5)	112.9 (4)	110.1 (3)	O(5)-C(16)-C(17)	-	127.5 (4)
C(1)-C(6)-C(7)	103.3 (4)	102.6 (3)	Cl-C(17)-C(16)	-	110.6 (3)
C(5)-C(6)-C(7)	113.4 (4)	119.6 (3)			

(c) Some comparable intramolecular non-bonded distances for both molecules.*

	(III)	(V)		(III)	(V)
O(1)···O(2)	2.60	2.76	C(2)···C(5)	2.96	2.96
O(1)···C(3)	3.67	3.37	C(3)···C(6)	2.99	2.96
{ O(1)···C(10)	2.83	-	{ C(5)···C(10)	-	3.07
{ O(1)···C(11)	-	2.78	{ C(5)···C(11)	3.31	-
{ O(1)···C(12)	2.72	-	{ C(5)···C(13)	2.86	-
{ O(1)···C(13)	-	2.71	{ C(5)···C(12)	-	2.96
O(3)···C(11)	3.26	3.26	C(6)···C(9)	3.05	3.08
O(4)···C(10)	3.38	3.36	C(7)···C(10)	2.95	2.29
C(1)···C(4)	2.96	2.96	C(9)···C(12)	2.97	2.91
C(1)···C(8)	2.26	2.26			

* Where the different stereochemistries require comparison of distances between different atoms, these are shown as successive pairs and bracketed.

Table 3 (cont.)

(d) Intermolecular distances (III)

O(1)···O(2 ⁱ)	2·83	O(3)···C(11 ^{iv})	3·79
O(1)···C(4 ⁱ)	3·23	O(3)···C(13 ^{iv})	3·50
O(1)···C(5 ⁱ)	3·58	O(3)···C(15 ^{iv})	3·54
O(1)···C(10 ⁱⁱ)	3·72	O(4)···C(8 ^{vi})	3·83
O(1)···H(O2 ⁱ)	1·98	C(3)···C(15 ^{iv})	3·86
O(2)···O(1 ⁱⁱ)	2·83	C(4)···C(15 ^{iv})	3·92
O(2)···C(2 ⁱⁱ)	3·83	C(5)···C(10 ⁱⁱ)	3·87
O(2)···C(6 ⁱⁱ)	3·99	C(8)···C(15 ^{iv})	3·98
O(2)···C(9 ⁱⁱⁱ)	3·67	C(9)···C(15 ^{iv})	3·86
O(2)···C(10 ⁱⁱⁱ)	3·44	H(O2)···O(1 ⁱⁱ)	1·98
O(2)···C(10 ^{iv})	3·91		

Roman numerals as superscripts refer to the equivalent positions which should be applied to the coordinates of the second atom:

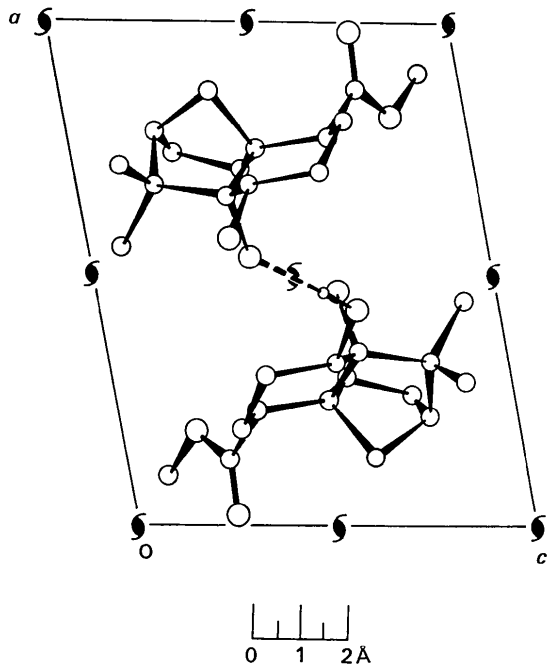
i	1-x, -½+y, 1-z	v	-x, ½+y, -z
ii	1-x, ½+y, 1-z	vi	x, y, -1+z
iii	x, 1+y, z	vii	x, y, 1+z
iv	-x, -½+y, 1-z		

(e) Intermolecular distances (V)

Cl(1)···O(2 ⁱ)	3·79	O(2)···O(3 ^{iv})	3·20
Cl(1)···O(5 ⁱⁱ)	3·58	O(3)···O(1 ^v)	2·87
Cl(1)···C(4 ⁱ)	3·80	O(3)···C(13 ^v)	3·57
Cl(1)···C(12 ⁱⁱ)	3·80	O(3)···H(O1 ^v)	1·99
Cl(1)···C(15 ⁱⁱⁱ)	3·53	O(4)···C(10 ^{iv})	3·65
Cl(1)···C(16 ⁱ)	3·62	O(5)···C(11 ^{vii})	3·46
Cl(1)···C(17 ⁱ)	3·67	O(5)···C(17 ⁱ)	3·52
O(1)···O(3 ^{iv})	2·87	H(O1)···O(3 ^{iv})	1·99
O(1)···C(15 ^{iv})	3·42		

