

Hiroyuki Oku,* Ryo Naito,
Keiichi Yamada and Ryoichi
KatakaiDepartment of Chemistry, Gunma University,
Kiryu, Gunma 376-8515, JapanCorrespondence e-mail:
katakai@chem.gunma-u.ac.jp

Key indicators

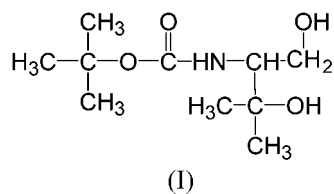
Single-crystal X-ray study
 $T = 173$ K
Mean $\sigma(\text{C}-\text{C}) = 0.010$ Å
Disorder in main residue
 R factor = 0.085
 wR factor = 0.244
Data-to-parameter ratio = 9.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.A synthetic intermediate of enantiopure *N*-protected
 β -hydroxyvaline, (2*R*)-2-[*N*-(*tert*-butoxycarbonyl)-
amino]-3-methylbutane-1,3-diol

Crystals of the title compound [systematic name: (2*R*)-*tert*-butyl *N*-(1,3-dihydroxy-3-methyl-2-butyl)carbamate], $\text{C}_{10}\text{H}_{21}\text{NO}_4$, were successfully grown from an ethyl acetate solution. There is one independent molecule in the asymmetric unit. The urethane linkage, $-\text{O}-\text{CO}-\text{NH}-$, is a *cis* conformer and the molecules are linked into a dimer by two $\text{N}-\text{H}\cdots\text{O}=\text{C}$ hydrogen bonds. The dimers are connected together by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds in which four hydroxy groups are involved.

Received 4 November 2004
Accepted 22 November 2004
Online 27 November 2004

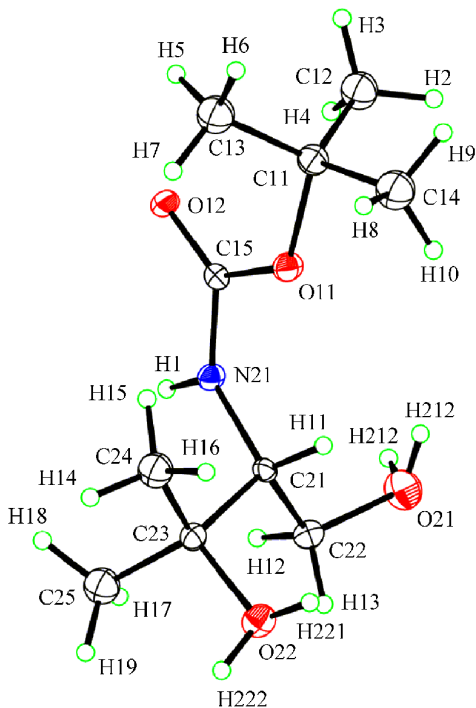
Comment

In need of enantiopure β -hydroxyvaline-containing peptide antibiotics, a chiral form of 2-*N*-(*tert*-butoxycarbonyl)amino-3-methylbutane-1,3-diol was recently reported as an effective intermediate for scale-up synthesis (Dettwiler & Lubell, 2003). Among various peptide antibiotics, β -hydroxyvaline is found, as in aureobasidines (Takesako *et al.*, 1991) and luzopeptides (Konishi *et al.*, 1981). In this paper, we report the structure of the title compound, (I), as one of our synthetic studies of antibacterial peptides containing unusual amino acids (Oku *et al.*, 2004; Yamada *et al.*, 2004; Urakawa *et al.*, 2004) and *N*-methylated amino acids (Endo *et al.*, 2003).



The molecular structure of (I) is shown in Fig. 1. Compound (I) has a *cis* conformation at the urethane linkage, $-\text{O}-\text{CO}-\text{NH}-$, and the molecules are linked into a dimer by two $\text{N}-\text{H}\cdots\text{O}=\text{C}$ hydrogen bonds (Fig. 2). The *cis* conformation is not common, but it is sometimes observed in short peptides (Oku *et al.*, 2003, 2004; Benedetti *et al.*, 1980). As found in this and other reported structures, the *cis* conformation is suitable for dimerization association in short peptide crystal structures.

