C513—H513···O62	1.00	2.96	3.050 (3)	86
N5—H5···O92^{i}	1.00	2.00	2.969 (3)	162
C9—H9···O102^{ii}	1.02	2.38	3.297 (4)	150
C23—H23*A*···O31^{iii}	1.00	2.44	3.233 (3)	136
C23—H23*B*···O55^{iv}	1.01	2.55	3.354 (3)	137
C510—H510···O62^{v}	1.01	2.61	3.189 (4)	117

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

The absolute configuration was assigned on the basis of the known chirality of the D-*manno* used in the synthesis. Since compound (I) crystallizes in a polar space group, polar axis restraints were applied by the method of Flack & Schwarzenbach (1988) and the absolute structure was established as described by Flack (1983). The H atoms were included at geometrically calculated positions. The displacement factors at room temperature are rather high and refinement of the terminal atoms gave the shift/s.u. greater than the normal values. It was in order to overcome these difficulties that the structure was studied at low temperature.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *SET*4 (Boer & Duisenberg, 1984) and *CELDIM* in *CAD*-4 *Software*. Data reduction: *XRAY*76 *System* (Stewart *et al.*, 1976). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *XRAY*76 *System*. Molecular graphics: *PLATON*94 (Spek, 1994). Software used to prepare material for publication: *PARST* (Nardelli, 1983*b*) and *PARSTCIF* (Nardelli, 1991).

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N-tert-Butoxycarbonyl-*N*,*N*′-ethylene-bridged (*S*)-tyrosyl-(*S*)-tyrosine methyl ester

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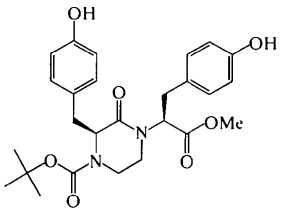
Abstract

The title compound, a pseudopeptide, methyl (2*S*)-3-(4-hydroxyphenyl)-2-[(3*S*)-4-(*tert*-butoxycarbonyl)-3-(4-hydroxybenzyl)-2-oxopiperazin-1-yl]propionate, $C_{26}H_{32}N_2O_7$, was crystallized from an H_2O/methanol solution. The two N-substituted chains on the piperazin-2-one (MKP) ring lie in the quasi-equatorial position and the third chain lies in the quasi-axial position. Each side chain on the tyrosines is located opposite the MKP ring. The MKP ring has a pseudo-chair form.

Comment

Peptides which are conformationally restricted through short-range cyclizations have been synthesized with the aim of clarifying the relationship between their biological activities, their conformations and their functionalities (Toniolo, 1990). The present authors have also prepared a series of structurally reinforced dipeptides containing *N*,*N*′-ethylene bridging and have studied their opiate activities (Takenaka *et al.*, 1993; Yamashita *et al.*, 1997). Although we have reported solid and solution structures of this series of oligopseudopeptides (Yamashita *et al.*, 1989; Kojima *et al.*, 1991) and macrocyclic pseudopeptides (Miyake *et al.*, 1996; Kojima *et al.*, 1995) which showed ionophorous (Kojima *et al.*, 1992) and enantioselective transport (Miyake *et al.*, 1993) properties, we have never obtained a crystal of a linear oligopseudopeptide containing a functional group on the side chains. This is the first paper describing the crystal structure of a pseudopeptide constructed from tyrosines, Boc-eYY-OMe,

where Boc is *tert*-butoxycarbonyl and eYY is (2*S*)-3-(4-hydroxyphenyl)-2-[(3*S*)-3-(4-hydroxybenzyl)-2-oxopiperazin-1-yl]propanoic acid (Yamashita *et al.*, 1993).