Roman numerals as superscripts refer to the equivalent positions which should be applied to the coordinates of the second atom:

i	-x, ½+y, ½-z	v	½-x, -½-y, 1-z
ii	-x, -½+y, ½-z	vi	1-x, -½+y, ½-z
iii	-1+x, y, z	vii	½-x, -y, -½+z
iv	-½+x, -½-y, 1-z		

Fig. 3. The molecular packing of (III) viewed down *b*.Table 4. *Least-squares planes*(i) Least-squares planes for (III) given in the form $lX' + mY' + nZ' = d$, where X' , Y' and Z' are coordinates in Å.

(a) Plane equations

Plane (1):	$-0.0813X' + 0.5867Y' - 0.8057Z' = -0.5378$
Plane (2):	$0.9401X' - 0.2905Y' - 0.1785Z' = 0.9957$
Plane (3):	$-0.9539X' + 0.2665Y' - 0.1381Z' = -3.2033$
Plane (4):	$-0.2696X' - 0.9548Y' - 0.1250Z' = -3.7347$
Plane (5):	$-0.6791X' + 0.7337Y' - 0.0212Z' = 0.0820$
Plane (6):	$-0.9319X' - 0.2987Y' - 0.2060Z' = -4.1196$

(b) Deviations of atoms (Å) from planes (starred atoms not used to define plane)

Plane (1):	O(3) 0.003, O(4) 0.001, C(2) 0.003, C(14) -0.008, C(15) 0.001
Plane (2):	C(1) 0.003, C(2) -0.003, C(3)* -0.739, C(4) 0.003, C(5) -0.003, C(6)* 0.558
Plane (3):	C(1)* 0.830, C(6) 0.043, C(7) -0.043, C(8)* 0.803, C(9) 0.044, C(10) -0.045
Plane (4):	C(1) -0.021, C(2) 0.014, C(8) 0.013, C(11) -0.006
Plane (5):	C(1) -0.015, C(6) 0.022, C(7) -0.021, C(8) 0.015
Plane (6):	C(1) 0.029, C(8) -0.029, C(9) 0.042, C(10) -0.042

(c) Dihedral angles between planes (°)

(1)-(4)	64.1, (2)-(3) 18.3, (2)-(4) 87.3,
(2)-(6)	41.2, (3)-(4) 88.9, (4)-(5) 59.0,
(4)-(6)	55.8, (5)-(6) 65.3

(ii) Least-squares planes for (V)

(a') Plane equations

Plane (1):	$0.0110X' - 0.9789Y' - 0.2039Z' = 0.0785$
Plane (2):	$0.3891X' + 0.5180Y' - 0.7618Z' = -3.0413$
Plane (3):	$-0.5467X' + 0.3792Y' - 0.7465Z' = -7.4655$
Plane (4):	$0.7704X' + 0.5103Y' - 0.3823Z' = 1.7362$
Plane (5):	$-0.0231X' + 0.5632Y' - 0.8260Z' = -5.8669$
Plane (6):	$-0.8990X' + 0.0728Y' - 0.4319Z' = -8.0944$
Plane (7):	$0.0668X' - 0.9053Y' - 0.4194Z' = -1.6920$

(b') Deviations of atoms (Å) from planes (starred atoms not used to define plane)

Plane (1):	O(3) 0.006, O(4) 0.019, C(2) -0.008, C(14) -0.004, C(15) -0.013
Plane (2):	C(1) 0.024, C(2) -0.024, C(3)* 0.668, C(4) 0.0024, C(5) -0.024, C(6)* -0.708
Plane (3):	C(1)* -0.814, C(6) -0.073, C(7) 0.074, C(8)* -0.817, C(9) -0.076, C(10) 0.075
Plane (4):	C(1) 0.046, C(2) 0.023, C(3) -0.033, C(8) -0.002, C(11) -0.035
Plane (5):	C(1) 0.042, C(6) -0.060, C(7) 0.060, C(8) -0.042, C(11)* -0.885
Plane (6):	C(1) -0.037, C(8) 0.038, C(9) -0.055, C(10) 0.054, C(11)* -0.887
Plane (7):	Cl(1) -0.071, O(2) -0.013, O(5) 0.038, C(5) -0.042, C(16) 0.025, C(17) 0.064

