

C26—C1—N2	119.1 (2)	O22A—C23A—C24A	108.7 (4)
C1—N2—C3	118.6 (2)	O25—C24A—C23A	103.0 (4)
C1—N2—P31	121.9 (2)	O22B—C21B—C20	101.5 (10)
C3—N2—P31	117.3 (2)	C23B—O22B—C21B	117.0 (9)
N2—C3—C4	111.9 (2)	O22B—C23B—C24B	116.0 (9)
C5—C4—C3	111.9 (2)	O25—C24B—C23B	113.1 (8)
N6—C5—C4	110.8 (3)	C26—O25—C24A	112.0 (3)
C7—N6—C5	117.2 (2)	C26—O25—C24B	131.2 (5)
C7—N6—P31	123.5 (2)	O25—C26—C27	124.8 (3)
C5—N6—P31	119.2 (2)	O25—C26—C1	114.8 (2)
C8—C7—C12	119.7 (2)	C27—C26—C1	120.4 (3)
C8—C7—N6	120.6 (2)	C28—C27—C26	119.1 (3)
C12—C7—N6	119.6 (2)	C29—C28—C27	121.5 (3)
C7—C8—C9	120.6 (3)	C28—C29—C30	119.4 (3)
C10—C9—C8	118.9 (3)	C29—C30—C1	121.2 (3)
C9—C10—C11	121.9 (3)	N6—P31—N2	97.26 (11)
C10—C11—C12	119.4 (3)	N6—P31—C33	111.82 (11)
O13—C12—C7	115.4 (2)	N2—P31—C33	102.68 (11)
O13—C12—C11	125.1 (3)	N6—P31—S32	112.74 (8)
C7—C12—C11	119.4 (3)	N2—P31—S32	120.37 (8)
C12—O13—C14	118.3 (2)	C33—P31—S32	110.99 (10)
O13—C14—C15	107.8 (3)	C38—C33—C34	118.0 (2)
O16—C15—C14	110.4 (3)	C38—C33—P31	121.1 (2)
C15—O16—C17	112.3 (3)	C34—C33—P31	120.9 (2)
O16—C17—C18	110.9 (3)	C35—C34—C33	120.9 (3)
O19—C18—C17	115.7 (3)	C36—C35—C34	120.2 (3)
C20—O19—C18	115.1 (3)	C35—C36—C37	119.9 (3)
O19—C20—C21A	114.5 (3)	C36—C37—C38	121.0 (3)
O19—C20—C21B	89.1 (6)	C33—C38—C37	120.1 (3)

Data collection, cell refinement and data reduction: local programs. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978); *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1098). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(1'R,2S,3R)-2-Hydroxy-2-(1-hydroxyethyl)-3-methyl-γ-butyrolactone

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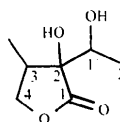
(Received 13 May 1994; accepted 14 July 1994)

Abstract

The determination of the structure of the title compound, C₇H₁₂O₄, allowed the unambiguous elucidation of the absolute configuration of a pheromone produced by the tropical butterfly *Prittwitzia hymaenea*. This unique pheromone is the 1'-epimer of the title compound. The lactone ring adopts a rather flat, almost ideal envelope conformation. The structure is stabilized by hydrogen bonds.

Comment

2-Hydroxy-2-(1-hydroxyethyl)-3-methyl-γ-butyrolactone, (I), has been identified as an Ithomiine butterfly pheromone, but no absolute or relative configuration has been reported (Edgar, Culvenor & Pliske, 1976). It is likely that this lactone is produced from 2,3-dihydroxy-2-(1-methylethyl)butanoic acids (viridifloric and trachelantic acids), obtained by the cleavage of pyrrolizidine alkaloids taken up from the plants that the butterflies feed upon (Edgar, Culvenor & Pliske, 1976). All enantiomers of the acids occur in these plant alkaloids.



(I)

In order to determine the relative and absolute configuration of the naturally occurring lactone, one enantiomer of each of the four diastereomers was synthesized starting from (*S*)-3-methyl- γ -butyrolactone. The sequence described by Schulz (1992) furnished the different diollactones, which were separated by HPLC. The assignment of the products was achieved through the structural analysis of one enantiomer, which proved to be (1'*R*,2*S*,3*R*)-2-hydroxy-2-(1-hydroxyethyl)-3-methyl- γ -butyrolactone. Based on the structure of this enantiomer, the 1'-epimer [Ithomiolide A, exhibiting a (1'*S*,2*S*,3*R*) configuration] could be identified as the natural pheromone (Schulz, 1992). This unusual type of lactone is not known from any other natural source.

