

P2—C13	2.116 (2)	O5—C51	1.417 (4)
P2—C15	2.130 (2)	O7—C71	1.471 (4)
P3—C111	2.101 (2)		
O3—P1—O7	111.15 (14)	C113—P3—C110	90.64 (8)
O3—P1—O1	111.05 (15)	C111—P3—C115	89.14 (8)
O7—P1—O1	110.10 (14)	C113—P3—C115	179.26 (8)
O3—P1—C11	106.70 (11)	C110—P3—C115	89.22 (7)
O7—P1—C11	112.85 (11)	C111—P3—C114	91.48 (9)
O1—P1—C11	104.79 (11)	C113—P3—C114	90.25 (7)
O5—P2—C14	121.66 (12)	C110—P3—C114	176.06 (10)
O5—P2—C12	124.12 (12)	C115—P3—C114	89.83 (6)
C14—P2—C12	114.08 (7)	C111—P3—C112	178.84 (9)
O5—P2—C13	85.61 (11)	C113—P3—C112	89.12 (7)
C14—P2—C13	91.01 (7)	C110—P3—C112	88.57 (9)
C12—P2—C13	90.07 (7)	C115—P3—C112	90.14 (7)
O5—P2—C15	93.48 (10)	C114—P3—C112	87.60 (7)
C14—P2—C15	90.39 (7)	C11—O1—P1	114.4 (2)
C12—P2—C15	89.55 (7)	C31—O3—P1	137.3 (2)
C13—P2—C15	178.59 (8)	C51—O5—P2	131.0 (2)
C111—P3—C113	91.60 (8)	C71—O7—P1	126.3 (2)
C111—P3—C110	92.34 (11)		

One butyl group, C39—C41, is disordered over two positions. The maximum difference peak of 1.5 e Å<sup>-3</sup> lies near C114 (in the PCl<sub>6</sub> anion) and may indicate a minor disorder component (or atomic displacements not well approximated by ellipsoids).

Data collection: XSCANS (Fait, 1991). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XP (Siemens, 1994). Software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1315). Services for accessing these data are described at the back of the journal.

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## Absolute Configuration of an Intermediate in the Asymmetric Synthesis of Natural $\beta$ -Hydroxy and $\beta$ -Amino Acids

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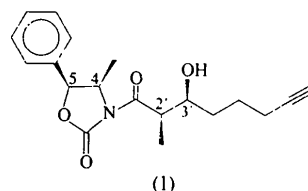
(Received 9 September 1996; accepted 18 April 1997)

## Abstract

The single-crystal X-ray structure determination of enantiomerically pure (4*R*,5*S*)-3-[(2*R*,3*S*)-3-hydroxy-2-methyl-7-octynoyl]-4-methyl-5-phenyl-1,3-oxazolidin-2-one, C<sub>19</sub>H<sub>23</sub>NO<sub>4</sub>, at 223 K is reported. The absolute configuration of this molecule has been determined.

## Comment

(4*R*,5*S*)-3-[(2*R*,3*S*)-3-Hydroxy-2-methyl-7-octynoyl]-4-methyl-5-phenyl-1,3-oxazolidin-2-one, (1), was prepared as an important intermediate in the asymmetric synthesis of the  $\beta$ -amino acid and  $\beta$ -hydroxy acid derivatives of onchidins (Rodríguez *et al.*, 1994; Fernández *et al.*, 1996), dimeric depsipeptides from the mollusc *Onchidium sp.* Compound (1) has been synthesized from enantiomerically pure commercially available (1*S*,2*R*)-norephedrine (Fernández *et al.*, 1996), thus fixing the absolute configurations of C atoms 4 and 5 in the title compound. This allows determination of the absolute configuration at C atoms 2' and 3', which is important in the context of the synthetic strategy to control the stereochemistry of the final  $\beta$ -hydroxy and  $\beta$ -amino acids.



A view of (1) showing the displacement ellipsoids, atomic numbering and the correct absolute configuration is given in Fig. 1. The absolute configuration of the molecule was also determined by refinement of the structure according to the method of Flack (1983).

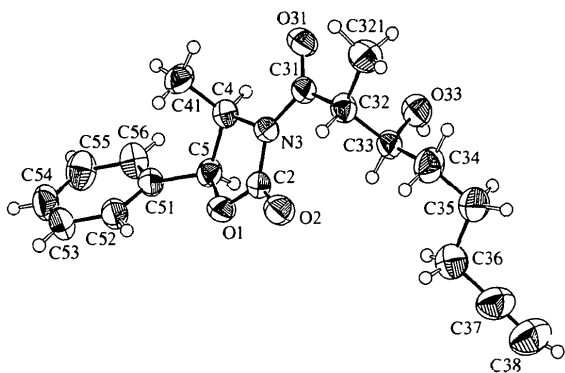


Fig. 1. Diagram of the molecule showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 60% probability level. H atoms are represented by spheres of arbitrary size.

