Acta Cryst. (1976). B32, 2396

The Structure of Guayacanin (with Acetone of Crystallization) $C_{30}H_{24}O_4 \cdot \frac{1}{3}(C_3H_6O)$, a Naturally Occurring Dibenzoxanthene from *Tabebuia guayacan*

BY ROSALIND Y. WONG, K. J. PALMER, G. D. MANNERS AND L. JURD

Western Regional Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Berkeley, California 94710, *U.S.A.*

(*Received* 15 *September* 1975; *accepted* 21 *February* 1976)

The crystal structure of guayacanin (with acetone of crystallization), $C_{30}H_{24}O_4 \cdot \frac{1}{3}(C_3H_6O)$, has been determined by X-ray diffraction. The crystals are rhombohedral, space group $R\bar{3}$ with hexagonal cell dimensions $a = 24{\cdot}677$ (7), $c = 20{\cdot}588$ (6) Å, $Z = 18$. The structure was solved by use of the programs *NORMAL* and *MULTAN*. The parameters were refined by full-matrix least squares to an R_1 index of 0·051 for 2681 reflections. The molecule has two chromene *gem* dimethyl groups, one of which is benzylically substituted. The molecule is approximately planar; repulsion between two hydrogen atoms produces an appreciable twist to the molecule. The crystal consists of clusters of six molecules; each cluster is centered on an inversion triad axis. The molecules in each cluster are held together by a network of hydrogen bonds. The only attractive force between clusters results from van der Waals interactions. The crystal contains two acetone molecules per cluster. The acetone molecules are disordered; the four heavy atoms partially occupy six positions and are centered on inversion triad axes. There are no bonds between the acetone molecules and the clusters.

Introduction

Long-term marine exposure tests (Southwell & Bultman, 1971) have shown that the Central American tree, *Tabebuia guayacan* Hemsl., is resistant to attack by marine boring organisms. As part of a study to identify the natural protective constituents the crystal structure of a new compound, guayacanin, which was recently isolated from the heartwood of *T. guayacan* (Manners, Jurd, Wong & Palmer, 1975), has been determined. Chemical and spectral data demonstrated that guayacanin is a novel prenylnapthaquinol dibenzoxanthene. From the chemical and spectral data two possible structures were postulated. The correct structure was determined by X-ray crystallography and the results are reported here.

Experimental procedure and refinement

Crystals of guayacanin were obtained from acetone as small, light-orange rhombohedra. Weissenberg and precession photographs were used to determine the space group. The precession photographs were compatible with Laue symmetry $\bar{3}$, and the hexagonal indices were found to obey the rule $-h+k+l=3n$. The primitive lattice is therefore rhombohedral and has the obverse orientation. The observed density of 1·287 g cm^{-3} requires eighteen molecules per hexagonal cell or six per rhombohedral cell. The structure was successfully solved in space group $R\bar{3}$. The unit-cell dimensions were refined by high-angle θ–2θ scans with a 1° take-off angle. The crystal data are summarized in Table 1.

Table 1. *Crystal data*

$(C_{30}H_{24}O_4) \cdot \frac{1}{3}(C_3H_6O)$	F.W. 467·873
$D_o = 1{\cdot}287$ g cm^{-3}	Space group $R\bar{3}$
$D_c = 1{\cdot}287$	$Z = 18$
Cu $K\alpha_1 = 1{\cdot}54051$ Å	$a = 24{\cdot}677$ (6) Å
Cu $K\alpha_2 = 1{\cdot}54433$	$c = 20{\cdot}588$ (6)
Cu $K\alpha = 1{\cdot}54518$	$F(000) = 4440$

The dimensions of the crystal used for intensity measurements were 0·223 × 0·220 × 0·235 mm. Intensity data were collected at room temperature with a G.E. automatic diffractometer equipped with a full-circle goniostat and controlled by an IBM 1800 time-sharing computer. The Ni-filtered copper 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 $0° \leq 2\theta \leq 115°$. The θ–2θ scan technique was used at a scan rate of 1° min^{-1}. The scan range varied to include both α_1 and α_2 peaks. Background counts were obtained 0·5° before and after the limits of the scan range. 5319 reflections were measured of which 3310 were unique; of these, 150 were measured as zero and 364 other reflections had $I \leq \sigma(I)$. These 514 reflections were excluded from the least-squares refinement. The value of $\sigma(I)$ was calculated from the expression $\sigma(I)^2 = C + (T_c/2T_b)^2(B_1 + B_2)$ where C is the total count in scan time T_c, and 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 $(\sum\sigma_i^2)^{1/2}/n$ or $(\sum\Delta_i^2)^{1/2}/(n-1)$ where σ_i and Δ_i are the standard deviation of the ith measure-

