

function minimized in the full-matrix least-squares calculations was  $\sum w(|F_o| - |F_c|)^2$  where  $w = 1.0/[\sigma^2(F) + 0.006F^2]$ . 307 variables were refined. The ratio of observations to parameters is 10:1. At convergence  $R = 0.039$ ,  $wR = 0.048$ ,  $S = 1.29$ ,  $\Delta/\sigma_{av} = 0.003$  while  $\Delta/\sigma_{max} = 0.059$  for a positional coordinate of an atom in the disordered THF. Final difference electron density excursions are  $-0.22$  and  $+0.28 \text{ \AA}^3$ . The absolute configuration of the methylphosphonothioate enantiomer was determined from the known configuration of the thymidiny moiety. Atomic scattering factors for neutral atoms are from *International Tables for X-ray Crystallography* (1974). Atomic fractional coordinates and equivalent isotropic displacement parameters are given in Table 1 for the title compound.\* Selected bond

\* Tables of parameters for the disordered THF atoms and for the H atoms, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51966 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distances and angles are given in Table 2. Fig. 1 shows the atom-numbering scheme.

**Related literature.** Methylphosphonothioates of nucleosides have not been reported. This structure was solved as part of an effort to introduce, with defined stereochemistry, chiral internucleotidic linkages into oligodeoxyribonucleotides. Continuing work will be published elsewhere.

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## Structure of a Protected C(1)-C(10) Subunit\* of C(2)-*epi*-Erythronolides A and B

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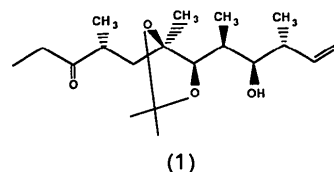
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**Abstract.** 1-[5-(2-Hydroxy-1,3-dimethyl-4-pentenyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl]-2-methyl-3-pentanone,  $C_{19}H_{34}O_4$ ,  $M_r = 326.48$ , monocline,  $P2_1$ ,  $a = 11.409$  (3),  $b = 7.889$  (2),  $c = 11.690$  (3)  $\text{\AA}$ ,  $\beta = 109.24$  (2) $^\circ$ ,  $V = 993.4$  (4)  $\text{\AA}^3$ ,  $Z = 2$ ,  $D_x = 1.09 \text{ g cm}^{-3}$ , Mo  $K\alpha$ ,  $\lambda = 0.71069 \text{ \AA}$ ,  $\mu = 0.6963 \text{ cm}^{-1}$ ,  $F(000) = 360$ ,  $T = 194 \text{ K}$ ,  $R = 0.0595$  for 1496 reflections [ $F_o \geq 4\sigma(F_o)$ ]. Molecules stack into columns parallel to the screw axis. Molecules are hydrogen bonded within each column. A hydrogen bond involving the hydroxyl group of one molecule and the carbonyl O of a second molecule (related by  $-x, -\frac{1}{2}+y, -z$ ) with an O...O distance of 2.859 (7)  $\text{\AA}$ , an H...O distance of 2.01 (7)  $\text{\AA}$  and an O—H...O angle of 164 (6) $^\circ$  is observed.

**Experimental.** (1) corresponds to the C(1)-C(10) portion of the 2-*epi*-erythromycins and was synthe-

sized by Lewis acid-mediated crotylstannane addition to an aldehyde (Keck & Abbott, 1984). The optical purity was established by an asymmetric aldol condensation (Evans, Bartroli & Shih, 1981) using a (1*S*,2*R*)-(+)-norephedrine hydrochloride derived reagent. Full synthetic details will be described elsewhere (Martin & Pacofsky, 1989). Crystals of (1) were obtained by slow evaporation from hexanes. The data crystal was a colorless needle and had dimensions 0.08  $\times$  0.12  $\times$  0.80 mm. The data were collected on a Nicolet R3 diffractometer, using a graphite monochromator, and equipped with a Nicolet LT-2 low-temperature delivery system (194 K). The lattice parameters were obtained from the least-squares refinement of 42 reflections with



\* [4*R*-(4 $\alpha$ ,5 $\beta$ )]-5-[(1*S*\*,2*R*\*,3*R*\*)-2-Hydroxy-1,3-dimethyl-4-pentenyl]-2,2,4-trimethyl-4-[(2*R*\*)-2-methyl-3-oxopentyl]-1,3-dioxolane.

