The Crystal Structure and Absolute Configuration of (+)-Isoolivil (with Acetone and Water of Crystallization), $C_{20}H_{24}O_7 \cdot C_3H_6O \cdot H_2O$

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The crystal structure of (+)-isoolivil, with water and acetone of crystallization, $C_{20}H_{24}O_7 \cdot C_3H_6O \cdot H_2O$ has been determined by X-ray diffraction. The (+)-isoolivil–acetone–water molecular complex crystallizes in the orthorhombic system, space group $P2_12_12_1$, with $a = 17 \cdot 245$ (6), $b = 20 \cdot 749$ (6) and $c = 6 \cdot 767$ (4) Å, $Z = 4$, $D_m = 1 \cdot 25$ g cm^{-3}; D_x for four formula units is $1 \cdot 24$ g cm^{-3}. The structure was solved by direct methods with *MULTAN*. The absolute configuration was determined by least-squares refinement of the parameters of the two enantiomers and application of Hamilton's statistical test. The final R_1 index is $0 \cdot 0489$ for 2779 reflections and $0 \cdot 0576$ when all reflections (3033) were included in the refinement. Each isoolivil molecule forms five intermolecular hydrogen bonds; the molecules pack together in the crystal to form channels running parallel to the c axis. Each isoolivil molecule is also hydrogen bonded to two different water molecules; each water molecule is in turn hydrogen bonded to the acetone molecule. The water and acetone molecules occupy fixed positions within the channels.

Introduction

Previous studies (Southwell & Bultman, 1971) on the heartwood constituents of the marine-borer-resistant Central American tree *Tabebuia guayacan* Hemsl. have led to the isolation and identification of several natural protective constituents (Wong, Palmer, Manners & Jurd, 1976; Manners, Jurd, Wong & Palmer, 1975). Further investigation of the heartwood yielded another constituent which NMR spectroscopy revealed to be (+)-isoolivil (I). The crystallographic study of (+)-isoolivil was undertaken to obtain an accurate description of the molecule geometry in the crystal since it possesses the unusual property of retaining the acetone and water of crystallization up to a temperature of about 90 °C, and to determine its absolute configuration. The results of this investigation are reported in this paper.

(I)

Experimental procedure and refinement

Crystals of (+)-isoolivil suitable for X-ray analysis were obtained from acetone. The crystals were colorless prisms elongated along **c**. Weissenberg and precession photographs were used to determine the unit-cell dimensions and space group. The unit cell is orthorhombic; the only systematic absences are $h00$, $0k0$, and $00l$ when h, k, and l are odd. The space group is therefore uniquely determined to be $P2_12_12_1$. Unit-cell dimensions were refined by high-angle θ–2θ scans obtained at a 1° take-off angle with Cu $K\alpha_1$ radiation.

Crystal data

$C_{20}H_{24}O_7 \cdot C_3H_6O \cdot H_2O$, F.W. $452 \cdot 50$, $a = 17 \cdot 245$ (6), $b = 20 \cdot 749$ (6), $c = 6 \cdot 767$ (4) Å; λ(Cu $K\alpha_1$) = $1 \cdot 5405$, λ(Cu $K\alpha_2$) = $1 \cdot 5443$ Å. Orthorhombic, space group $P2_12_12_1$, $Z = 4$, $F(000) = 968$, $D_m = 1 \cdot 25$, $D_x = 1 \cdot 24$ g cm^{-3}.

The dimensions of the crystal used for intensity measurements were $0 \cdot 147 \times 0 \cdot 176 \times 0 \cdot 206$ mm parallel to **a**, **b** and **c** respectively. Intensity data were collected at room temperature with a GE automatic diffractometer equipped with a full-circle goniostat and controlled by an IBM 1800 time-sharing computer. The Ni-filtered Cu radiation was detected by a scintillation counter equipped with a single-channel pulse-height analyzer. One quarter of the reciprocal sphere was recorded in the range $0° \le 2\theta \le 110°$. The θ–2θ scan technique was used at a scan rate of 1° min^{-1}.
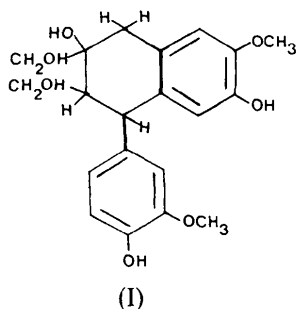
Table 1. *Positional and thermal parameters and their standard deviations in* $C_{20}H_{24}O_7 \cdot C_3H_6O \cdot H_2O$