Unprotected diols were found as OH groups. From a difference Fourier map, each OH group was found to be disordered around the $\text{C}-\text{O}$ axis, resulting in two conformers of the OH group. Therefore, there are two possible patterns of hydrogen bonding, each composed of four interactions as shown in Fig. 3. One, shown in green arrows from donors (H atoms) to acceptors (O atoms), has a right-handed orientation: $\text{O}22-\text{H}22\cdots\text{O}21^{\text{iii}}-\text{H}211^{\text{iii}}\cdots\text{O}21^{\text{v}}-\text{H}212^{\text{v}}\cdots\text{O}22^{\text{ii}}-\text{H}221^{\text{ii}}\cdots\text{O}22$ (symmetry codes are as in Fig. 3). The other, shown in blue arrows, has a left-handed orientation: $\text{O}22-\text{H}221\cdots\text{O}22^{\text{ii}}-\text{H}222^{\text{ii}}\cdots\text{O}21^{\text{v}}-\text{H}211^{\text{v}}\cdots\text{O}21^{\text{iii}}-\text{H}212^{\text{iii}}\cdots$

**Figure 1**

A view of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 20% probability level.

O22. Two of the four hydrogen bonds are composed of crystallographically equivalent O atoms, such as O21ⁱⁱⁱ...O21^v and O22ⁱⁱⁱ...O22. In these pairs, there is a twofold axis between the equivalent O atoms, as shown in Fig. 3. The dimers of (I) connected by two N—H...O=C hydrogen bonds are thus aggregated together by mutual —OH...OH— hydrogen bonds.

Experimental

The title peptide, (I), was prepared from Boc-D-Ser-OH in three steps (overall yield 71%) according to the reported procedure (Dettwiler *et al.*, 2003). Crystals of the title compound were successfully grown from ethyl acetate–hexane. Analytical data (melting point, ¹H NMR and $[\alpha]_D^{20}$) are in accordance with the expected structure; m.p. = 337–338 K, $[\alpha]_D^{20} = +5.1^\circ$ (*c* 1.0, methanol).

Crystal data

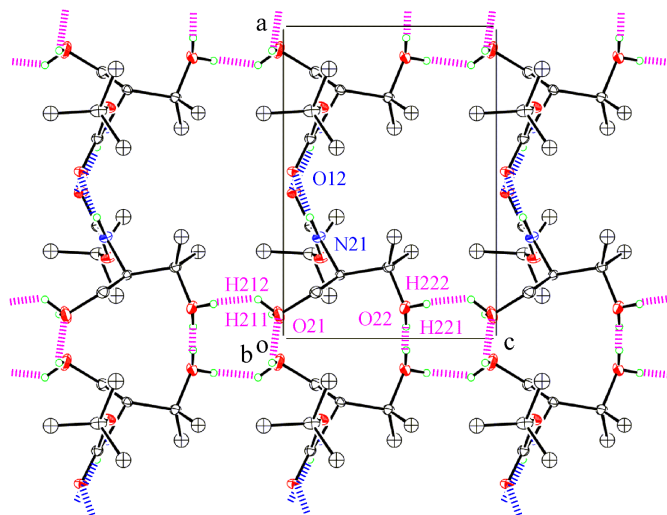
C₁₀H₂₁NO₄
M_r = 219.28
 Orthorhombic, *P*2₁2₁2
a = 9.833 (8) Å
b = 18.994 (17) Å
c = 6.713 (8) Å
V = 1254 (2) Å³
Z = 4
D_x = 1.162 Mg m⁻³

Cu *K*α radiation
 Cell parameters from 8702 reflections
 $\theta = 4.5\text{--}66.6^\circ$
 $\mu = 0.74\text{ mm}^{-1}$
T = 173.1 K
 Prism, colorless
 0.25 × 0.25 × 0.05 mm