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>) for non-H atoms of C<sub>19</sub>H<sub>34</sub>O<sub>4</sub>

For anisotropic atoms, the  $U$  value is  $U_{eq}$ , calculated as  $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$  where  $A_{ij}$  is the dot product of the  $i$ th and  $j$ th direct-space unit-cell vectors.

	$x$	$y$	$z$	$U$
C1	0.0515 (6)	-0.378630	0.4754 (6)	0.050 (3)
C2	0.1343 (5)	-0.3463 (14)	0.4214 (5)	0.040 (2)
C3	0.2266 (5)	-0.2054 (13)	0.4527 (5)	0.031 (2)
C4	0.2051 (5)	-0.0901 (13)	0.3436 (5)	0.025 (2)
C5	0.2952 (5)	0.0616 (13)	0.3638 (5)	0.027 (2)
C6	0.2723 (4)	0.1637 (13)	0.2463 (4)	0.026 (2)
C7	0.2968 (5)	0.0748 (13)	0.1369 (5)	0.026 (2)
C8	0.1808 (5)	-0.0073 (14)	0.0484 (5)	0.027 (2)
C9	0.1844 (5)	-0.0165 (13)	-0.0822 (4)	0.030 (2)
C10	0.1604 (5)	0.1521 (13)	-0.1435 (4)	0.029 (2)
C11	0.2477 (6)	0.2096 (15)	-0.2082 (6)	0.040 (2)
C12	0.2257 (7)	0.382 (2)	-0.2633 (8)	0.055 (3)
O13	0.0706 (3)	0.2371 (12)	-0.1445 (3)	0.0371 (15)
C14	0.0859 (8)	-0.144 (2)	-0.1579 (6)	0.052 (3)
O15	0.3285 (3)	0.2202 (12)	0.0769 (3)	0.0319 (13)
C16	0.4081 (5)	-0.0435 (13)	0.1743 (5)	0.031 (2)
O17	0.3564 (3)	0.3017 (12)	0.2692 (3)	0.0352 (14)
C18	0.2855 (6)	0.1801 (14)	0.4638 (6)	0.041 (3)
O19	0.0841 (3)	-0.0181 (12)	0.3048 (3)	0.0328 (14)
C20	0.3580 (6)	-0.280 (2)	0.4963 (7)	0.051 (3)
C21	0.2523 (8)	0.4926 (15)	0.1061 (7)	0.053 (3)
C22	0.3542 (5)	0.3616 (13)	0.1546 (5)	0.036 (2)
C23	0.4812 (8)	0.434 (2)	0.1689 (8)	0.058 (3)

Table 2. Bond lengths (Å) and angles (°) for non-H atoms of C<sub>19</sub>H<sub>34</sub>O<sub>4</sub>