ment 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, $(0{\cdot}05I)^2$, was included in the calculation of $\sigma^2(F^2)$: $\sigma^2(F^2)=[\sigma^2(I)+(0{\cdot}05I)^2]/(\mathrm{Lp})^2$, 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 small, $\mu(\mathrm{Cu}\ K\alpha)=6{\cdot}88\ \mathrm{cm}^{-1}$; consequently, a correction for absorption was not made. All calculations were carried out on the Berkeley Lawrence Laboratory's CDC 7600 computer with programs furnished by A. Zalkin.

Normalized structure factors $|E|$ were calculated by the program *NORMAL* written by G. T. Grainger and revised by Main (1972). The crystal structure was solved by direct methods using the *MULTAN* program (Germain, Main & Woolfson, 1971). The correct structure was not revealed until the coordinates of 30 atoms comprising a planar, fused, six-membered ring structure were used in *NORMAL*. An E Fourier synthesis revealed the parameters of the 34 heavy atoms. The O atoms were distinguished from the C atoms by the magnitude of the isotropic thermal parameters after the parameters of the 34 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 $\sum w(\Delta F)^2$ where $\Delta F=|F_c|-|F_o|$, F_o and F_c being 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 $I<\sigma(I)$. Scattering factors for all atoms except H were taken from Cromer & Waber (1965). The H scattering factors were from Stewart, Davidson & Simpson (1965).

A Fourier difference synthesis led to the determination of the positional parameters for the 24 H atoms. Least-squares refinement of the parameters of the 34 heavy atoms with anisotropic temperature factors and 24 H atoms with isotropic temperature factors with no restriction on their positional parameters gave a discrepancy index R_1, defined as $\sum||F_o|-|F_c||/\sum|F_o|$, of 0·097.

The NMR spectrum of crystalline guayacanin dissolved in $CDCl_3$ (Manners *et al.*, 1975) indicated

Table 2. *Positional and thermal parameters and their standard deviations in guayacanin (with acetone of crystallization)*, $C_{30}H_{24}O_4\cdot\frac{1}{3}(C_3H_6O)$

Estimated standard deviations are indicated in parentheses. The thermal parameters are in Å². The temperature factor is $\exp(-T)$ where $T=\frac{1}{4}\sum\sum h_ih_jB_{ij}a_i^*a_j^*$ for the anisotropic case and $T=B(\sin\theta/\lambda)^2$ for the isotropic case.