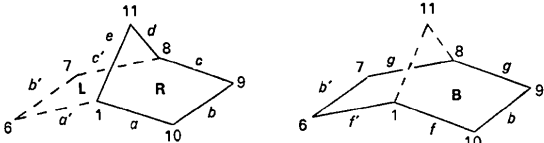
(c') Dihedral angles between planes (°)

(1)-(4)	65.6, (2)-(3) 56.5, (2)-(4) 31.4,
(2)-(6)	89.0, (3)-(4) 86.7, (4)-(5) 54.2,
(4)-(6)	60.6, (5)-(6) 65.3

[1.557 (8) in (III); 1.559 (5) Å in (V)] and mean endocyclic valency angles [101.4 (4)° in (III); 101.0 (3)° in (V)] suggests little difference between the two bicyclo-[2,2,1]heptyl residues, a more detailed examination of the torsion angles for these two systems (Table 5) reveals the extent to which these residues differ from each other and from the theoretical values calculated for the

norbornane skeleton (Altona & Sundaralingam, 1970). The negative, non-zero values of the torsion angles b and b' indicate that the bicyclo[2,2,1]heptyl moieties of both (III) and (V) exhibit twisting of the *Synchro*(—) type. It is also evident that on average the most marked deviations from the theoretical values, and also the greatest differences between the two molecules themselves, occur for those rings (L and B) which are most directly involved in the fusion to the cyclohexane ring. Moreover, the differences from theoretical values are greatest for (V), in which the cyclohexane-bicyclo[2,2,1]heptyl fusion is *trans*.

Table 5. Comparison of skeletal twisting



Torsion angles (°)	Bornane	(III)	(V)	
Ring L	a'	36	+39.2	+43.6
	b'	0	-3.4	-9.6
	c'	36	-33.8	-27.8
	d'	56	+57.8	+54.3
	e'	56	-59.4	-59.3
Ring R	a	36	-29.1	-28.6
	b	0	-6.9	-8.7
	c	36	+40.9	+43.0
	d	56	-57.8	-60.0
	e	56	+52.5	+53.8
Ring B	f	71	+75.6	+75.8
	g	71	-66.8	-65.7
	f'	71	-67.1	-62.5
	g'	71	+73.8	+78.5

Ring L: C(1), C(6), C(7), C(8), C(11)
 Ring R: C(1), C(10), C(9), C(8), C(11)
 Ring B: C(1), C(6), C(7), C(8), C(9), C(10).

In particular, the non-zero values for the torsion angle b' (Table 5), indicate that the twisting of the two molecules is such that complete eclipsing of the substituents on C(6) and C(7) is avoided. It is remarkable that in both molecules the C(6)–C(7) bond [1.593 (7) Å in (III); 1.588 (5) Å in (V)] is longer than might otherwise be expected for a C(sp^3)–C(sp^3) bond, and this may well be a genuine effect since similar lengthening has been noted in other bridged hydrocarbons, particularly for C(sp^3)–C(sp^3) bonds which either radiate from bridgehead positions (Beisler, Silverton, Penttila, Horn & Fales, 1971), or which bear almost eclipsed substituents (Gilardi, 1972). However, our observation must be assessed in the context of several other apparently 'lengthened' bonds [1.581 (9) Å for C(7)–C(8) in (III); 1.578 (5) Å for C(1)–C(10) in (V)], where there is no such obvious correlation between molecular strain and the observed values.

In addition to the small differences between the torsion angles of (III) and (V), differences are also observed between several corresponding valency angles. As one would expect, these differences are most marked for angles around C(6), since this is the site of the *cis*- and *trans*-fusion of the cyclohexane and bicyclo[2,2,1]heptyl moieties in the two molecules. Thus the *trans*-fusion in (V) results in a value of 119.6 (3)° for C(5) C(6) C(7), compared with 113.4 (4)° in (III), while the value of 108.8 (4)° for O(1) C(6) C(1) in (III) [104.8 (3)° in (V)] is consistent with a release of the potential steric crowding of the 6 α -hydroxy group and the α -2-carbon bridge in (III).

The carbomethoxy-bearing cyclohexane rings of (III) and (V) are also somewhat different. Both adopt chair conformations, but whereas in (III) atoms C(1), C(2), C(4) and C(5) are closely coplanar with C(3) and C(6) respectively -0.739 and $+0.558$ Å removed from this plane, in (V) the atoms C(1), C(2), C(4) and C(5) are slightly less planar, with C(3) and C(6) lying $+0.668$ and -0.708 Å distant from the plane. [The reversal of the deviations of C(3) and C(6) results from the *trans*-fusion in (V) as opposed to the *cis*-fusion in (III)]. It is also noticeable that the O(1)···C(3) intramolecular separation in (III) is 0.3 Å greater than in (V).