Estimated standard deviations are indicated in parentheses. The thermal parameters are in Å^2. The temperature factor is $\exp(-T)$ where $T = \frac{1}{4}\Sigma\Sigma h_i h_j B_{ij}\, a_i^* a_j^*$ for the anisotropic case and $T = B(\sin\theta/\lambda)^2$ for the isotropic case.

	x	y	z	B11	B22	B33	B12	B13	B23
O1	.0006(2)	.5389(1)	.1454(4)	4.7(1)	2.0(1)	3.5(1)	-.3(1)	-.5(1)	-.29(9)
O2	-.1089(2)	.4675(1)	-.2652(3)	4.3(1)	4.5(1)	2.5(1)	.1(1)	-.4(1)	-.5(1)
O3	-.1269(2)	.5066(1)	.3592(5)	5.1(2)	4.1(2)	2.8(1)	1.0(1)	.0(1)	-.1(1)
O4	.2739(2)	.3677(2)	.4595(5)	4.2(2)	6.7(2)	5.2(2)	.1(1)	-.8(1)	2.4(1)
O5	.3222(2)	.4136(2)	.1144(4)	3.6(1)	7.3(2)	5.0(2)	.3(1)	.8(1)	2.3(1)
O6	.0091(2)	.1675(1)	.1897(4)	7.4(2)	2.4(1)	4.9(1)	-.1(1)	2.6(1)	-.3(1)
O7	-.0623(2)	.1458(1)	.5346(5)	5.3(2)	2.1(1)	4.7(1)	.0(1)	1.7(1)	.6(1)
O8	-.2455(2)	.4131(2)	-.1846(6)	4.7(2)	6.3(2)	6.9(2)	-.0(1)	-.1(1)	-.3(2)
O9	-.2767(3)	.3462(2)	.1681(8)	12.6(4)	8.5(3)	11.6(3)	-3.3(3)	-3.5(3)	4.1(3)
C1	.0503(2)	.4630(2)	-.0833(6)	4.1(2)	2.7(2)	2.8(2)	-.2(2)	.2(2)	.4(2)
C2	-.0224(2)	.4856(2)	.0180(5)	3.8(2)	2.1(2)	2.4(1)	-.1(1)	-.2(1)	-.4(1)
C3	-.0558(2)	.4309(2)	.1448(5)	3.8(2)	2.0(1)	2.5(1)	-.2(1)	-.5(1)	-.5(1)
C4	.0018(2)	.4045(2)	.2993(5)	3.8(2)	1.8(1)	2.4(2)	-.1(1)	.1(1)	.2(1)
C5	.1427(2)	.3868(2)	.3698(6)	3.4(2)	3.0(2)	3.3(2)	-.3(1)	-.4(2)	.6(1)
C6	.2200(2)	.3892(2)	.3238(6)	3.4(2)	3.0(2)	3.9(2)	.1(1)	-.3(2)	1.3(2)
C7	.2437(2)	.4143(2)	.1406(6)	3.1(2)	3.5(2)	3.8(2)	.0(1)	.5(2)	.6(2)
C8	.1891(2)	.4375(2)	.0124(6)	4.0(2)	3.4(2)	3.0(2)	-.2(2)	.4(2)	.7(2)
C9	.1094(2)	.4352(2)	.0584(5)	3.7(2)	2.4(2)	2.6(2)	-.1(1)	-.1(1)	-.1(1)
C10	.0860(2)	.4087(2)	.2379(5)	3.8(2)	1.9(1)	2.6(2)	-.3(1)	.1(1)	.3(1)
C11	-.0186(2)	.3355(2)	.3604(5)	2.9(2)	2.3(2)	2.7(2)	.1(1)	.1(1)	.2(1)
C12	.0025(2)	.2843(2)	.2394(6)	3.9(2)	2.5(2)	2.9(2)	-.2(1)	.5(2)	.0(1)
C13	-.0112(2)	.2207(2)	.2971(6)	3.5(2)	2.1(2)	3.8(2)	-.1(1)	.2(2)	-.1(1)
C14	-.0480(2)	.2079(2)	.4733(6)	3.0(2)	2.4(2)	3.7(2)	-.3(1)	.7(2)	.7(1)
C15	-.0696(2)	.2588(2)	.5935(6)	4.8(2)	2.9(2)	3.5(2)	.0(2)	1.7(2)	.4(2)
C16	-.0561(2)	.3214(2)	.5385(6)	4.5(2)	2.4(2)	3.3(2)	.3(2)	1.2(2)	-.2(2)
C17	-.0801(3)	.5135(2)	-.1286(6)	4.3(2)	3.1(2)	2.7(2)	.3(2)	.0(2)	.3(2)
C18	-.1329(2)	.4481(2)	.2452(6)	3.4(2)	3.4(2)	3.4(2)	-.2(2)	-.1(2)	.5(2)
C19	.3522(4)	.4382(3)	-.065(1)	4.0(3)	6.7(3)	5.2(3)	-.3(2)	1.4(2)	.6(3)
C20	.0522(5)	.1753(3)	.014(1)	13.4(5)	4.5(3)	5.8(3)	.8(3)	5.4(4)	-.7(2)
C21	-.2731(4)	.2946(3)	.245(1)	9.5(5)	6.3(4)	13.6(6)	-2.0(3)	-4.6(4)	3.9(4)
C22	-.2360(7)	.2393(5)	.145(1)	19.4(9)	12.7(6)	11.7(6)	7.5(6)	1.4(6)	-.3(5)
C23	-.3059(6)	.2882(4)	.468(1)	16.4(7)	11.9(6)	10.1(5)	-.9(5)	1.1(5)	4.5(5)

