5α-Hydroxy-4αH,1,6,11βH-guai-2,10(15)-dien-6,12-olide

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Abstract. $C_{15}H_{20}O_3$, orthorhombic, $P2_12_12_1$; $a = 10 \cdot 544$ (4), $b = 22 \cdot 854$ (9), $c = 5 \cdot 827$ (3) Å; $Z = 4$, $D_x = 1 \cdot 175$ g cm^{-3}, μ(Cu $K\bar{\alpha}$) $= 7 \cdot 6$ cm^{-1}; final residual $R = 0 \cdot 048$. The title compound adopts a 5α-hydroxy-1βH-conformation at the ring junction.

Introduction. The title hydroazulene intermediate (I) was prepared from α-santonin by a novel method (Fujimoto, Shimizu & Tatsuno, 1976a, b). For the synthesis of guaiane-type sesquiterpenoids starting from (I), it was necessary to establish the stereochemistry of the compound (I). Colourless prismatic crystals elongated along **c** were grown from an ether solution by evaporation. Oscillation and Weissenberg photographs showed that the crystal is orthorhombic with the systematic absences: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; and $00l$, $l = 2n + 1$, consistent with the space group $P2_12_12_1$. A specimen, $0 \cdot 2 \times 0 \cdot 2 \times 0 \cdot 7$ mm, was selected for cell-parameter and intensity measurements. The cell parameters were determined from 18 high-angle reflections measured on a Rigaku four-circle diffractometer (Cu $K\alpha$, $\lambda = 1 \cdot 54178$ Å). The intensity data were collected on the diffractometer with graphite-monochromatized Cu $K\alpha$ radiation; the ω–2θ scan mode with a scan speed in ω of $2°$ min^{-1} was used. Background counts were taken for 10 s on each side of a reflection. Five standard reflections were monitored after every 52 reflections; the fluctuations in F_o were less than $\pm 1 \cdot 5\%$ throughout the data collection. Of the 1498 independent reflections that were measured within the range $2\theta < 135°$, 1301 reflections with $I > \sigma(I)$ were used for the analysis. Intensities were corrected for Lorentz and polarization effects, but not for absorption ($\mu r = 0 \cdot 08$).

(I)
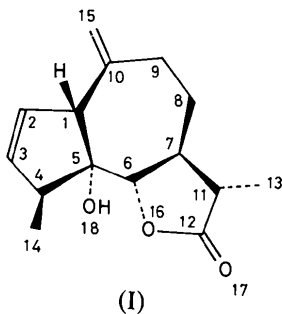
The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). With 143 normalized structure factors ($E_{min} = 1 \cdot 6$) and 900 Σ_2 relationships, 16 sets of phases were generated. The E Fourier map computed from the set with the highest figure of merit revealed all 18 non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically by a block-diagonal least-squares method ($R = 0 \cdot 098$); all 20 H atoms were located on a difference map and refined isotropically. The weighting scheme was: $w(F_o) = 1/[\sigma^2(F_o) + kF_o^2]$, where the factor $k = 0 \cdot 0022$ was so chosen as to make the average values of $w(F_o - F_c)^2$ over appropriately divided F_o ranges nearly constant. The five low-angle reflections with the largest amplitudes, *i.e.* 021, 120, 101, 102 and 110, were found to be significantly affected by extinction; therefore they were given zero weights in the final refinement. The final residual was $R = 0 \cdot 048$ for the 1301 observed reflections ($R = 0 \cdot 044$ without the five reflections with zero weights). The atomic scattering factors for C and O were from *International Tables for X-ray Crystallography* (1974), while those for H were from Stewart, Davidson & Simpson (1965). The calculations were performed on the FACOM 230-75 computer of this

Table 1. *Positional parameters* ($\times 10^5$) *and equivalent isotropic thermal parameters of non-hydrogen atoms*

	x	y	z	B_{eq} (Å^2)
C(1)	46273 (27)	17200 (13)	28546 (56)	4·2
C(2)	33167 (28)	16821 (15)	18058 (78)	5·6
C(3)	30104 (29)	11381 (16)	13186 (79)	5·8
C(4)	40196 (28)	7110 (13)	20165 (68)	4·8
C(5)	52022 (26)	11220 (10)	21414 (51)	3·6
C(6)	62349 (26)	9501 (10)	38032 (52)	3·4
C(7)	73776 (26)	13548 (11)	38610 (53)	3·6
C(8)	71615 (29)	19153 (12)	52202 (71)	4·8
C(9)	65007 (34)	24008 (12)	38591 (76)	5·5
C(10)	54365 (29)	22457 (12)	22604 (59)	4·4
C(11)	83846 (26)	9377 (12)	47706 (64)	4·3
C(12)	80068 (28)	3700 (12)	36961 (50)	3·9
C(13)	97688 (32)	10982 (16)	43286 (108)	7·6
C(14)	36883 (33)	4003 (18)	42469 (87)	6·9
C(15)	52007 (37)	25685 (16)	4454 (80)	6·3
O(16)	67684 (18)	3832 (7)	31374 (35)	3·7
O(17)	86485 (22)	−471 (8)	32147 (42)	5·0
O(18)	57102 (17)	11801 (8)	−1031 (37)	4·1