	x ($\times10^4$)	y ($\times10^4$)	z ($\times10^4$)	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	2862·6 (7)	2016·9 (7)	2779·8 (7)	3·65 (8)	3·68 (8)	3·44 (8)	2·41 (7)	0·26 (6)	0·38 (6)
O(2)	1929·3 (7)	400·4 (7)	4392·0 (8)	2·80 (8)	3·31 (8)	4·40 (9)	1·52 (6)	0·13 (6)	0·62 (6)
O(3)	4723·7 (8)	1513·8 (8)	2110·9 (8)	4·54 (9)	5·3 (1)	3·28 (8)	3·55 (8)	0·92 (7)	1·05 (7)
O(4)	979·3 (8)	671·8 (9)	4555·0 (9)	3·33 (8)	4·06 (9)	4·57 (9)	1·96 (7)	0·76 (7)	0·69 (7)
C(1)	2392 (1)	1659 (1)	3211 (1)	3·1 (1)	3·4 (1)	2·8 (1)	1·8 (1)	−0·16 (9)	−0·24 (9)
C(2)	1902 (1)	1795 (1)	3268 (1)	3·9 (1)	3·9 (1)	2·9 (1)	2·4 (1)	−0·65 (9)	−0·55 (9)
C(3)	1879 (2)	2267 (2)	2904 (1)	5·0 (2)	5·6 (2)	3·7 (1)	3·7 (1)	0·4 (1)	0·7 (1)
C(4)	1398 (2)	2381 (2)	2974 (1)	6·6 (2)	7·4 (2)	3·7 (1)	5·5 (2)	0·2 (1)	0·7 (1)
C(5)	904 (2)	2017 (2)	3403 (1)	4·8 (2)	7·1 (2)	3·6 (1)	4·3 (2)	−0·5 (1)	−0·4 (1)
C(6)	911 (1)	1560 (1)	3762 (1)	3·6 (1)	5·4 (2)	3·4 (1)	2·9 (1)	−0·2 (1)	−0·5 (1)
C(7)	1413 (1)	1439 (1)	3714 (1)	3·1 (1)	4·0 (1)	2·9 (1)	2·0 (1)	−0·48 (9)	−0·64 (9)
C(8)	1445 (1)	981 (1)	4107 (1)	2·8 (1)	3·4 (1)	3·3 (1)	1·4 (1)	−0·11 (9)	−0·54 (9)
C(9)	1930 (1)	867 (1)	4030 (1)	2·9 (1)	2·9 (1)	3·4 (1)	1·41 (9)	−0·33 (9)	−0·14 (9)
C(10)	2544 (1)	491 (1)	4558 (1)	3·0 (1)	3·6 (1)	3·3 (1)	1·8 (1)	0·26 (9)	0·47 (9)
C(11)	2973 (1)	715 (1)	3978 (1)	3·2 (1)	3·4 (1)	3·6 (1)	1·9 (1)	−0·03 (9)	0·21 (9)
C(12)	2919 (1)	1065 (1)	3508 (1)	3·0 (1)	2·8 (1)	3·1 (1)	1·53 (9)	−0·09 (9)	−0·19 (9)
C(13)	2408 (1)	1200 (1)	3572 (1)	2·9 (1)	3·0 (1)	3·1 (1)	1·62 (9)	−0·30 (9)	−0·38 (9)
C(14)	3344 (1)	1379 (1)	2963 (1)	3·0 (1)	3·1 (1)	2·8 (1)	1·64 (9)	−0·39 (9)	−0·31 (9)
C(15)	3817 (1)	1238 (1)	2755 (1)	3·3 (1)	3·2 (1)	2·8 (1)	2·0 (1)	−0·07 (9)	0·03 (9)
C(16)	3810 (1)	655 (1)	2905 (1)	4·4 (1)	3·5 (1)	3·2 (1)	2·4 (1)	0·4 (1)	0·3 (1)
C(17)	4322 (1)	616 (1)	2790 (1)	5·5 (2)	4·4 (1)	3·2 (1)	3·5 (1)	0·3 (1)	0·3 (1)
C(18)	4905 (1)	1178 (1)	2563 (1)	4·5 (1)	5·1 (1)	3·7 (1)	3·5 (1)	0·6 (1)	0·9 (1)
C(19)	4265 (1)	1628 (1)	2320 (1)	3·4 (1)	3·4 (1)	2·6 (1)	2·0 (1)	−0·16 (9)	−0·21 (9)
C(20)	4258 (1)	2142 (1)	2026 (1)	3·2 (1)	3·0 (1)	2·7 (1)	1·48 (9)	−0·22 (9)	−0·08 (9)
C(21)	4721 (1)	2541 (1)	1577 (1)	3·6 (1)	3·9 (1)	3·4 (1)	1·7 (1)	0·2 (1)	0·3 (1)
C(22)	4693 (1)	3031 (1)	1303 (1)	4·5 (1)	3·7 (1)	4·1 (1)	1·6 (1)	0·4 (1)	0·8 (1)
C(23)	4210 (1)	3141 (1)	1466 (1)	4·9 (2)	3·3 (1)	4·5 (1)	2·2 (1)	−0·1 (1)	0·6 (1)
C(24)	3754 (1)	2766 (1)	1895 (1)	4·6 (1)	3·1 (1)	3·4 (1)	2·2 (1)	−0·2 (1)	−0·0 (1)
C(25)	3767 (1)	2258 (1)	2187 (1)	3·2 (1)	2·9 (1)	2·6 (1)	1·48 (9)	−0·48 (9)	−0·28 (9)
C(26)	3317 (1)	1861 (1)	2655 (1)	3·3 (1)	3·1 (1)	2·8 (1)	1·88 (9)	−0·45 (9)	−0·44 (9)
C(27)	2412 (2)	−148 (2)	4785 (2)	4·2 (1)	4·3 (2)	5·4 (2)	2·4 (1)	1·0 (1)	1·5 (1)
C(28)	2814 (2)	964 (2)	5103 (2)	4·0 (2)	5·3 (2)	3·8 (1)	2·3 (1)	0·0 (1)	−0·1 (1)
C(29)	5323 (2)	1015 (3)	2173 (2)	7·1 (2)	7·9 (2)	5·7 (2)	6·0 (2)	2·4 (2)	2·3 (2)
C(30)	5267 (2)	1618 (2)	3123 (2)	4·9 (2)	6·0 (2)	4·8 (2)	3·2 (2)	−0·4 (1)	0·7 (1)

