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The Absolute Configuration of an Iodo Derivative of Xerantholide

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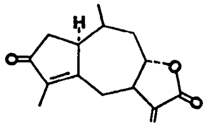
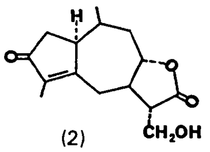
Abstract. (1*R*,7*S*,8*S*,9*S*)-13-Iodoguaia-4-en-3-one-7,8α-olide, $C_{15}H_{19}IO_3$, $M_r = 374{\cdot}22$, monoclinic, $P2_1$, $a = 7{\cdot}403\,(1)$, $b = 8{\cdot}820\,(1)$, $c = 12{\cdot}054\,(2)$ Å, $\beta = 90{\cdot}41\,(2)^\circ$, $V = 787{\cdot}0\,(3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}579$ g cm^{-3}, $\lambda(\text{Cu }K\alpha) = 1{\cdot}54178$ Å, $\mu = 162{\cdot}12$ cm^{-1}, $F(000) = 372$, $T = 295$ K, $R = 0{\cdot}056$ for 1144 independent reflections. The $-CH_2I$ moiety lies in a crystal cavity which results in a large anisotropic thermal motion. The coordinates from the iodine structure were used in a molecular-mechanics calculation to rationalize the differences in physical properties of the two hydroxymethylene derivatives of xerantholide.

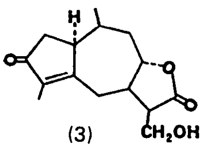
Introduction. During investigations of the chemical transformation of xerantholide (1) the two C(11) hydroxymethylene derivatives (2) and (3) were prepared (Miski & Mabry, 1987). These two members of a diastereomeric pair exhibited quite different chemical and physical properties. The IR spectrum (KBr) of (2) indicates that the hydroxyl group is hydrogen-bonded intramolecularly to the lactone carbonyl while no strong hydrogen bonding is indicated in the spectrum of (3). Compound (2) also loses water more readily than (3). Since molecular models did not provide a definitive rationalization, a structural analysis was suggested. Good single crystals of the hydroxy derivatives could not be prepared; however, a usable crystal of the iodide (4) was obtained.



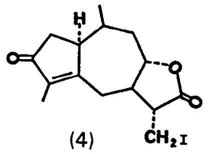
(1)



(2)



(3)



(4)

Experimental. A colorless prismatic crystal of dimensions 0·25 × 0·16 × 0·09 mm was selected; Nicolet *R*3*m*/μ update of a $P2_1$ diffractometer; data collected in the Wyckoff mode (2θ fixed, ω varied)

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($4{\cdot}0 \leq 2\theta \leq 115°$), graphite-monochromated Cu $K\alpha$ radiation, lattice parameters from least-squares refinement of 15 reflections ($40{\cdot}93 \leq 2\theta \leq 52{\cdot}97°$) with angles measured by a centering routine; systematic absences $0k0$, $k = 2n + 1$, Laue symmetry 2, consistent with space group $P2_1$, two monitored reflections showed no variation in intensity greater than $3\sigma(I)$; 1144 independent reflections ($0 \leq h \leq 9$, $0 \leq k \leq 10$, $-14 \leq l \leq 14$) and their Friedel pairs collected (2288 total reflections); Lorentz and polarization corrections applied, empirical absorption correction applied (maximum and minimum transmission factors of 0·154 and 0·020); neither direct methods nor refinement of iodine coordinates from a Patterson map produced recognizable fragments; the I coordinates were translated through the cell and the best set was used in a refinement of the 200 largest E values; a six-atom fragment yielded the complete molecule upon cycling; block-cascade least-squares refinement with riding model for H led to a final $R = 0{\cdot}051$, $wR = 0{\cdot}074$, $S = 1{\cdot}59$, $(\Delta/\sigma)_{\max} = 0{\cdot}03$, largest peaks in the final difference map of $+1{\cdot}36$ and $-0{\cdot}78$ e Å^{-3} within 1 Å of the I atom; $\sum w(|F_o| - |F_c|)^2$ minimized, 172 parameters, all 1144 reflections considered observed, $w = [\sigma^2(F) + 0{\cdot}0025F^2]^{-1}$; refinement with all observed Friedel pairs (2288 reflections) led to an R factor of 0·053 and a variable η (in inf_i'') for absolute configuration refined to 1·17(7) (Rogers, 1981); all computer programs (*SHELXTL*, control and data transfer) supplied by Nicolet for Desktop 30 Microeclipse and Nova 4/C configuration; atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Table 1 lists atomic positional parameters and U_{eq} values, while Table 2 lists selected interatomic distances and valence angles.*