Table 2. Positional parameters (× 10⁴) and isotropic thermal parameters of hydrogen atoms

The C—H and O—H (marked with an asterisk) distances (Å) are also given in the last column; the estimated standard deviations are 0·03–0·05 Å.

|	x	y	z	B (Å²)	r(C—H) or r(O—H)
H(1)	4504 (24)	1732 (12)	4438 (53)	4·6 (7)	0·93
H(2)	2739 (38)	2021 (18)	1480 (85)	9·3 (11)	1·00
H(3)	2262 (29)	1028 (13)	647 (59)	5·7 (7)	0·92
H(4)	4159 (23)	410 (12)	949 (54)	3·8 (6)	0·94
H(6)	5906 (23)	937 (12)	5414 (53)	4·1 (7)	1·00
H(7)	7579 (24)	1428 (10)	2332 (46)	3·1 (5)	0·93
H(8A)	6698 (23)	1812 (11)	6655 (58)	4·3 (7)	1·00
H(8B)	7956 (26)	2043 (13)	5997 (58)	5·2 (7)	1·00
H(9A)	6352 (35)	2723 (16)	4744 (80)	8·1 (10)	0·91
H(9B)	7206 (38)	2583 (15)	2835 (74)	8·7 (10)	1·04
H(11)	8253 (23)	879 (12)	6635 (56)	4·2 (6)	1·10
H(13A)	9993 (31)	1480 (14)	5371 (69)	8·1 (9)	1·09
H(13B)	9899 (41)	1100 (16)	2674 (81)	9·5 (11)	0·97
H(13C)	10422 (37)	782 (19)	5187 (94)	9·8 (11)	1·12
H(14A)	4250 (30)	125 (16)	4694 (83)	8·1 (10)	0·90
H(14B)	3283 (29)	687 (16)	5574 (82)	9·2 (10)	1·10
H(14C)	2848 (32)	189 (15)	4107 (80)	8·0 (10)	1·01
H(15A)	4499 (34)	2508 (16)	−543 (70)	8·2 (10)	0·95
H(15B)	5661 (30)	2908 (17)	253 (71)	7·6 (10)	0·92
H(18)	6028 (25)	831 (13)	−531 (60)	4·8 (7)	0·90*
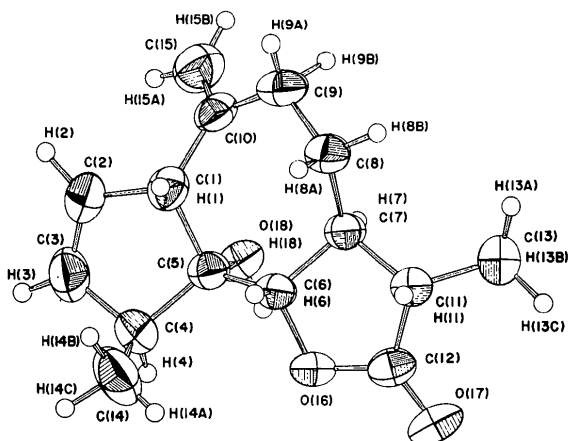
Fig. 1. Conformation of the molecule. The thermal ellipsoids are at the 50% probability level.

Institute, with the *UNICS* II program system (Sakurai, Iwasaki, Watanabe, Kobayashi, Bando & Nakamichi, 1974). The atomic parameters of the non-hydrogen atoms are given in Table 1* and those of the hydrogen atoms in Table 2.

Discussion. The stereochemistry of (I) can be seen from Fig. 1, an *ORTEP* drawing (Johnson, 1965) of the

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33177 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
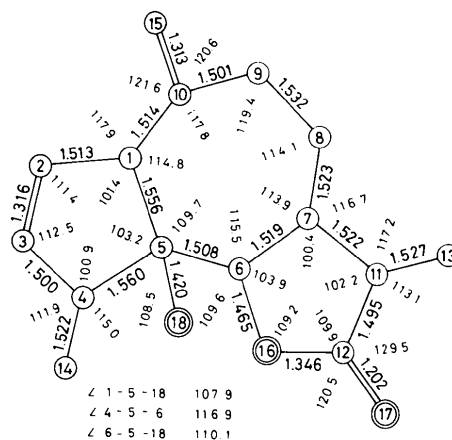