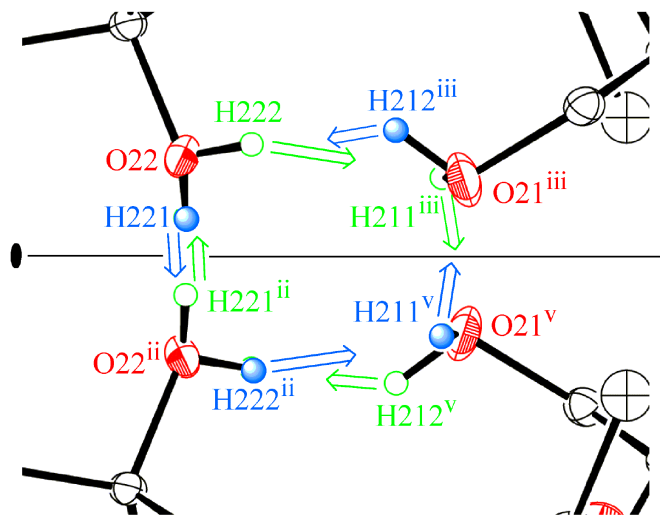
Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)
T_{min} = 0.765, *T_{max}* = 0.964
 10 309 measured reflections

1318 independent reflections
 965 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.045
 $\theta_{\text{max}} = 68.1^\circ$
h = -11 → 11
k = -22 → 22
l = -8 → 8

**Figure 2**

A packing diagram of (I), projected down the *b* axis. Hydrogen bonds are shown as dashed lines.

**Figure 3**

A detail from the packing diagram of (I), projected down the *b* axis. Two hydrogen-bonded states are found in —OH...OH— interactions. One is shown in green arrows (right-handed orientation); the other is shown in blue arrows (left handed). [Symmetry codes: (ii) $-x, 1 - y, z$; (iii) $x, y, 1 + z$; (v) $-x, 1 - y, 1 + z$.]

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.085$
 $wR(F^2) = 0.244$
S = 1.07
 1318 reflections
 133 parameters

H-atom parameters constrained
 $w = 1/[0.007F_o^2 + \sigma(F_o^2)]/(4F_o^2)$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.59\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.43\text{ e \AA}^{-3}$

Table 1

Torsion angles for the urethane linkage ($^\circ$).

C11—O11—C15—N21	175.5 (5)	C15—N21—C21—C22	-135.8 (6)
C21—N21—C15—O11	4.8 (8)	C15—N21—C21—C23	97.8 (6)

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N21-H1\cdots O12^i$	0.95	1.97	2.916 (6)	174
$O21-H211\cdots O21^{ii}$	0.78	2.15	2.717 (8)	129
$O22-H222\cdots O21^{iii}$	0.82	2.11	2.742 (6)	133
$O21-H212\cdots O22^{iv}$	0.82	2.11	2.742 (6)	134
$O22-H221\cdots O22^{ii}$	0.85	1.95	2.799 (6)	177

Symmetry codes: (i) $1-x, 1-y, z$; (ii) $-x, 1-y, z$; (iii) $x, y, 1+z$; (iv) $x, y, z-1$.

The methyl C atoms were refined isotropically; all other non-H atoms were refined anisotropically. This procedure was adopted because of the limited number of observed reflections. H atoms were positioned geometrically, with $C-H = 0.95$ Å, except for hydroxy H atoms H211, H212, H221 and H222, which were located in a difference Fourier map with occupancies of 0.5. The H atoms were refined using a riding model, with U_{iso} constrained to be $1.2U_{eq}$ of the carrier atom. In the absence of significant anomalous scattering effects, Friedel pairs were averaged and the absolute configuration could not be determined from the diffraction experiment. The absolute configuration of the compound was, however, confirmed from the spectroscopic data.

Data collection: *RAPID-AUTO* (Rigaku/MS & Rigaku Corporation, 2003); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS & Rigaku Corporation, 2003); program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 1996); molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *CrystalStructure*.

HO acknowledges a Grant-in-Aid for Scientific Research on Priority Areas (No. 14078101 and 16033211, Reaction Control of Dynamic Complexes) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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