Area detector scans	R_{int} = 0.053
Absorption correction: none	θ_{max} = 27.70°
15 309 measured reflections	$h = -10 \rightarrow 9$
7744 independent reflections	$k = -34 \rightarrow 35$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = -0.001$
$R[F^2 > 2\sigma(F^2)] = 0.051$	$\Delta\rho_{max} = 0.160$ e Å^{-3}
$wR(F^2) = 0.156$	$\Delta\rho_{min} = -0.184$ e Å^{-3}
$S = 1.000$	Extinction correction: none
7740 reflections	Scattering factors from *International Tables for Crystallography* (Vol. C)
539 parameters	
H atoms not refined	
$w = 1/[\sigma^2(F_o^2) + (0.0639P)^2 + 0.1876P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Selected intermolecular distances (Å)*

C14···C7^{i}	3.780 (3)	C35···C36^{iii}	3.925 (3)
C14···C15^{ii}	4.273 (3)	C35···C36^{iv}	5.798 (3)
C15···C6^{i}	3.936 (3)	C36···C35^{iii}	3.925 (3)
C15···C14^{ii}	4.273 (3)	C36···C35^{iv}	5.798 (3)

Symmetry codes: (i) $1-x, 2-y, 2-z$; (ii) $-x, 2-y, 1-z$; (iii) $1-x, 1-y, 2-z$; (iv) $2-x, 1-y, 2-z$.

The data collection conditions by R-AXIS IICS are as follows: number of frames measured 19, oscillation range per frame 10.0°, exposure time per frame 45 min and crystal-to-detector distance 143.0 mm.

Data collection: *OSCILL* in *R-AXIS IICS Software* (Rigaku Corporation, 1994). Cell refinement: *SCALE* in *R-AXIS IICS Software*. Data reduction: *SCALE* in *R-AXIS IICS Software*. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994) in *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1061). Services for accessing these data are described at the back of the journal.

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β-D-3′-Deoxyadenosine (Cordycepin)

P. Karthe,[a] N. Gautham,[a] Anil Kumar[b] and S. B. Katti[b]

[a]*Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras 600 025, India, and* [b]*Division of Biopolymers, Central Drug Research Institute, Lucknow 226 001, India. E-mail: crystal@giasmd01.vsnl.net.in*

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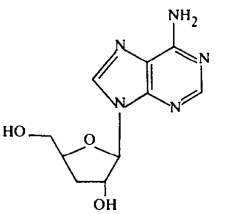
Abstract

In the title compound, $C_{10}H_{13}N_5O_3$, the nucleoside adopts an *anti* conformation with C3′-*endo* sugar puckering. The overall molecular conformation is similar to that of both adenosine and 2′-deoxyadenosine.

Comment

3′-Deoxynucleosides could function as possible inhibitors of RNA synthesis and, thus, may be useful in the treatment of cancer, as well as viral and other infections (Bazin & Chattopadhyaya, 1985; Rainny & Santi, 1983). As part of our program to study their molecular conformations (Karthe, Gautham, Kumar & Katti, 1997), we report here the structure of 3′-deoxyadenosine, (I).



(I)

An *ORTEP*92 (Vicković, 1994) view of the molecule with the atom-numbering scheme is shown in Fig. 1. The conformation of the base with respect to the ribose moiety is *anti* with the glycosidic torsion angle χ_{CN}, O4′—C1′—N9—C4, equal to −172.5 (6)°. In α-D-2′-deoxyadenosine (Watson, Sutor & Tollin, 1965) and also in β-D-adenosine (Lai & Marsh, 1972), the conformation is *anti*. The sugar pucker in the present structure is C3′-*endo*, as observed in adenosine. The pseudorotation phase angle (*P*) and the maximum amplitude of puckering (τ_M) are 4.4 and 38.4°, respectively. In 2′-deoxyadenosine, the sugar pucker is C3′-*exo*. The torsion angles φ_{OO} (O5′—C5′—C4′—O4′) and φ_{OC} (O5′—C5′—C4′—C3′) are 57.3 (8) and 175.5 (6)°, respectively. The conformation about the C4′—C5′ bond

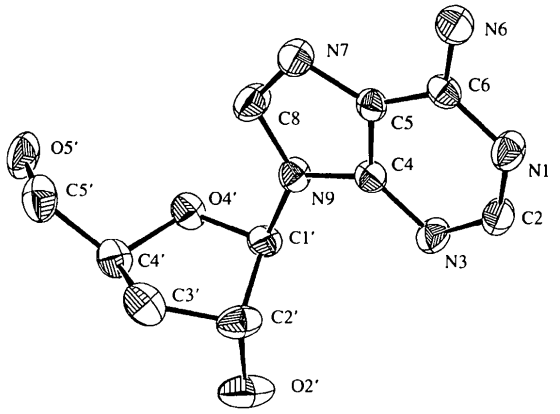


Fig. 1. Displacement ellipsoid plot of the title molecule (50% probability ellipsoids) with the atom-numbering scheme adopted.