The X-ray analysis supports the expected (Evans, Bartroli & Shih, 1981; Gage & Evans, 1989) configuration at all the chiral centres. The torsion angles C321—C32—C33—O33 and C41—C4—C5—C51 are  $-61.8(2)$  and  $26.9(3)^\circ$ , respectively. Bond lengths and angles in this compound fall within normal ranges. The oxazolidinone ring has structural features that are comparable with those of similar compounds (Marsch, Schaefer, Kukkola & Myers, 1992), being non-planar; the atom set N3, C2, O2, O1 defines a virtual plane, but atom C4 sits above and atom C5 sits below this plane.

## Experimental

Compound (1) was prepared in optically pure form by an enantioselective aldol condensation reaction using Evans' methodology (Evans *et al.*, 1981; Gage & Evans, 1989). Suitable crystals were obtained from an ethyl acetate–hexane (1:6) solution.

### Crystal data

$C_{19}H_{23}NO_4$   
 $M_r = 329.38$   
 Orthorhombic  
 $P2_12_1$   
 $a = 6.9300(2) \text{ \AA}$   
 $b = 15.5478(15) \text{ \AA}$   
 $c = 16.5453(13) \text{ \AA}$   
 $V = 1782.7(2) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.227 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Cu  $K\alpha$  radiation  
 $\lambda = 1.5418 \text{ \AA}$   
 Cell parameters from 25 reflections  
 $\theta = 17.80\text{--}26.74^\circ$   
 $\mu = 0.698 \text{ mm}^{-1}$   
 $T = 223(2) \text{ K}$   
 Prism  
 $0.40 \times 0.30 \times 0.25 \text{ mm}$   
 Colourless

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega$  scans  
 Absorption correction:  $\psi$  scans (North, Phillips & Mathews, 1968)  
 $T_{\min} = 0.823$ ,  $T_{\max} = 0.840$

2769 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.022$   
 $\theta_{\text{max}} = 64.79^\circ$   
 $h = 0 \rightarrow 7$   
 $k = -1 \rightarrow 18$   
 $l = -19 \rightarrow 19$

3467 measured reflections  
 2858 independent reflections

3 standard reflections  
 every 200 reflections  
 intensity decay: none

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.095$   
 $S = 1.043$   
 2858 reflections  
 310 parameters  
 All H atoms refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 0.3437P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.272 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.139 \text{ e \AA}^{-3}$

Extinction correction: *SHELXL93* (Sheldrick, 1993)  
 Extinction coefficient: 0.0081 (6)  
 Scattering factors from *International Tables for Crystallography* (Vol. C)  
 Absolute configuration: Flack (1983)  
 Flack parameter =  $-0.04(22)$

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1—C2	1.341 (2)	C32—C33	1.536 (3)
O1—C5	1.453 (2)	C33—C34	1.532 (3)
O2—C2	1.198 (2)	C34—C35	1.521 (3)
O31—C31	1.218 (2)	C35—C36	1.507 (4)
O33—C33	1.421 (2)	C36—C37	1.481 (4)
N3—C2	1.390 (2)	C37—C38	1.187 (4)
N3—C31	1.396 (2)	C51—C56	1.384 (3)
N3—C4	1.479 (2)	C51—C52	1.384 (3)
C4—C41	1.513 (3)	C52—C53	1.389 (3)
C4—C5	1.539 (3)	C53—C54	1.370 (3)
C5—C51	1.506 (2)	C54—C55	1.373 (3)
C31—C32	1.509 (2)	C55—C56	1.389 (3)
C32—C321	1.523 (3)		
C2—O1—C5	110.45 (14)	C31—C32—C35	109.75 (15)
C2—N3—C31	128.13 (14)	C321—C32—C33	112.8 (2)
C2—N3—C4	110.33 (14)	O33—C33—C34	110.6 (2)
C31—N3—C4	121.31 (14)	O33—C33—C32	108.0 (2)
O2—C2—O1	121.8 (2)	C34—C33—C32	110.8 (2)
O2—C2—N3	129.4 (2)	C35—C34—C33	115.0 (2)
O1—C2—N3	108.80 (14)	C36—C35—C34	112.2 (2)
N3—C4—C41	111.6 (2)	C37—C36—C35	112.5 (2)
N3—C4—C5	99.68 (14)	C38—C37—C36	178.7 (3)
C41—C4—C5	115.4 (2)	C56—C51—C52	119.0 (2)
O1—C5—C51	109.0 (2)	C56—C51—C5	118.8 (2)
O1—C5—C4	103.46 (15)	C52—C51—C5	122.1 (2)
C51—C5—C4	118.4 (2)	C51—C52—C53	120.0 (2)
O31—C31—N3	117.4 (2)	C54—C53—C52	120.6 (2)
O31—C31—C32	123.5 (2)	C53—C54—C55	119.7 (2)
N3—C31—C32	119.2 (2)	C54—C55—C56	120.2 (2)
C31—C32—C321	109.8 (2)	C51—C56—C55	120.4 (2)