Boc-eYY-OMe

The *ORTEP*II (Johnson, 1976) drawing of Boc-eYY-OMe is shown in Fig. 1. The two N-substituted chains on the piperazin-2-one (MKP) ring lie in the quasi-equatorial position and the third chain is in the quasi-axial position. Each side chain on the tyrosines is located on the opposite face of the MKP ring. The torsion angles (IUPAC–IUB, 1970) of the peptide backbone [C1—C2—N3—C19 −127.7 (3)° and N3—C2—C1—N6 −8.5 (3)°] in the MKP ring are within the ranges observed in cyclic peptides possessing the MKP ring (Kojima *et al.*, 1995; Miyake *et al.*, 1996) and the other torsion angles outside the MKP ring are within the allowed regions of the Ramachandran plot (Ramachandran & Sasisekharan, 1968). Intermolecular hydrogen bonds (Table 2) mediated by both functional groups on the side chains of the tyrosines fix the conformations of the urethane bonds [O21—C19—N3—C2 is *cis* (IUPAC–IUB, 1970)] in the solid state, while the structure in solution is in an equilibrium of *cis* and *trans* conformations (1:2 in perdeuterated dimethyl sulfoxide), as described previously by Kojima *et al.* (1991).

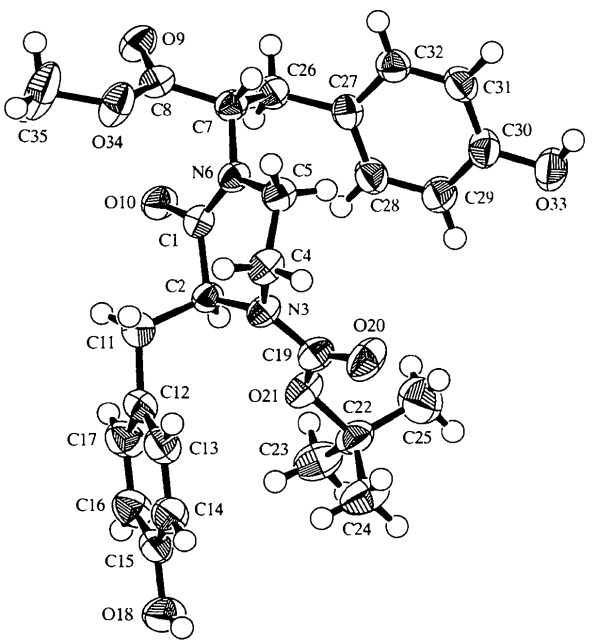


Fig. 1. *ORTEP*II drawing (Johnson, 1976) of Boc-eYY-OMe with the atom-numbering scheme. Ellipsoids for non-H atoms correspond to the 70% probability level and H atoms are shown as spheres of an arbitrary radius.

The piperazin-2-one ring is in a near-chair conformation. The C1—C2—C11—C12 torsion angle is 166.5 (2)°, indicating that the α–β conformation of the side chain on atom C2 is the U_I form (Kojima *et al.*, 1991). This result, that *cis*-peptide bonding on the N-terminal end of eYY induces a U_I form, is the same as for previous data that were obtained for macrocyclic pseudopeptides containing *N*,*N*′-ethylene-bridged phenylalanylphenylalanine (Miyake *et al.*, 1996).

Experimental

The ethyl analogue of the title compound, Boc-eYY-OEt, was prepared from di-*tert*-butyldicarbonate [$(Boc)_2O$] and *N*,*N*′-ethylene-bridged-(*S*)-tyrosyl-(*S*)-tyrosine ethyl ester (eYY-OEt; Yamashita *et al.*, 1993) prepared earlier. The title methyl ester (Boc-eYY-OMe) was obtained quantitatively from a solution of Boc-eYY-OEt in the presence of NaOMe in methanol by ester exchange (m.p. 371–376 K). Analysis calculated for $C_{26}H_{32}N_2O_7 \cdot \frac{1}{2}H_2O$: C 63.27, H 6.74, N 5.68%; found: C 63.27, H 6.69, N 5.70%. A single crystal suitable for X-ray analysis was obtained from a 1:1 H_2O/methanol solution as a non-hydrated one. IR (KBr): 1744, 1696 (*sh*), and 1665 cm^{-1} for ν(C=O) of ester, urethane and amide, respectively; FAB MS *m*/*z* 485 [$M + H^+$]; $[\alpha]_D$ = +14.5 (in methanol).