is thus *gauche-gauche*. This is the same as in 2′-deoxyadenosine and adenosine. Indeed, the overall molecular conformation is very similar in the three compounds; only the ribose conformations are different. The absence of the 2′-O atom appears to be associated with the C3′-*exo* conformation in the structure of 2′-deoxyadenosine.

In the crystal, each molecule is hydrogen bonded to four symmetry-related molecules. The NH_2 group of the base forms a three-centred hydrogen bond with the O5′ atom of a symmetry-related molecule at $(x-\frac{1}{2}, -y+\frac{3}{2}, -z+2)$ and the N7 atom of a symmetry-related molecule at $(x-\frac{1}{2}, -y+\frac{3}{2}, -z+3)$.

Experimental

Thin plate-like crystals were grown by slow evaporation of an aqueous solution of the compound at room temperature.

Crystal data

$C_{10}H_{13}N_5O_3$
M_r = 251.25
Orthorhombic
$P2_12_12$
a = 10.231 (4) Å
b = 22.752 (7) Å
c = 4.817 (2) Å
V = 1121.3 (7) Å^3
Z = 4
D_x = 1.488 Mg m^{-3}
D_m = 1.495 Mg m^{-3}
D_m measured by flotation
Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 21 reflections
θ = 6–12°
μ = 0.114 mm^{-1}
T = 293 (2) K
Thin plate
0.30 × 0.10 × 0.05 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1194 measured reflections
1194 independent reflections
715 reflections with $I > 2\sigma(I)$
θ_{max} = 25°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 26$
$l = 0 \rightarrow 5$
3 standard reflections every 100 reflections
intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.128
S = 0.844
1193 reflections
216 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + 4.6216P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 0.264 e Å^{-3}
$\Delta\rho_{min}$ = −0.238 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.007 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
N1	0.2843 (5)	0.8454 (3)	1.3446 (14)	0.036 (2)
C2	0.3013 (7)	0.8903 (3)	1.1721 (19)	0.039 (2)
N3	0.4007 (5)	0.9027 (2)	1.0056 (14)	0.034 (2)
C4	0.4947 (6)	0.8615 (3)	1.0294 (15)	0.027 (2)
C5	0.4920 (6)	0.8128 (3)	1.1968 (15)	0.026 (2)
C6	0.3810 (7)	0.8046 (3)	1.3612 (16)	0.028 (2)
N6	0.3633 (6)	0.7597 (2)	1.5368 (15)	0.039 (2)
N7	0.6063 (6)	0.7803 (2)	1.1629 (14)	0.035 (2)
C8	0.6726 (7)	0.8101 (3)	0.9779 (17)	0.038 (2)
N9	0.6104 (5)	0.8597 (2)	0.8861 (12)	0.0273 (14)
C1′	0.6567 (6)	0.9052 (3)	0.6917 (16)	0.027 (2)
C2′	0.6962 (8)	0.9607 (3)	0.8453 (17)	0.038 (2)
O2′	0.6874 (5)	1.0079 (2)	0.6516 (11)	0.052 (2)
C3′	0.8390 (8)	0.9478 (3)	0.9192 (17)	0.041 (2)
C4′	0.8839 (7)	0.9162 (3)	0.6570 (17)	0.032 (2)
O4′	0.7705 (4)	0.8840 (2)	0.5603 (10)	0.0306 (12)
C5′	0.9962 (8)	0.8741 (3)	0.6954 (18)	0.044 (2)
O5′	1.0211 (5)	0.8445 (2)	0.4390 (12)	0.045 (2)

Table 2. *Selected torsion angles (°)*

O4′—C1′—C2′—C3′	−30.6 (7)	C2′—C1′—O4′—C4′	9.6 (7)
C1′—C2′—C3′—C4′	38.3 (7)	C3′—C4′—O4′—C1′	15.7 (7)
C2′—C3′—C4′—O4′	−33.6 (7)		

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP* (Frenz, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*92 (Vicković, 1994). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1055). Services for accessing these data are described at the back of the journal.