Table 2 (*cont.*)

	x ($\times 10^3$)	y ($\times 10^3$)	z ($\times 10^3$)	B
C(31)	0	0	149 (2)	11·5 (9)
C(32)	0	0	220 (2)	8·8 (6)
C(33)	0	0	281 (2)	9·3 (6)
C(34)	42·4 (9)	75·3 (9)	202·5 (9)	7·4 (4)
H(1)	221 (1)	249 (1)	264 (1)	4·1 (7)
H(2)	139 (1)	270 (1)	270 (1)	4·3 (6)
H(3)	55 (1)	208 (1)	346 (1)	3·9 (6)
H(4)	59 (1)	132 (1)	405 (1)	3·1 (5)
H(5)	334 (1)	62 (1)	400 (1)	3·6 (5)
H(6)	339 (1)	25 (1)	306 (1)	3·2 (5)
H(7)	435 (1)	24 (1)	285 (1)	4·2 (6)
H(8)	510 (1)	251 (1)	143 (1)	4·8 (7)
H(9)	501 (1)	332 (1)	99 (2)	5·4 (7)
H(10)	418 (1)	347 (1)	128 (1)	4·1 (6)
H(11)	340 (1)	286 (1)	203 (1)	3·8 (6)
H(12)	101 (2)	38 (2)	477 (2)	7·1 (9)
H(13)	282 (2)	−13 (1)	495 (2)	5·7 (7)
H(14)	223 (1)	−48 (2)	443 (2)	5·0 (7)
H(15)	210 (1)	−32 (1)	514 (1)	4·7 (7)
H(16)	289 (1)	137 (2)	496 (1)	4·6 (7)
H(17)	324 (2)	106 (1)	521 (1)	4·4 (7)
H(18)	251 (2)	84 (2)	545 (2)	6·4 (8)
H(19)	504 (2)	73 (2)	181 (2)	7·0 (10)
H(20)	544 (1)	77 (1)	245 (1)	5·0 (7)
H(21)	560 (2)	133 (2)	196 (2)	5·7 (9)
H(22)	540 (1)	137 (1)	344 (1)	4·8 (6)
H(23)	498 (2)	170 (1)	340 (2)	5·9 (8)
H(24)	563 (2)	202 (2)	292 (2)	6·6 (8)

that there are two acetone molecules per cluster of six guayacanin molecules. The calculated density for this composition is in excellent agreement with the observed value (Table 1). A Fourier difference synthesis reveals four peaks, C(31), C(32), C(33) and C(34), at (0·0,0·0,0·16), (0·0,0·0,0·22), (0·0,0·0,0·28) and (0·04, 0·07,0·20) with electron densities of 1·3, 1·7, 1·3 and 1·3 respectively. The next highest peak has an electron density of 0·54. These peaks are incompatible with the geometry of acetone. However, the distances C(32)–C(33) and C(32)–C(34) of 1·24 and 1·45 Å, respectively, are close to those expected for C=O and C–C.