Discussion. Fig. 1 shows the absolute configuration of (4) which confirms the assigned configuration of xerantholide (1) (Rychlewska, 1981; Watson, Kashyap, Miski & Mabry, 1985). In the solid state the CH_2I moiety lies in a cavity and thermal motion of the lactone ring leads to a larger thermal motion of the attached I atom. Inaccuracies due to the empirical absorption correction and the large thermal motion of the heavy atom lead to relatively large standard deviations. Librational corrections of bond lengths show increases of 0·004 to 0·011 Å in C—C and C—O bonds. The C—I distance is increased by 0·017 Å to 2·120 (14) Å. While the corrections are large, they are less than 3σ.

Table 1. *Atomic positional parameters* ($\times 10^4$) *and* U_{eq} (Å$^2 \times 10^3$) *values*

	x	y	z	U_{eq}
I(1)	277 (2)	5122 (7)	2270 (1)	137·4 (7)
C(1)	3850 (10)	−247 (14)	3673 (8)	59 (4)
C(2)	4437 (12)	−1135 (21)	4725 (9)	79 (4)
C(3)	2828 (12)	−1917 (15)	5118 (8)	57 (3)
O(3)	2766 (9)	−2789 (13)	5934 (7)	75 (3)
C(4)	1323 (10)	−1530 (12)	4434 (8)	45 (3)
C(5)	1834 (9)	583 (12)	3608 (7)	40 (2)
C(6)	616 (10)	67 (14)	2762 (7)	45 (3)
C(7)	1485 (10)	1248 (12)	2009 (7)	41 (2)
C(8)	2913 (12)	608 (14)	1238 (8)	57 (3)
O(8)	2930 (10)	1692 (13)	317 (7)	83 (3)
C(9)	4762 (12)	525 (14)	1703 (10)	67 (4)
C(10)	4950 (9)	−666 (19)	2650 (9)	67 (4)
C(11)	157 (12)	2006 (14)	1177 (8)	52 (3)
C(12)	1410 (16)	2488 (17)	281 (9)	71 (4)
O(12)	1159 (13)	3455 (14)	−416 (8)	91 (4)
C(13)	−1072 (16)	3226 (16)	1605 (9)	68 (4)
C(14)	4637 (19)	−2260 (21)	2262 (15)	92 (6)
C(15)	−558 (11)	−2039 (14)	4666 (9)	57 (3)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Selected interatomic distances* (Å), *valence angles* (°) *and torsion angles* (°)

C(1)—C(2)	1·55 (2)	C(7)—C(11)	1·55 (1)
C(1)—C(5)	1·52 (1)	C(8)—C(9)	1·48 (1)
C(1)—C(10)	1·53 (1)	C(8)—O(8)	1·47 (1)
C(2)—C(3)	1·46 (2)	C(9)—C(10)	1·56 (2)
C(3)—C(4)	1·42 (1)	C(10)—C(14)	1·50 (3)
C(3)—O(3)	1·25 (2)	O(8)—C(12)	1·33 (2)
C(4)—C(5)	1·36 (1)	C(11)—C(12)	1·49 (2)
C(4)—C(15)	1·49 (1)	C(11)—C(13)	1·50 (2)
C(5)—C(6)	1·47 (1)	C(12)—O(12)	1·21 (2)
C(6)—C(7)	1·53 (1)	C(13)—I(1)	2·10 (1)
C(7)—C(8)	1·52 (1)		

C(1)C(2)C(3)	106·3 (8)	C(7)C(8)O(8)	103·3 (8)
C(2)C(3)C(4)	110(1)	C(8)O(8)C(12)	111·0 (8)
C(3)C(4)C(5)	110·6 (8)	O(8)C(12)C(11)	111(1)
C(4)C(5)C(1)	111·1 (7)	C(12)C(11)C(7)	101·3 (8)
C(5)C(1)C(2)	102·3 (8)	C(11)C(7)C(8)	101·8 (7)
C(11)C(13)I(1)	114·4 (8)		