The presence of the chloroacetate function in (V) also induces differences between the two molecules. Such effects are evidenced by the O(1)···O(2) intramolecular separations [0.2 Å greater in (V)], and also by the valency angles C(5)–C(6)–C(7) [119.6 (3)° in (V); 113.4 (4)° in (III)], O(1)–C(6)–C(5) [107.3 (3)° in (V); 104.9 (4)° in (III)] and O(2)–C(5)–C(4) [108.0 (3)° in (V); 112.1 (4)° in (III)].

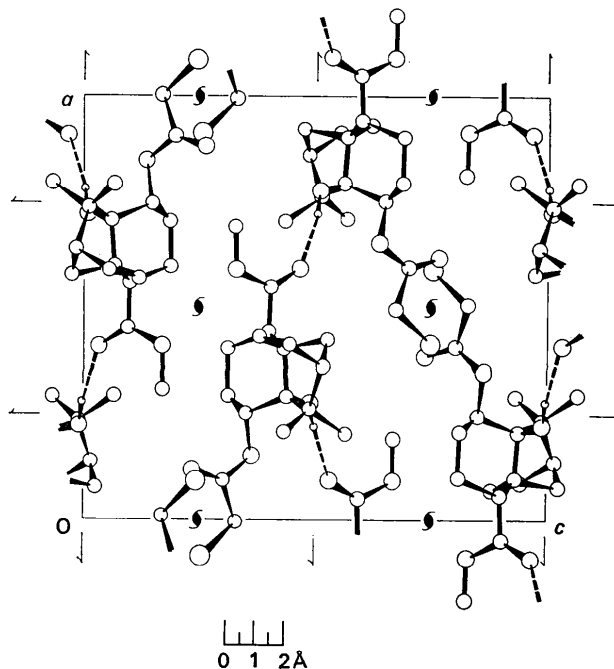


Fig. 4. The molecular packing of (V) viewed down b .

With the exception of those dimensions which have already been discussed, the remaining features of the molecules agree well with literature values for similar bond types. Examinations of the crystal-packing arrangements of (III) and (V) reveal O-H...O hydrogen bonding in both cases. For (III), a helix of hydrogen-bonded molecules [O...O 2.83 Å, O...H 1.98 Å, angle O-H...O 173°] extends in the **b** direction, while for (V) there are two independent and unlinked helices [O...O 2.87 Å, O...H 1.99 Å, angle O-H...O 169°] extending in the **a** direction.

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The Geometry of Hydrogen Bonds from Donor Water Molecules

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Analysis of the observed geometry of about 190 hydrogen bonds where the water molecule act as donor shows that the equilibrium configuration of the bond is linear and that the bending of the bond is isotropic.

The most direct and accurate information on the geometry of the hydrogen bond has been derived from neutron-diffraction studies of crystals. However, each crystal structure is a compromise between many competing interactions, and the observed geometry is therefore expected to be distorted from the inherent equilibrium configuration. To determine the equilibrium configuration, distortions from other interactions have to be corrected for or removed. It is generally assumed that the hydrogen bond is linear, but recently *ab initio* calculations by Kistenmacher, Popkie & Clementi (1973) on water molecule-anion complexes show that the configuration of maximal stability is non-linear.

We shall study in this paper the geometry of the hydrogen bonds formed by water molecules when the water molecule acts as a hydrogen-bond donor: H-O-H...A. We shall also obtain information on the equilibrium configuration from analysis of the approximately 190 bonds of this type presently known. Our basic assumption will be that the variations in geometry from one structure to another will be random. We therefore expect the averaged quantities to

be representative for the equilibrium configuration and that the random character of the distortions will result in Gaussian distributions.

There are interactions that cannot be removed in this way. It is expected that the hydrogen-bond length will be shortened in molecular solids owing to compression from the long-range attractive forces making the observed distances systematically too small. We shall therefore concentrate on characterizing the shape of the hydrogen bond.

To describe the shape we shall use the two angles defined in Fig. 1, θ and φ , where θ is the angle between the O-H vector and the H...A vector, and φ is the angle between the projection of the H...A vector in the *xy* plane and the plane of the water molecule. The data we will use have been taken from the survey by Ferraris & Franchini-Angela (1972). A similar review has recently been published by Falk & Knop (1973).

Fig. 2 is a histogram showing the number of bonds grouped according to the deviation from linearity. In this histogram bifurcated bonds are also included as separate bonds. It is seen that the most probable value for θ is not in the region 0-5°, but in the region 5-10°. The deviation from linearity can be very large. Hamilton & Ibers (1968) concluded from a similar plot that

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