Unfortunately, the triad axis parallel to C(32)–C(33) does not generate a peak 180° from C(34) nor can the peak labelled C(31) be rationally explained as part of the acetone molecule; the ∠C(31)–C(32)–C(34) is only 77°. In the least-squares refinement, the two atoms composing the carbonyl group were arbitrarily divided among the three positions along the inversion triad axis and given a weight of 0·074 ($\frac{1}{3}\times\frac{2}{3}\times\frac{1}{3}$ – one acetone per three guayacanin molecules, two atoms occupying three positions and lying on an inversion triad axis). The two methyl carbon atoms were assumed to occupy the three equivalent positions about the inversion axis; C(34) was, therefore, assigned a weight of 0·22 ($\frac{1}{3}\times\frac{2}{3}$). Inclusion of these peaks, with isotropic temperature factors and assuming that they were all carbon atoms, in the least-squares refinement reduced the R_1 index to 0·076.

A comparison of F_{obs} and F_{calc} revealed that the agreement was poor when $\sin\theta/\lambda < 0{\cdot}18$. Elimination of the 115 reflections below this limit reduced R_1 to the final values of 0·051 for 2681 data and 0·077 for all 3310 data. $R_2=[\sum w|\Delta F|^2/\sum w|F_o|^2]^{1/2}$ is 0·054 and the standard deviation of an observation of unit weight is 1·38. All parameter shifts in the final cycle of least-squares refinement are less than $0{\cdot}3\sigma$. No attempt was made to locate the hydrogen atoms of the disordered acetone molecules. The final positional and thermal parameters for all atoms and their estimated standard deviations are listed in Table 2.*

Results and discussion

The structure of guayacanin is illustrated in the *ORTEP* drawing (Johnson, 1965) shown in Fig. 1. The molecule consists of two chromene *gem*-dimethyl groups, one of which is benzylically substituted. A schematic drawing of the molecule with the atom numbering system used in this paper and the interatomic distances between the heavy atoms, except the disordered acetone molecule, is presented in Fig. 2. Distances involving H atoms are listed in Table 3. Bond angles involving the heavy atoms are tabulated in Table 4. The observed bond lengths and angles of the aromatic rings are generally normal and are in good agreement with those reported for 2-hydroxy-1,3,4,7-tetramethoxyxanthone (Stout, Lin & Singh, 1969).

The four aromatic rings in the molecule are essentially planar. The two planes formed by C(1), C(7), C(8), C(9), C(13), C(12), O(1) and C(14), C(15),

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31695 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

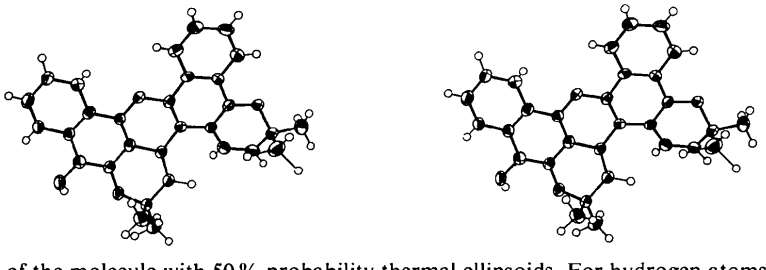

Fig. 1. Stereoscopic view of the molecule with 50% probability thermal ellipsoids. For hydrogen atoms an arbitrary temperature parameter of 1·0 Å^2 was used.

C(19), C(20), C(25), C(26), C(12), O(1), respectively, intersect at an angle of 173·1°; the molecule is thus slightly butterfly-shaped. The three heterocyclic rings have a flattened boat form. There are four possible conformations of the molecule due to the two dimethyl groups on the chromene rings. The observed conformation appears to be dictated primarily by the repulsion between the two hydrogen atoms H(5) and H(6).

From inspection of a molecular model the distance between these two hydrogen atoms is a maximum when the axial methyl groups are on the same side of the molecular plane (*cis*). It is not apparent from the model why the conformation illustrated in Fig. 1 is more stable than that with the two axial methyl groups pointing away from the viewer. When the two axial methyl groups are *trans*, the H(5)–H(6) distance is very short, and it is obvious why the two *trans* conformations are unstable.

The repulsion between H(5) and H(6) increases the angles C(11)–C(12)–C(14) and C(14)–C(15)–C(16)

Table 3. *Distances* (Å) *involving hydrogen atoms*

The e.s.d.'s are 0·05 Å.