The hydroxyl groups O2—H20 and O5—H50 in the title compound form intermolecular hydrogen bonds, details of which are given in Table 3. The hydrogen bonds involving the O2—H20 group form an infinite one-dimensional chain along [010]. Other distances and angles are, in general, as expected. The conformation of the five-membered lactone ring is defined by the ring-puckering parameters $Q = 0.273(3) \text{ \AA}$ and $\Phi = 104.9(6)^\circ$ (Cremer & Pople, 1975); the ring adopts a rather flat, almost ideal E_{C3} conformation.

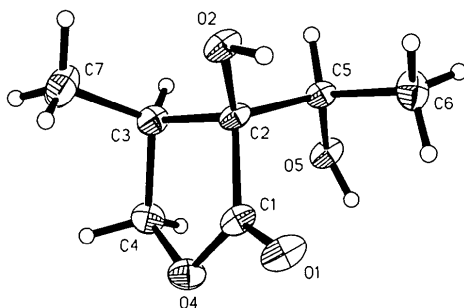


Fig. 1. *SHELXTL-Plus* drawing (Sheldrick, 1992) of the molecular conformation of the title compound showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

Experimental

Suitable single crystals of the title compound, which melted at 327–328 K, were obtained from dichloromethane/hexane (4:1).

Crystal data

$C_7H_{12}O_4$
 $M_r = 160.17$
 Monoclinic
 $C2$
 $a = 15.783(2) \text{ \AA}$
 $b = 5.458(1) \text{ \AA}$
 $c = 9.586(1) \text{ \AA}$
 $\beta = 104.97(1)^\circ$
 $V = 797.7(2) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.334 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation
 $\lambda = 1.54178 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 42.6\text{--}50.7^\circ$
 $\mu = 0.929 \text{ mm}^{-1}$
 $T = 173(1) \text{ K}$
 Transparent block
 $0.5 \times 0.3 \times 0.3 \text{ mm}$
 Colorless

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
 $2\theta/\omega$ scans
 Absorption correction: none
 1910 measured reflections
 1632 independent reflections
 1610 observed reflections
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0613$
 $\theta_{\text{max}} = 76.5^\circ$
 $h = 0 \rightarrow 19$
 $k = 0 \rightarrow 6$
 $l = -12 \rightarrow 12$
 3 standard reflections
 frequency: 120 min
 intensity variation: 10%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0831$
 $wR(F^2) = 0.2126$
 $S = 1.045$
 1632 reflections
 117 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.1869P)^2 + 0.6131P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = -0.035$
 $\Delta\rho_{\text{max}} = 0.665 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.488 \text{ e \AA}^{-3}$

Extinction correction:
 $F_c^* = kF_c[1 + (0.001\chi \times F_c^2\lambda^3/\sin 2\theta)]^{-1/4}$
 Extinction coefficient:
 $\chi = 0.007(2)$
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
 Absolute configuration: Flack (1983)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O1	0.7014 (2)	0.4372 (4)	0.5369 (2)	0.0239 (6)
O2	0.7138 (1)	0.3989 (4)	0.8428 (2)	0.0200 (5)
O4	0.6146 (1)	0.7567 (4)	0.5472 (2)	0.0238 (6)
O5	0.7915 (1)	0.9976 (4)	0.7503 (2)	0.0208 (5)
C1	0.6759 (2)	0.5917 (5)	0.6063 (3)	0.0182 (6)
C2	0.7070 (2)	0.6264 (5)	0.7709 (3)	0.0159 (6)
C3	0.6326 (2)	0.7826 (6)	0.8020 (3)	0.0203 (7)
C4	0.5953 (2)	0.9128 (6)	0.6578 (3)	0.0227 (7)
C5	0.7967 (2)	0.7583 (5)	0.8147 (3)	0.0170 (6)
C6	0.8721 (2)	0.6126 (6)	0.7842 (4)	0.0259 (7)
C7	0.5626 (2)	0.6300 (8)	0.8450 (4)	0.0355 (9)

Table 2. Selected geometric parameters (\AA , $^\circ$)