1	2	3	1-2	1-2-3
C2	C1		1.323 (11)	
C3	C2	C1	1.492 (12)	125.7 (7)
C4	C3	C20	1.520 (11)	112.3 (6)
C4	C3	C2		109.5 (5)
C20	C3	C2	1.533 (10)	109.2 (8)
C5	C4	O19	1.544 (12)	105.5 (8)
C5	C4	C3		114.8 (4)
O19	C4	C3	1.421 (8)	112.2 (5)
C6	C5	C18	1.538 (10)	109.2 (8)
C6	C5	C4		111.1 (4)
C18	C5	C4	1.529 (12)	112.3 (6)
C7	C6	O17	1.563 (10)	101.9 (5)
C7	C6	C5		118.2 (8)
O17	C6	C5	1.417 (11)	109.2 (4)
C8	C7	O15	1.530 (8)	107.8 (5)
C8	C7	C16		112.9 (8)
C8	C7	C6		113.3 (5)
O15	C7	C16	1.451 (12)	107.9 (5)
O15	C7	C6		100.5 (7)
C16	C7	C6	1.520 (11)	113.5 (4)
C9	C8	C7	1.542 (8)	113.0 (5)
C10	C9	C14	1.492 (14)	108.8 (5)
C10	C9	C8		111.9 (7)
C14	C9	C8	1.551 (12)	110.1 (6)
C11	C10	O13	1.506 (11)	121.4 (9)
C11	C10	C9		117.5 (7)
O13	C10	C9	1.221 (10)	121.0 (7)
C12	C11	C10	1.49 (2)	116.6 (8)
C22	O15	C7	1.408 (12)	110.3 (5)
C22	O17	C6	1.413 (8)	106.2 (5)
C21	C22	C23	1.518 (13)	111.7 (9)
C21	C22	O15		109.1 (5)
C21	C22	O17		110.7 (6)
C23	C22	O15	1.515 (12)	111.0 (7)
C23	C22	O17		107.7 (5)
O15	C22	O17		106.4 (8)

14.0 < 2θ < 23.0°. The data were collected using the ω-scan technique (3792 reflections, of which 1896 were unique,  $R_{int} = 0.0453$  from averaging symmetry equivalent reflections), with a 2θ range from 4.0–50.0°, with a 1.2° ω scan at 5–10° min<sup>-1</sup> ( $h = -13 \rightarrow 13$ ,  $k = 0 \rightarrow 9$ ,  $l = -13 \rightarrow 13$ ). Four reflections ( $\bar{1}00$ ; 125; 311; 003) were remeasured every 196 reflections to monitor instrument and crystal stability (maximum correction on  $I$  was < 2%). The data were also corrected for Lp effects but not for absorption. Reflections having  $F_o < 4[\sigma(F_o)]$  were considered unobserved (400 reflections). Data reduction and decay correction were performed using the Nicolet XRD *SHELXTL-Plus* software package (Sheldrick, 1987). The structure was solved by direct methods (Sheldrick, 1987) and refined by full-matrix least squares (Sheldrick, 1976). In all, 339 parameters were refined. The non-H atoms were refined with anisotropic thermal parameters. Most of the H-atom positions were obtained from a Δ*F* map. Methyl H atoms of C12, C18 and C20 were initially calculated in idealized positions but were refined unconstrained during the final refinement cycles. The H atoms were refined with isotropic thermal parameters. The positional parameters and  $U$  for H6 did not refine to reasonable values (poor bond lengths and angles and negative  $U$ ) in the latter stages of refinement. The position of H6 was allowed to ride on C6 and the  $U$  was fixed at 1.2 ×  $U_{eq}$  of C6 for the last refinement cycles. The function  $\sum w(|F_o| - |F_c|)^2$  was minimized, where  $w = 1/[\sigma(F_o)]^2$  and  $\sigma(F_o) = (0.5kI^{-1/2} \{[\sigma(I)]^2 + (0.02I)^2\}^{1/2})$ . The intensity,  $I$ , is given by  $(I_{peak} - I_{background}) \times (\text{scan rate})$ ; 0.02 is a factor to downweight intense reflections and to account for instrument instability and  $k$  is the correction due to Lp effects and decay.  $\sigma(I)$  was estimated from counting statistics;  $\sigma(I) = [(I_{peak} + I_{background})^{1/2} \times (\text{scan rate})]$ . The final  $R = 0.0595$  for 1496 reflections, with