Table 1 (*cont.*)

	X	Y	Z	B
H1	.072(2)	.501(2)	-.147(6)	3.3(8)
H2	.034(2)	.430(2)	-.161(6)	4.0(10)
H3	-.066(2)	.395(2)	.067(6)	3.1(8)
H4	.000(2)	.433(1)	.408(4)	1.4(6)
H5	.120(1)	.372(1)	.550(4)	-.2(5)
H6	.207(2)	.458(1)	-.106(5)	1.6(7)
H7	.027(2)	.295(2)	.108(5)	2.5(7)
H8	-.098(2)	.250(2)	.706(6)	2.8(8)
H9	-.068(2)	.355(2)	.621(5)	2.2(7)
H10	-.043(3)	.549(2)	.240(7)	6.2(13)
H11	-.119(2)	.534(1)	-.076(4)	1.1(7)
H12	-.053(2)	.548(2)	-.196(5)	1.3(6)
H13	-.162(3)	.460(2)	-.207(8)	7.6(15)
H14	-.151(2)	.415(2)	.334(6)	3.4(8)
H15	-.178(2)	.448(2)	.153(6)	4.1(9)
H16	-.123(2)	.498(2)	.452(6)	2.6(12)
H17	.318(4)	.378(4)	.49(1)	11.6(25)
H18	.335(3)	.495(3)	-.104(8)	8.4(15)
H19	.331(3)	.423(2)	-.157(7)	3.8(13)
H20	.408(3)	.436(2)	-.054(5)	3.2(9)
H21	.090(4)	.210(3)	-.02(1)	11.7(23)
H22	.010(3)	.196(3)	-.085(9)	8.0(17)
H23	.068(3)	.126(3)	-.057(8)	8.2(14)
H24	-.043(3)	.122(2)	.451(7)	5.1(13)
WH1	-.251(6)	.390(6)	-.07(2)	22.5(42)
WH2	-.285(4)	.462(4)	-.15(1)	13.0(22)