O1—C1	1.205 (4)	C2—C3	1.541 (4)
O2—C2	1.411 (3)	C2—C5	1.547 (3)
O4—C1	1.337 (3)	C3—C7	1.523 (4)
O4—C4	1.453 (4)	C3—C4	1.530 (4)
O5—C5	1.438 (4)	C5—C6	1.521 (4)
C1—C2	1.538 (4)		
C1—O4—C4	110.6 (2)	C3—C2—C5	112.3 (2)
O1—C1—O4	123.1 (2)	C7—C3—C4	111.2 (2)
O1—C1—C2	126.1 (3)	C7—C3—C2	113.1 (3)
O4—C1—C2	110.9 (2)	C4—C3—C2	102.5 (2)
O2—C2—C1	110.9 (2)	O4—C4—C3	106.4 (2)
O2—C2—C3	110.9 (2)	O5—C5—C6	110.7 (2)
C1—C2—C3	102.1 (2)	O5—C5—C2	111.0 (2)
O2—C2—C5	109.2 (2)	C6—C5—C2	114.3 (2)
C1—C2—C5	111.3 (2)		

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H20...O5 ⁱ	0.84	1.95 (2)	2.765 (3)	162 (2)
O5—H50...O1 ⁱⁱ	0.84	1.97 (1)	2.805 (3)	173 (3)

Symmetry codes: (i) $x, y - 1, z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$.

During the collection of the intensity data a loss of intensity of about 30% and a shift of the peak position was detected in two of the three standard reflections (after 612 reflections). The centering of the crystal in the X-ray beam was checked optically. After recentering all 25 control reflections, the data collection was continued with a loss of 10% in the intensity of all three standard reflections. A linear decay correction (Kopf, 1987) was applied to the data to compensate for this. The decay of the crystal and other problems with the crystal quality (only a miniscule amount of the compound was available) may explain the rather high values of *R*. From the systematic absences (*hkl*: $h + k = 2n$) the possible space groups *C*2 (No. 5), *C*_m (No. 8) and *C*2/*m* (No. 12) were deduced. With *Z* = 4 and $|E^2 - 1| = 0.727$ (the theoretical value for a non-centrosymmetric space group being 0.736), and given the knowledge that the title compound was chiral, the only possible space group was *C*2. The positions of all H atoms were refined with distance restraints for the C—H bonds (Sheldrick, 1993). Friedel opposites were collected for each reflection. These Friedel pairs were regarded as symmetry independent and were not merged. The absolute structure was determined by refinement of the Flack enantiomorph parameter, *x*, which refined to -0.4 (4) (Flack, 1983). Polar-axis restraints were applied using the method of Flack & Schwarzenbach (1988) in order to fix the origin in *y*.

Data collection and cell refinement: *CAD-4 Software* (Enraf-Nonius, 1989). Data reduction: *CADSHL* (Kopf, 1987). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1992). Software used to prepare material for publication: *CIF2TEX* (Kopf, 1992a) and *FCF2FOC* (Kopf, 1992b).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1199). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Chiral Bicyclic 1-Acetoxy Phosphonamide

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Abstract

The crystal structure of a chiral non-racemic 1-acetoxy phosphonamide, 2-(1-acetoxy-3-methylbutyl)-1,3-(2,2-dimethylpropyl)-2,3,3a,4,5,6,7,7a-octahydro-1*H*-1,3,2-benzodiazaphosphole 2-oxide, m.p. = 385.5–386 K, C₂₃H₄₅N₂O₃P, has been determined by X-ray diffraction. The title compound consists of a five-membered ring with a tetrahedrally coordinated P atom. In addition to the two N atoms of the five-membered ring, the P atom is bonded to an O atom and the C₁ atom of the acetoxyalkyl chain. The five-membered ring is *trans* fused to a cyclohexane ring in a chair conformation.

Comment

Recently, we reported the preparation and reactions of chiral phosphorous acid diamides (Koeller & Spilling, 1991; Blazis, De la Cruz, Koeller & Spilling, 1993). Treatment of phosphorous acid diamide (1) with LDA in THF solution followed by addition of isovaleraldehyde to the resulting anion gave the 1-hydroxy phosphonamides (2) in a 3.4:1 ratio of diastereoisomers (Fig. 1). Treatment of (2) with acetic anhydride, triethylamine and DMAP in CH₂Cl₂ gave the acetates (3a) and (3b), which could be separated by chromatography on silica gel. The more polar acetate (3b) crystallized from diethyl ether and hexane to give crystals suitable for X-ray diffraction analysis. Evidence for the relative configuration of C(1) was not available by standard spectroscopic methods, but single-crystal X-ray diffraction analysis allowed assignment of the relative configuration of the new chiral center as *S*, resulting from the *R,R* diamide. The phosphorous acid diamide showed the same facial selectivity as previously observed in the reaction with cinnamaldehyde (Koeller, Rath & Spilling, 1993). The molecular structure is shown in Fig. 2.