C(1)C(5)C(6)C(7)	−6 (1)	C(7)C(8)O(8)C(12)	−20 (1)
C(5)C(6)C(7)C(8)	68 (1)	C(8)O(8)C(12)C(11)	−1 (1)
C(6)C(7)C(8)C(9)	−87 (1)	O(8)C(12)C(11)C(7)	21 (1)
C(7)C(8)C(9)C(10)	68 (1)	C(12)C(11)C(7)C(8)	−32 (1)
C(8)C(9)C(10)C(1)	−66 (1)	C(11)C(7)C(8)O(8)	32 (1)
C(9)C(10)C(1)C(5)	79 (1)	C(7)C(11)C(13)I(1)	61 (1)
C(10)C(1)C(5)C(6)	−59 (2)	C(12)C(11)C(13)I(1)	−59 (1)

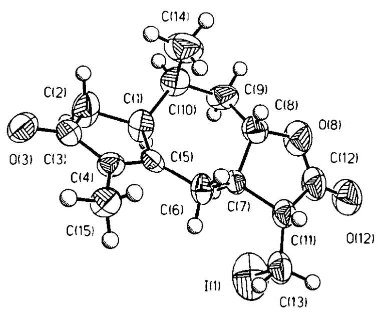

Fig. 1. Drawing of compound (4). The thermal ellipsoids are drawn at the 30% probability level. H atoms are shown as spheres of arbitrary size.

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* Lists of structure factors, H-atom parameters, and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44129 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

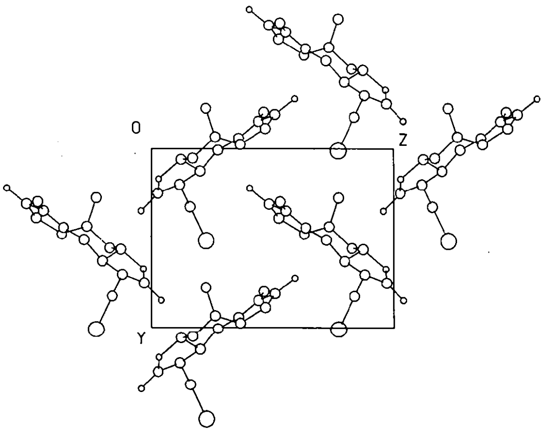

Fig. 2. Packing diagram for compound (4).

The cyclopentene ring is almost planar while the five-membered lactone ring exhibits an envelope conformation. The seven-membered ring is in a chair conformation (Toromanoff, 1980).

The coordinates from the X-ray study were used as input for a molecular-mechanics (Allinger & Yuh, 1980) comparison of the C(11) epimers (2) and (3). In (2) the conformation with the hydroxyl hydrogen-bonded to the carbonyl is about 13 kJ mol^{-1} more stable than the conformer with the hydroxyl rotated in a nonbonding position. In compound (3) the hydrogen-bonded conformer is only about 0·2 kJ mol^{-1} more stable. This is due to a steric interaction between the C(13) and C(6) hydrogen atoms in the hydrogen-bonded conformer of (3), and there is little energy gained by intramolecular hydrogen bonding. It is more difficult to rationalize the easier loss of water by (2) to form (1) since the mechanism of dehydration is still not understood completely.

A packing diagram for (4) is given in Fig. 2.

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Structure of Benzamidinium Pyruvate

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Abstract. $C_{10}H_{12}N_2O_3$, $M_r = 208·22$, monoclinic, $P2_1/n$, $a = 5·756$ (3), $b = 18·994$ (13), $c = 9·766$ (8) Å, $\beta = 98·53$ (5)°, $V = 1055·9$ (1) Å^3, $Z = 4$, $D_m = 1·311$ (2), $D_x = 1·309$ (1) Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·106$ mm^{-1}, $F(000) = 440$, $T = 296$ K, $R = 0·044$ for 1262 unique observed reflections. The structure contains inter- and intramolecular hydrogen bridges between the amidine nitrogens and the carboxy-

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