The scan range varied to include both α_1 and α_2 peaks. Background counts were obtained $0\cdot5°$ before and after the limits of the scan range. 3481 reflections were measured of which 3033 were unique; of these, 120 were measured as zero, and 134 other reflections had $I \leq \sigma(I)$. These 254 reflections were excluded from the least-squares refinement. The value of $\sigma(I)$ was calculated from the expression $\sigma^2(I) = C + (T_c/2T_b)^2(B_1 + B_2)$, where C is the total count in scan time T_c, B_1 and B_2 are the two background counts taken for $T_b = 20$ s. When a reflection was measured more than once, the intensities were averaged and the standard deviation was set equal to the greater of $(\Sigma \sigma_i^2)^{1/2}/n$ or $(\Sigma\Delta_i^2)^{1/2}/(n - 1)$ where σ_i and Δ_i are the standard deviations of the ith measurement and the deviation of the ith measurement from the average, respectively, and n is the number of measurements. To reduce the weight given to intense reflections and to compensate for non-random errors an additional term, $(0\cdot05I)^2$, was included in the calculation of $\sigma^2(F^2)$: $\sigma^2(F^2) = [\sigma^2(I) + (0\cdot05I)^2]/(Lp)^2$, where Lp is the Lorentz–polarization factor. Two standard reflections were measured every 48 reflections; no significant change in their intensity was noted during the experiment. The linear absorption coefficient is $\mu(\text{Cu } K\alpha) = 7\cdot99$ cm^{-1}; consequently, a correction for absorption was not made. A correction for secondary extinction was applied during the final stages of refinement as discussed below. All calculations were carried out on the Lawrence Berkeley Laboratory's CDC 7600 computer with programs furnished by A. Zalkin.

Normalized structure factors $|E|$ were calculated by Wilson's method. The crystal structure was solved by direct methods with the phase determination program *MULTAN* (Germain, Main & Woolfson, 1971), based on the weighted tangent formula. An E Fourier synthesis revealed the parameters of the 32 heavy atoms. The O atoms were distinguished from the C atoms by the magnitude of the isotropic thermal parameters after the parameters of the 32 heavy atoms had been refined by least squares as C atoms.

The positional and thermal parameters were refined with a full-matrix, least-squares program which minimizes the function $\Sigma\, w(\Delta F)^2$ where $\Delta F = |F_o| - |F_c|$; F_o and F_c are the observed and calculated structure factors. The weighting factor w was taken equal to $1/\sigma^2(F)$, where $\sigma(F) = F_o - [F_o^2 - \sigma(F_o^2)]^{1/2}$ when $I > \sigma(I)$ and equal to zero when $I \leq \sigma(I)$. Scattering fac-

tors for all atoms except H were taken from Cromer & Waber (1965). The H scattering factors were from Stewart, Davidson & Simpson (1965). A correction for anomalous dispersion was applied to the scattering factor for O (Cromer, 1965).

Least-squares refinement of the parameters of the 32 heavy atoms with anisotropic temperature factors gave a discrepancy index R_1, defined as $\Sigma \, ||F_o| - |F_c||/\Sigma \, |F_o|$, of 0·078. A Fourier difference synthesis enabled the positional parameters for the 32 H atoms to be determined. Inclusion of H atoms in the least-squares refinement, with isotropic temperature factors and no restriction on their positional or thermal parameters, reduced R_1 to the final value of 0·0493. At this stage the very intense reflections had $F_o < F_c$. A correction for secondary extinction was made by applying the equation $F_{corr.} = [1 + (EF)I]F_o$ where I is the net intensity, EF the extinction factor, and F_o and F_{corr} the observed and corrected structure factors respectively (Zachariasen, 1963). By trial, the best value for EF appeared to be 1×10^{-7}. Generally, this correction led to a small improvement in the agreement between F_o and F_c but did not significantly improve the discrepancy between these two values for 200 and 020.