H(1)—C(3)	0·91	H(13)–C(27)	1·03
H(2)—C(4)	1·00	H(14)–C(27)	1·01
H(3)—C(5)	0·96	H(15)–C(27)	0·98
H(4)—C(6)	0·93	H(16)–C(28)	0·97
H(5)—C(11)	1·04	H(17)–C(28)	0·98
H(6)—C(16)	1·07	H(18)–C(28)	0·97
H(7)—C(17)	0·97	H(19)–C(29)	1·04
H(8)—C(21)	1·03	H(20)–C(29)	0·96
H(9)—C(22)	0·98	H(21)–C(29)	0·85
H(10)–C(23)	0·94	H(22)–C(30)	1·07
H(11)–C(24)	1·06	H(23)–C(30)	1·01
H(12)–O(4)	0·88	H(24)–C(30)	1·03

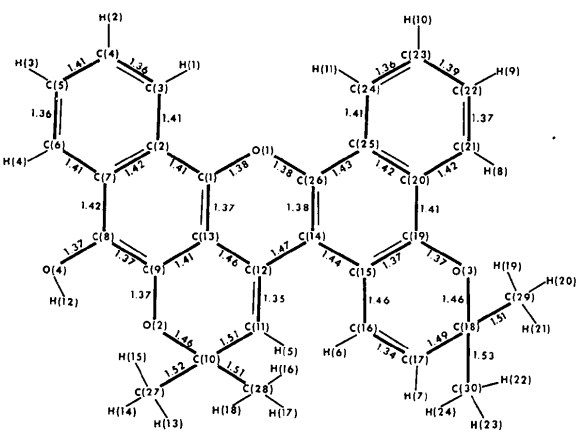

Fig. 2. The atom numbering scheme used in this paper and the bond distances between heavy atoms. Estimated standard deviations are 0·01 Å. This view corresponds to that in Fig. 1.

Table 4. *Bond angles* (°) *involving heavy atoms*

E.s.d.'s are 0·6°.

C(1)—O(1)—C(26)	119·0	C(12)–C(14)–C(15)	123·6
C(9)—O(2)—C(10)	115·7	C(12)–C(14)–C(26)	118·5
C(18)–O(3)—C(19)	115·9	C(15)–C(14)–C(26)	117·8
O(1)—C(1)—C(2)	116·6	C(14)–C(15)–C(16)	124·2
O(1)—C(1)—C(13)	121·2	C(14)–C(15)–C(19)	119·3
C(2)—C(1)—C(13)	122·2	C(16)–C(15)–C(19)	116·0
C(1)—C(2)—C(3)	123·1	C(15)–C(16)–C(17)	119·2
C(1)—C(2)—C(7)	118·1	C(16)–C(17)–C(18)	119·7
C(3)—C(2)—C(7)	118·7	O(3)—C(18)–C(17)	107·6
C(2)—C(3)—C(4)	121·1	O(3)—C(18)–C(29)	104·8
C(3)—C(4)—C(5)	120·1	O(3)—C(18)–C(30)	108·3
C(4)—C(5)—C(6)	120·5	C(17)–C(18)–C(29)	112·8
C(5)—C(6)—C(7)	120·9	C(17)–C(18)–C(30)	112·1
C(2)—C(7)—C(6)	118·6	C(29)–C(18)–C(30)	110·8
C(2)—C(7)—C(8)	119·4	O(3)—C(19)–C(15)	121·3
C(6)—C(7)—C(8)	122·0	O(3)—C(19)–C(20)	115·7
O(4)—C(8)—C(7)	117·5	C(15)–C(19)–C(20)	122·8
O(4)—C(8)—C(9)	122·6	C(19)–C(20)–C(21)	122·4
C(7)—C(8)—C(9)	119·9	C(19)–C(20)–C(25)	118·4
O(2)—C(9)—C(8)	118·4	C(21)–C(20)–C(25)	119·2
O(2)—C(9)—C(13)	120·1	C(20)–C(21)–C(22)	120·3
C(8)—C(9)—C(13)	121·4	C(21)–C(22)–C(23)	120·1
O(2)—C(10)–C(11)	110·9	C(22)–C(23)–C(24)	121·4
O(2)—C(10)–C(27)	104·3	C(23)–C(24)–C(25)	120·2
O(2)—C(10)–C(28)	108·4	C(20)–C(25)–C(24)	118·9
C(11)–C(10)–C(27)	111·9	C(20)–C(25)–C(26)	118·1
C(11)–C(10)–C(28)	110·4	C(24)–C(25)–C(26)	122·9
C(27)–C(10)–C(28)	110·9	O(1)—C(26)–C(14)	123·5
C(10)–C(11)–C(12)	121·9	O(1)—C(26)–C(25)	113·4
C(11)–C(12)–C(13)	117·0	C(14)–C(26)–C(25)	123·1
C(11)–C(12)–C(14)	127·9	C(31)–C(32)–C(33)	180·0
C(13)–C(12)–C(14)	114·9	C(31)–C(32)–C(34)	77·5
C(1)—C(13)–C(9)	118·8	C(33)–C(32)–C(34)	102·6
C(1)—C(13)–C(12)	121·5		
C(9)—C(13)–C(12)	119·7		