Fig. 2. Bond distances (Å) and angles (°) of the non-hydrogen atoms. The estimated standard deviations are 0·03–0·05 Å and 0·2–0·3° respectively.

molecule viewed down **c**. The 1β,5α-conformation of (I) differs from the 1,5α-conformation of 2-bromo-dihydroisophoto-α-santonic lactone acetate (II), of which the absolute configuration as well as the molecular conformation has been established (Asher & Sim, 1965). The bond distances and angles of the non-hydrogen atoms are shown in Fig. 2; the C—H and O—H distances are included in Table 2. Most of them are normal compared with those in related structures (Asher & Sim, 1965). The average bond distances are: $C(sp^3)$—$C(sp^3)$ = 1·530, $C(sp^3)$—$C(sp^2)$ = 1·505, C=C = 1·315, $C(sp^3)$—O = 1·443, $C(sp^2)$—O = 1·346 and C=O = 1·202 Å; only the $C(sp^3)$—$C(sp^3)$ distances associated with C(5), *i.e.* 1·560, 1·556 and 1·508 Å, deviate significantly from the average distance.

(II)
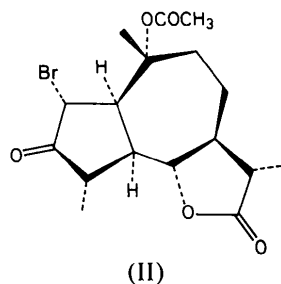
The cycloheptane ring adopts a flattened-chair conformation with an average bond angle of 115°. The five atoms, C(5)—C(6) and C(8)—C(9)—C(10), form an equatorial plane (±0·04 Å), whereas the two apical atoms, C(1) and C(7), deviate from the mean plane by +0·79 and −0·76 Å respectively. The chair conformation is similar to that in (II), but in the latter C(10) instead of C(1) is apical. As expected from the C(2)=C(3) double bond, the six atoms of the cyclopentene ring, C(1)—C(2).H(2)=C(3).H(3)—C(4), are coplanar (±0·02 Å) and only C(5) deviates, by 0·52 Å,
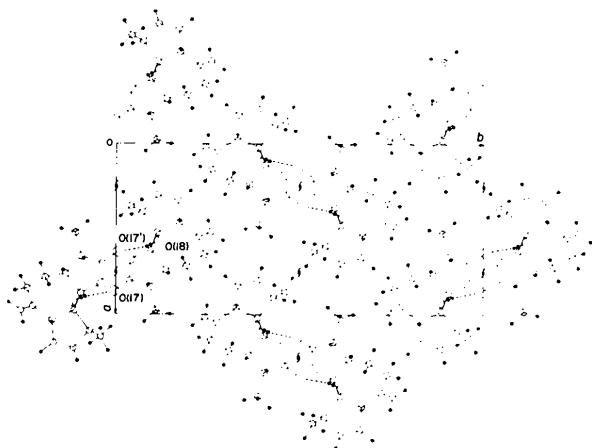
Fig. 3. Molecular packing viewed down c. The broken lines indicate the O–H···O hydrogen bonds.

from the plane. The structure of the lactone ring is essentially the same as in (II); the five atoms, C(6)–O(16)–C(12).O(17)–C(11), are coplanar (± 0.02 Å) and only C(7) deviates, by 0.52 Å, from the plane. In both five-membered rings, the bond angles at the C(sp^3) atoms are systematically smaller than the tetrahedral value, the average being $102°$.

The molecular packing viewed down c is shown in Fig. 3. The hydroxyl group O(18)–H(18) of a molecule is hydrogen-bonded to the carbonyl O(17′) of an adjacent molecule in a helical sequence; thus, an infinite molecular column is formed along c through O–H···O hydrogen bonds. The hydrogen-bond distances are O(18)···O(17′) = 2.850 and H(18)···O(17′) = 1.97 Å. Molecular columns are stacked with normal van der Waals contacts.

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Perchloro-1,2,3-triphenylnaphthalene

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Abstract. $C_{28}Cl_{20}$, monoclinic, $P2_1/a$, $a = 23.426$ (4), $b = 13.284$ (2), $c = 11.592$ (2) Å, $\beta = 98.29$ (7)°, $Z = 4$, $D_x = 1.945$ g cm^{-3}. The structure has been determined by direct methods and refined to $R = 0.059$ for 5607 independent reflexions. The naphthalene system is very distorted owing to repulsions among its bulky substituents.

Introduction. Transparent, colourless crystals suitable for X-ray studies were grown by slow evaporation of a toluene solution at room temperature. Preliminary unit-cell parameters and the space group were obtained from Weissenberg photographs.

The dimensions of the crystal selected were $0.3 \times 0.3 \times 0.3$ mm. Precise lattice parameters were