The absolute configuration was determined by least-squares refinement of the parameters of the two enantiomers. The results of the best refinements in the two cases are as follows:

	1	2
R_1 for 2779 reflections	0·0489	0·0493
R_1 for all (3033) reflections	0·0576	0·0579
R_2 (defined as $[\Sigma \, w \, |\Delta F|^2/\Sigma \, w|F_o|^2]^{1/2}$	0·0545	0·0552
Standard deviation of an observation of unit weight	1·440	1·459

According to Hamilton's (1965) statistical test, the enantiomer with lower R_2 index has a probability of being correct to a significance level better than 0·5%. All parameter shifts in the final cycle of least-squares refinement were less than 0·2σ for all heavy-atom parameters except those of water and acetone which are 0·5σ. This structure was used to calculate the final positional and thermal parameters for all atoms and their estimated standard deviations (Table 1).*

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32143 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
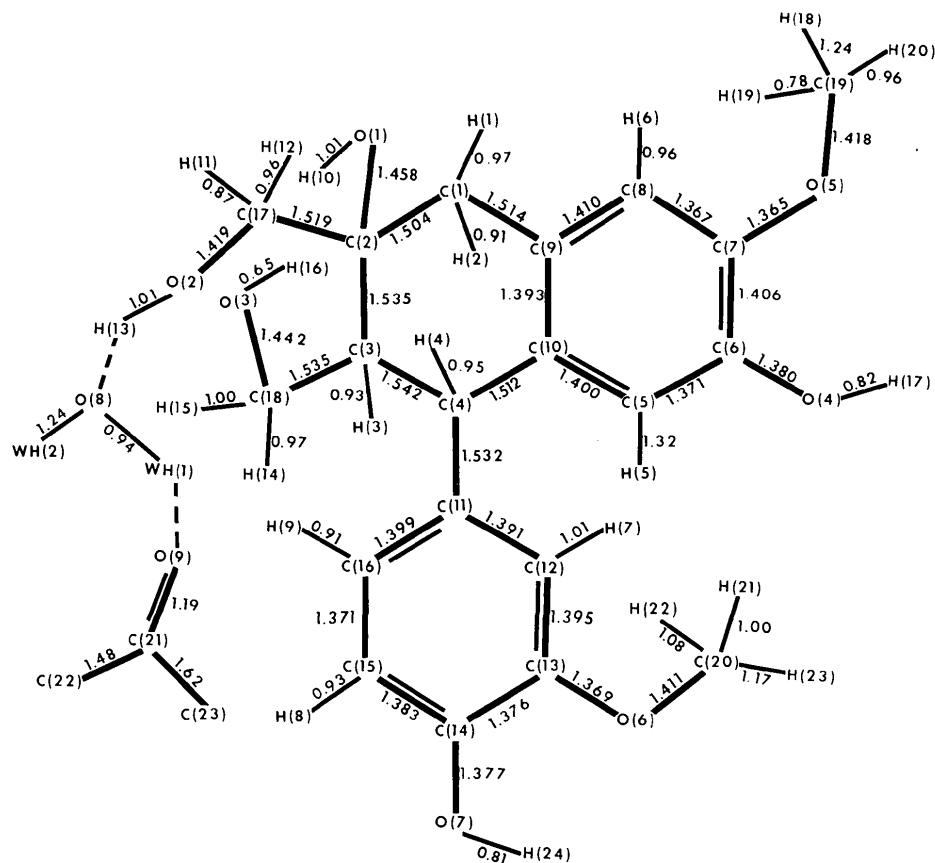

Fig. 1. The atom-numbering scheme and the bond distances. The e.s.d.'s are 0·008 Å for heavy atoms and 0·09 Å for H atoms. This view corresponds to that shown in Fig. 2.

Results and discussion

A schematic drawing of the molecule with the atom-numbering system and the interatomic distances is shown in Fig. 1. Bond angles between the heavy atoms are in Table 2.