Crystal data

$C_{26}H_{32}N_2O_7$	Mo $K\alpha$ radiation
M_r = 484.55	λ = 0.7107 Å
Monoclinic	Cell parameters from 25 reflections
$P2_1$	θ = 12.8–17.1°
a = 9.641 (4) Å	μ = 0.087 mm^{-1}
b = 10.251 (4) Å	T = 150 K
c = 13.893 (5) Å	Prismatic
β = 101.00 (3)°	0.35 × 0.33 × 0.05 mm
V = 1347.8 (8) $Å^3$	Colourless
Z = 2	
D_x = 1.194 Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-7*R* diffractometer	R_{int} = 0.023
$\omega/2\theta$ scans	θ_{max} = 30°
Absorption correction: none	h = 0 → 11
4100 measured reflections	k = 0 → 12
3830 independent reflections	l = −17 → 17
3256 reflections with $I > 2\sigma(I)$	3 standard reflections every 150 reflections intensity decay: 2.5%

Refinement

Refinement on F	$w = 1/[\sigma^2(F_o) + 0.00006\|F_o\|^2]$
R = 0.039	$(\Delta/\sigma)_{max} < 0.001$
wR = 0.042	

S = 1.962	$\Delta\rho_{max}$ = 0.29 e Å^{-3}
3256 reflections	$\Delta\rho_{min}$ = −0.14 e Å^{-3}
316 parameters	Extinction correction: none
H-atom parameters not refined	Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O10—C1	1.233 (2)	N6—C5	1.470 (3)
N3—C2	1.467 (3)	N6—C7	1.466 (3)
N3—C4	1.443 (3)	C1—C2	1.519 (3)
N3—C19	1.360 (3)	C2—C11	1.544 (3)
N6—C1	1.342 (3)	C4—C5	1.508 (3)
C2—N3—C4	114.6 (2)	O10—C1—C2	118.2 (2)
C2—N3—C19	123.2 (2)	N6—C1—C2	120.4 (2)
C4—N3—C19	121.5 (2)	N3—C2—C1	111.1 (2)
C1—N6—C5	124.9 (2)	N3—C2—C11	112.3 (2)
C1—N6—C7	116.8 (2)	C1—C2—C11	110.3 (2)
C5—N6—C7	118.1 (2)	N3—C4—C5	109.9 (2)
O10—C1—N6	121.4 (2)	N6—C5—C4	110.2 (2)
O10—C1—N6—C5	177.5 (2)	C1—C2—N3—C4	42.8 (2)
O10—C1—N6—C7	−8.4 (3)	C1—C2—N3—C19	−127.7 (3)
O10—C1—C2—N3	170.3 (2)	C1—C2—C11—C12	166.5 (2)
O10—C1—C2—C11	−64.5 (3)	C2—N3—C4—C5	−64.1 (2)
O20—C19—N3—C2	171.6 (3)	C2—C1—N6—C5	−3.8 (3)
O20—C19—N3—C4	1.7 (4)	C2—C1—N6—C7	170.3 (2)
N3—C2—C1—N6	−8.5 (3)	C4—N3—C2—C11	−81.3 (4)
N3—C4—C5—N6	47.6 (2)	C4—C5—N6—C7	170.0 (2)
N6—C1—C2—C11	116.7 (2)	C5—N6—C7—C8	−132.4 (3)
C1—N6—C5—C4	−15.9 (3)	C5—C4—N3—C19	106.5 (2)
C1—N6—C7—C8	53.0 (3)	C11—C2—N3—C19	108.2 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O18—H13···O20^{i}	0.747	1.911	2.648 (2)	170
O33—H29···O18^{ii}	0.816	1.964	2.771 (3)	170

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

All H atoms were fixed at geometrically favourable positions. The absolute configuration of the molecule is derived from the known (*S*)-configuration of the tyrosine moieties.

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku Corporation, 1988). Cell refinement: *Rigaku/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985) and *DIRDIF*94 (Beurskens *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Absolute configuration of the active stereoisomer of new rice fungicide Carpropamid

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Abstract

The absolute configuration of the active component of fungicide Carpropamid of a diastereoisomeric mixture was determined to be (1*S*,3*R*)-*N*-[(*R*)-1-(4-chlorophenyl)ethyl]-2,2-dichloro-1-ethyl-3-methylcyclopropanecarboxamide, $C_{15}H_{18}Cl_3NO$. Two molecules are tightly coupled in the crystal. The intermolecular hydrogen bonding between C=O and H—N is responsible for this assembly.