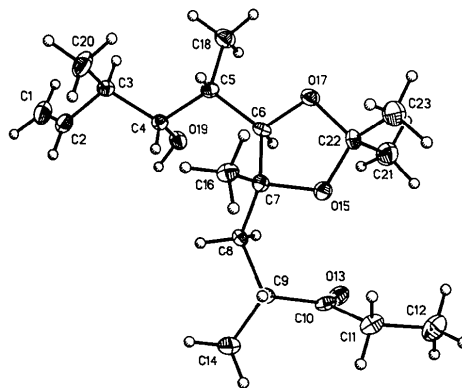


Fig. 1. View of (1) showing the atom-labeling scheme. Ellipsoids are scaled to the 30% probability level. H atoms are of arbitrary size. One methyl H atom on C14 is obscured from view.

$wR = 0.0582$  ( $R_{\text{all}} = 0.0774$ ,  $wR_{\text{all}} = 0.0611$ ) and a goodness of fit = 1.577. The maximum  $|\Delta/\sigma| < 0.1$  in the final refinement cycle and the minimum and maximum peaks in the final  $\Delta F$  map were  $-0.24$  and  $0.26 \text{ e } \text{\AA}^{-3}$ , respectively. Differentiation between enantiomorphs could not be made on the basis of the X-ray results ( $wR = 0.0582$  for the enantiomorph). The scattering factors for the non-H atoms were taken from Cromer & Mann (1968), with the anomalous-dispersion corrections taken from the work of Cromer & Liberman (1970). The scattering factors for the H atoms were obtained from Stewart, Davidson & Simpson (1965). Values used to calculate the linear absorption coefficient are from *International Tables for X-ray Crystallography* (1974).<sup>\*</sup> Figures were generated using *SHELXTL-Plus* (Sheldrick, 1987). The positional and thermal parameters for non-H atoms are listed in Table 1, while the bond lengths and angles for the non-H atoms are listed in Table 2. The atom-labeling scheme is shown in Fig. 1. Other computer programs used in this work are listed in reference 11 of Gadol & Davis (1982).

**Related literature.** The crystal structure of the related C(1)–C(10) subunit of the erythromycins has been reported (Lynch, Pacofsky, Martin & Davis, 1989). The total synthesis of erythronolide B has been

<sup>\*</sup> Tables of anisotropic thermal parameters, H-atom positional parameters, bond distances and angles involving H atoms, structure factor amplitudes and a unit-cell packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51865 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Structure of 3 $\beta$ ,3 $\alpha\beta$ ,6-Trimethyl-3 $\alpha$ ,7 $\alpha\beta$ -dihydro-2(3H),5(4H)-benzo[b]furandione

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**Abstract.**  $\text{C}_{11}\text{H}_{14}\text{O}_3$ ,  $M_r = 194.23$ , orthorhombic,  $P2_12_12_1$ ,  $a = 6.648$  (2),  $b = 6.710$  (1),  $c = 22.941$  (3)  $\text{\AA}$ ,  $V = 1023.4$  (4)  $\text{\AA}^3$ ,  $Z = 4$ ,  $D_x = 1.261 \text{ g cm}^{-3}$ , Mo  $K\alpha$  radiation (graphite monochromator),  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu = 0.85 \text{ cm}^{-1}$ ,  $F(000) = 416$ ,  $T = 295$  (1) K,  $R = 0.033$  for 183 variables and the 862 reflections having  $I > 2\sigma(I)$ . This structure confirms the stereochemistry at C(3 $\alpha$ ) and C(7 $\alpha$ ) of a

reported (Sviridov, Ermolenko, Yashunsky, Borodkin & Kochetkov, 1987*a,b*).

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model substrate used to evaluate a manganese triacetate oxidation step needed for a quassinoid synthesis. There are no unusual bond lengths or angles.

**Experimental.** The title compound was synthesized (Jeganathan, Richardson & Watt, 1989) and crystallized from ether as colorless, thick, rectangular plates; the dimensions of the data crystal were  $0.22 \times$