The structure and absolute configuration of (+)-isoolivil are illustrated in the stereoscopic drawing (Johnson, 1965), Fig. 2. The molecule has a lignan skeleton (Swan, Klyne & MacLean, 1967) with the asymmetric configuration of $2S$, $3S$, and $4S$. The molecular structure, including the configuration about the asymmetric centers C(2), C(3) and C(4), confirms that postulated from NMR data (Smith, 1963; Ayres & Mhasalkar, 1964; Kato, 1964). The two H atoms H(3) and H(4) are *trans*, and the two CH_2OH groups bonded to C(2) and C(3) are in a *gauche*-diequatorial conformation with their OH groups pointing away from each other. From inspection of a molecular model, other conformations of O(3) appear possible. The observed orientation is preferred because it enhances the forma-

tion of a hydrogen bond between O(1) and O(3) to form a five-membered chelate ring, O(1), O(3), C(2), C(3) and C(18); the observed O(1)—O(3) distance is 2·716 Å.

In the crystal the isoolivil molecules form a molecular complex with acetone and water in the ratio 1 : 1 : 1. Each isoolivil molecule is hydrogen bonded to two different water molecules, and the water molecule in turn forms a hydrogen bond to the carbonyl O of the acetone molecule. Fig. 3 illustrates the molecular packing in the crystal as seen looking down c with a horizontal. As shown in Fig. 3, the isoolivil molecules form channel-like spaces which are about 7–8 Å in diameter and parallel to c; they are bound together by a network of intermolecular hydrogen bonds. The hydrogen-bond distances are in Table 3. The cavities leading from one channel to another are small in diameter. Both solvate molecules are in these channel-like spaces and occupy definite crystallographic positions in the crystal, unlike the situation observed in guayacanin (Wong *et al.*, 1976) and guayin (Manners *et al.*, 1975), where the enclosed acetone molecules are found to be disordered. The thermal stability of the solvated isoolivil crystals is apparently due to the combination of hydrogen bonds and the structural arrangement, which only allows the escape of the water and acetone molecules by diffusion along the channels.

The intramolecular bond distances are normal. The average C—C bond length in the two benzene rings, 1·39 Å, agrees exactly with the accepted value of the aromatic C—C bond length (Sutton, 1965). Excluding the common C(9)—C(10) bond, the C—C bond lengths of the cyclohexene ring vary between 1·504 and 1·542 Å with a mean of 1·521 Å, which is in good agreement with the aliphatic C—C bond of 1·537 Å (Sutton, 1965). The C—C and C=O bond lengths in the acetone molecule are 1·547 (mean) and 1·193 Å respectively; $\angle CCO$ and $\angle CCC$ are 119·5° (mean) and 121·0°. These observed values are in good agreement with those reported for acetone by Romers & Greutzberg (1956).

The mean bond angles in both benzene rings are 120·0°. The average value of the bond angles in the cyclohexene ring is 115·7°, which is slightly higher than the expected value of 113°. Generally, the C—C bond distances and angles in the tetralin ring of (+)-isoolivil agree closely with those reported for 1,2,3,4-tetra-chlorotetralin (Lasheen, 1952). The six C atoms C(5) to

Table 2. *Bond angles* (°) *involving heavy atoms*

The e.s.d.'s are 0·6°.