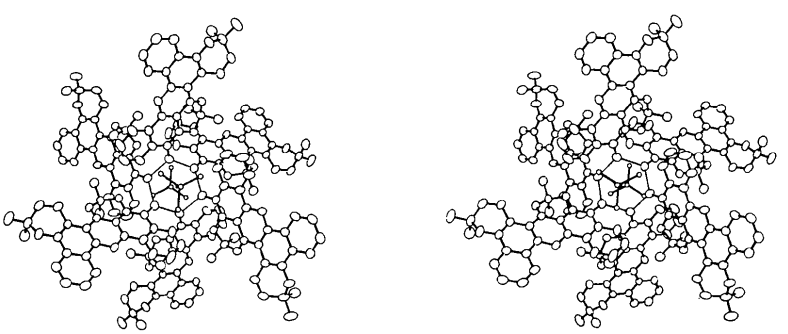

Fig. 3. Stereoscopic view of the molecular packing viewed down **c** with **a** horizontal. The thermal ellipsoids are drawn at the 50% level except for the acetone molecules; for these atoms an arbitrary temperature parameter of 1·0 Å^2 was used.

from their nominal value of 120° to 127·9 and 124·2° respectively. The C(11)–C(16) distance is thereby increased to 3·07 as compared with 2·56 Å for C(12)–C(15). The H(5)–H(6) interaction leads to considerable stress in the molecule which results in a twist about the C(14)–C(15) and C(15)–C(16) bonds, so that C(16) is forced below the plane formed by C(1), C(13), C(14) and C(26) by 0·55 Å. C(11) is displaced 0·48 Å above this plane as viewed in Fig. 2. Both of these displacements increase the H(5)–H(6) distance, and thus reduce the steric hindrance between these two hydrogen atoms. The four carbon–methyl bond distances are in excellent agreement with the C–C single bond value of 1·52 Å (Dewar & Schmeising, 1960). The C–H bond distances are generally normal and similar to those observed in other organic crystals.

A network of intermolecular hydrogen bonds between the phenolic hydroxyl atoms, O(4), produces a cluster of six molecules. Each cluster is centered on an inversion triad axis. The O(4)···O(4′) distance is 2·82 Å. The intermolecular hydrogen bonds and the molecular packing within a cluster are shown in Fig. 3. This view is parallel to the *c* axis, with the *a* axis horizontal. The only attractive force between the clusters of six molecules is that due to van der Waals interactions.

The acetone molecules are disordered, the four heavy atoms partially occupying six positions. The acetone molecules are centered on the inversion triad axis (Fig. 3) and there are two of them between each cluster of six guayacanin molecules. There are no hydrogen atoms available to form intermolecular hydrogen bonds between guayacanin and acetone. This undoubtedly accounts for the fact that the acetone molecules are disordered.

Thermal parameters of all atoms are within the normal range except for the slightly higher values for the methyl carbon atoms C(27) to C(30).

The authors wish to thank Dr A. Zalkin for the use of his computer programs and Professor D. H. Templeton for his helpful discussion.

References

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Dewar, M. J. S. & Schmeising, H. N. (1960). *Tetrahedron*, **11**, 96–120.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

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

Main, P. (1972). Univ. of York, England.

Manners, G. D., Jurd, L., Wong, R. Y. & Palmer, K. J. (1975). *Tetrahedron*, **31**, 3019–3024.

Southwell, C. R. & Bultman, J. D. (1971). *Biotropica*, **3**, 81–107.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Stout, G. H., Lin, S. T. & Singh, I. (1969). *Tetrahedron*, **25**, 1975–1983.