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Acetyl-ΔPhe-L-Ala-ΔPhe-D-Ala Methyl Ester

ANGELA TUZI,[a] ADRIANO FISSI[b] AND OSVALDO PIERONI[b,c]

[a]*Dipartimento di Chimica, Universitá di Napoli 'Federico II', Via Mezzocannone 4, 80134 Napoli, Italy,* [b]*CNR, Istituto di Biofisica, Via S. Lorenzo 26, 56100 Pisa, Italy, and* [c]*Dipartimento di Chimica e Chimica Industriale, Via Risorgimento 35, 56100 Pisa, Italy. E-mail: tuzi@chemna.dichi.unina.it*

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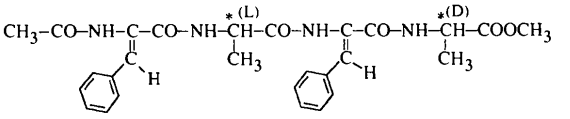
Abstract

The peptide chain of acetylphenylalanine-L-alanine-phenylalanine-D-alanine methyl ester, $C_{27}H_{30}N_4O_6$, adopts a 3_{10}-helical conformation having right-handed screw sense. The 3_{10}-helix is stabilized by intramolecular hydrogen bonds, between CO of the acetyl group and NH of ΔPhe^3, and between CO of ΔPhe^1 and NH of D-Ala^4. The hydrogen bonds form two consecutive ten-membered rings whose (φ, ψ) torsion angles are quite close to the standard values for type-III β-turns. In the crystal, the molecules are linked head-to-tail by intermolecular hydrogen bonds to form continuous helical columns. These are aligned along axes parallel to the *c* axis, with neighbouring columns running in opposite directions. There are no lateral hydrogen bonds between helical columns, but only hydrophobic interactions provided by the interdigitation of apolar side chains of the dehydro-phenylalanine residues, as well as of the C-terminal methyl ester groups.

Comment

Incorporation of α,β-unsaturated amino-acidic residues in a peptide sequence produces remarkable conformational consequences and can induce structural motifs which are not available when the same residues are saturated. Various types of helical structures have been found to occur depending on the specific sequence and positioning of dehydro residues (Rajashankar, Ramakumar, Jain & Chauhan, 1995; Tuzi *et al.*, 1996). 3_{10}-Helices have been observed for peptides containing two alternate dehydro-phenylalanine (ΔPhe) residues (Ciajolo, Tuzi, Pratesi, Fissi & Pieroni, 1991, 1992). Here we describe the crystal and molecular structure of the tetrapeptide Ac-ΔPhe^1-L-Ala^2-ΔPhe^3-D-Ala^4-OMe, (I).



(I)

In helix-forming peptides, the role of the chiral residues is known to be different depending on whether they are located at an internal position or at the C-terminal position; more specifically, if they are both of the L configuration, the alanine in position 2 would favour the right-handed screw sense whereas the alanine in position 4 would prefer the opposite left-handed sense (Pieroni, Fissi, Pratesi, Temussi & Ciardelli, 1993; Tuzi *et al.*, 1996). The presence of an alanine residue having D configuration at the C-terminal position, therefore, may be expected to produce a more marked propensity toward formation of a right-handed helix.

Relevant bond lengths, angles and torsion angles are reported in Table 1. They are in good agreement with corresponding values usually observed in peptides, including those containing dehydro-phenylalanine residues (Singh, Narula & Patel, 1990). The C=C double bonds show a *trans* configuration of the phenyl ring with respect to the C=O group. As already observed in analogous compounds (Ciajolo *et al.*, 1991, 1992), the slight shortening of N—C^α and C^α—CO bonds in ΔPhe^1 and ΔPhe^3 seems to indicate partial conjugation of the styryl side chains with the peptide chain. Complete conjugation, however, is hindered for steric reasons. In fact, for Phe^1, the plane of the C=C double bond (including atoms C1*A*, C1*B*, C1C, N1 and C1′) forms a skew angle of 132.7 (2)° with the plane of the preceding peptide bond (including atoms N1, C2, O1 and C1*A*) and an angle of 30.8 (2)° with the plane of the next peptide bond (involving atoms N2, C1′, O1′ and C1*A*). For Phe^3, the values of the corresponding angles are 61.6 (1) and 150.7 (2)°. The styryl groups themselves are not planar; in ΔPhe^1, the planes of the phenyl ring and the C=C double-bond plane form an angle of 34.4 (2)°, while in ΔPhe^3, they deviate from planarity to a minor extent [6.0 (9)°].

The molecular conformation of the peptide is shown in Fig. 1. It is characterized by the presence of two intramolecular hydrogen bonds (C=O of the acetyl