C(7)—O(5)—C(19)	118·0	C(1)—C(9)—C(8)	120·3
C(13)—O(6)—C(20)	119·3	C(1)—C(9)—C(10)	120·5
C(2)—C(1)—C(9)	113·1	C(8)—C(9)—C(10)	119·2
O(1)—C(2)—C(1)	106·2	C(4)—C(10)—C(5)	118·5
O(1)—C(2)—C(3)	109·4	C(4)—C(10)—C(9)	122·7
O(1)—C(2)—C(17)	105·9	C(5)—C(10)—C(9)	118·8
C(1)—C(2)—C(3)	109·7	C(4)—C(11)—C(12)	119·7
C(1)—C(2)—C(17)	111·5	C(4)—C(11)—C(16)	122·3
C(3)—C(2)—C(17)	113·7	C(12)—C(11)—C(16)	117·9
C(2)—C(3)—C(4)	113·6	C(11)—C(12)—C(13)	120·9
C(2)—C(3)—C(18)	113·6	O(6)—C(13)—C(12)	124·8
C(4)—C(3)—C(18)	109·9	O(6)—C(13)—C(14)	115·0
C(3)—C(4)—C(10)	114·3	C(12)—C(13)—C(14)	120·2
C(3)—C(4)—C(11)	111·5	O(7)—C(14)—C(13)	121·6
C(10)—C(4)—C(11)	110·4	O(7)—C(14)—C(15)	119·3
C(6)—C(5)—C(10)	121·6	C(13)—C(14)—C(15)	119·1
O(4)—C(6)—C(5)	119·5	C(14)—C(15)—C(16)	121·1
O(4)—C(6)—C(7)	120·8	C(11)—C(16)—C(15)	120·7
C(5)—C(6)—C(7)	119·7	O(2)—C(17)—C(2)	113·5
O(5)—C(7)—C(6)	113·5	O(3)—C(18)—C(3)	111·8
O(5)—C(7)—C(8)	127·2	O(9)—C(21)—C(22)	121·2
C(6)—C(7)—C(8)	119·4	O(9)—C(21)—C(23)	117·8
C(7)—C(8)—C(9)	121·3	C(22)—C(21)—C(23)	121·0

Fig. 2. Stereoscopic view of the molecule. The ellipsoids are drawn at the 50% probability level.
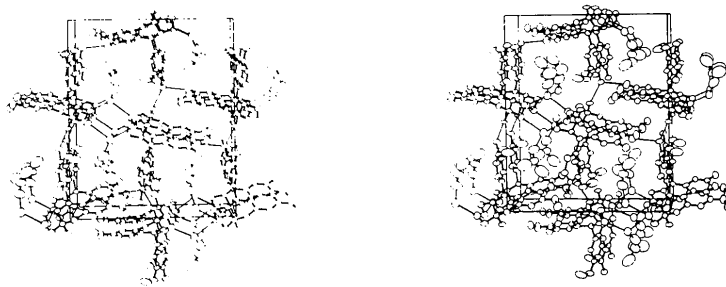
Fig. 3. Stereoscopic view of the molecular packing viewing down c with a horizontal.

Table 3. *Hydrogen-bond distances and angles in*
(+)-*isoolivil*

E.s.d.'s are 0·008 Å and 0·9° for distances and angles respectively.

O(1)–H(10)···O(3)	2·716 Å	138·3°
O(2)–H(13)···O(8)	2·669	150·3
O(3^i)–H(16^i)···O(2)	2·685	176·4
O(4)–H(17)···O(7^{iv})	2·838	145·6
O(7^{ii})–H(24^{ii})···O(1)	2·744	153·5
O(8)–WH(1)···O(9)	2·812	172·7
O(8^{iii})–WH(2^{iii})···O(3)	2·776	146·4

Symmetry code

(i) $x, y, z - 1$ (iii) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$

(ii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$ (iv) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$

C(10), constituting the benzene ring, together with C(1), C(4), O(4) and O(5), are coplanar within experimental error. The other benzene ring, C(11) to C(16), is planar; the maximum deviation from the mean ring plane is 0·008 Å. The dihedral angle between the two planes C(5) to C(10) and C(11) to C(16) is 77·8°. The observed conformation reduces the steric hindrance between H(5) and H(7), and H(9) and H(14).

The thermal parameters of most of the atoms are within the normal range; the exceptions are the higher values for C(20) and H(21) of the methyl group and C(21), C(22), C(23) and O(9) of the acetone molecule. The first is presumably due to methyl torsion and the latter to the fact that the acetone molecules are only weakly held in position by the single hydrogen bond to water and, therefore, undergo appreciable thermal motion. In addition, the thermal parameters of H(17) and the water H atoms, WH(1) and WH(2), are also higher than nor-

mal. No attempt was made to locate the H atoms of the acetone molecule.

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