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software* and *SDP* (Frenz, 1983). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1994). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1016). Services for accessing these data are described at the back of the journal.

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## Structure and Conformation of Photosynthetic Pigments and Related Compounds. 10. Comparison of a Phytychlorin and Phytoporphyrin Derived from Chlorophyll *a*

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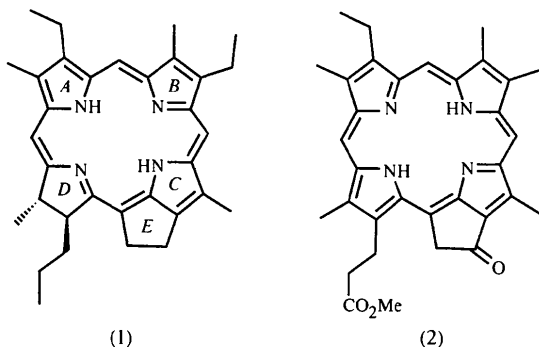
### Abstract

The crystal and molecular structures of 17-decarboxyethyl-13<sup>1</sup>-deoxy-17-propylphytychlorin, C<sub>33</sub>H<sub>40</sub>N<sub>4</sub>, (1), and phytoporphyrin methyl ester, C<sub>34</sub>H<sub>36</sub>N<sub>4</sub>O<sub>3</sub>, (2), are compared. Compound (1) shows structural parameters similar to those of other naturally occurring phytychlorins. Owing to the absence of any heteroatom functionalities at the periphery, no close contacts are observed in the packing of (1), in contrast to those normally found in other chlorophyll derivatives. Compound (2) presents the first structure of a free-base pheophorphyrin and forms chains stabilized by C—H···O=C and π–π

interactions. In contrast to the structure of (1) and other chlorins, the two pyrrole H atoms in (2) are located at rings *B* and *D*.

### Comment

The structure of the phytychlorin (1) derived from chlorophyll *a* was determined in order to obtain information on the crystal packing of a pheophorbide *a* derivative containing no O functionalities. This was achieved in (1) by removal of the 13<sup>1</sup> oxo group and substitution of the 17-propionic acid group present in chlorophyll *a* with a propionyl group.



Compound (1) crystallized with two crystallographically independent molecules in the asymmetric unit, mainly distinguished by the conformation of the C17 propionyl groups (Fig. 1). The structural parameters of the macrocycles agree well with those of other pheophorbides related to chlorophyll *a* (Hoppe, Will, Gassmann & Weichselgartner, 1969; Gassmann, Strell, Brandl, Sturm & Hoppe, 1971; Fischer, Templeton, Zalkin & Calvin, 1972; Kratky, Isenring & Dunitz, 1977; Smith, Goff, Fajer & Barkigia, 1982, 1983; Senge & Smith, 1992). The hydrophorphyrin character is clearly evidenced by the elongated C17—C18 and C37—C38 bond lengths [1.552 (5) and 1.551 (5) Å, respectively]. With the exception of the reduced ring *D*, both macrocycles are almost planar. The average deviation of the 26 atoms comprising the phytychlorin macrocycle system is 0.031 Å in (1) and 0.065 Å in (2). The largest deviations from the respective N<sub>4</sub> planes are observed for C18 [0.28 (5) Å] and C38 [0.42 (5) Å].

The chlorins form molecular stacks in the crystal, repeating the (1)–(1)–(2)–(2)–(1) motif. Whereas the interplanar separations of the N<sub>4</sub> planes are of the order of 3.5 Å, there is almost no π overlap of the ring systems as indicated by center-to-center separations of the order of 7.9 (1) Å and lateral shifts of the macrocycle centers against each other by about 7.03 (3) Å [geometrical parameters as defined by Scheidt & Lee (1987)]. Thus, in contrast to other phytychlorins, in the absence of any heteroatom functionalities at the phytychlorin periphery, no close contacts and only very weak π–π interactions are observed.