Professor Shafiq-ur-Rehman, Taxonomist, Department of Botany, University of Azad Jammu and Kashmir, Pakistan, for help in plant collection and identification, and the University of Calgary for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1439). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1141–1143

(1′*S*,5′*S*,6′*R*,8′*S*)-1-[(6′-Acetoxy-8′-hydroxy-2′-oxabicyclo[3.2.1]oct-5′-yl)oxymethyl]-N^4-benzoylcytosine†

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(*Received 13 January 1998; accepted 29 January 1998*)

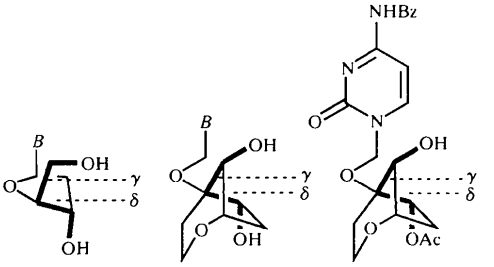
Abstract

The structure of the title compound, $C_{21}H_{23}N_3O_7$, has been determined at 193 K. The equivalent DNA-backbone torsion angles δ (O6′—C6′—C5′—C8′) and γ (C6′—C5′—C8′—O8′) are 157.3 (4) and 67.5 (5)°, respectively. An intramolecular hydrogen bond involving the hydroxy O8′ and carbonyl O2 atoms helps fix the molecule in an extended arrangement with the torsion angle between the bicyclo and pyrimidinyl moieties (C5′—O1—C1—N1) being 159.9 (4)°.

† Systematic name: (1*S*,5*S*,6*R*,8*S*)-5-[(4-benzamido-1,2-dihydro-2-oxopyrimidin-1-yl)methyloxy]-8-hydroxy-2-oxabicyclo[3.2.1]oct-6-yl acetate.

Comment

In our research programme on the synthesis and evaluation of the pairing properties of nucleic acid analogues, we became interested in oligonucleotides built from the bicyclo[3.2.1] nucleoside (1). In this class of nucleoside analogues, the natural deoxyribofuranose unit is replaced by a synthetic bicyclic sugar surrogate to which the nucleobases are attached *via* a flexible linker. Extrapolated to the oligomeric level, these structural changes bring about a locked conformation around the DNA-backbone torsion angles δ and γ in a geometry which conforms with that observed in DNA duplexes of the *B* type, while at the same time the structural preorganization imposed by the (cyclic) furanose unit in natural DNA is missing. In order to have access to precise geometrical data associated with the torsion angles δ and γ, as well as with the flexible base-linker unit of this class of nucleoside analogues, we synthesized (2) and studied its crystal structure.



Deoxyribonucleosides (1) (2)

The DNA-backbone torsion angles of interest are δ [O6′—C6′—C5′—C8′ 157.3 (4)°] and γ [C6′—C5′—C8′—O8′ 67.5 (5)°]. They compare well with the respective torsion angles found for natural DNA duplexes of the *B* type, with values of δ 122±30° and γ 57±10° (Saenger, 1984). The planes of the aromatic rings of the benzoyl protecting group and the cytosine core unit are slightly twisted at the C7—C8 bond [torsion angle C9—C8—C7—N4 is −16.1 (7)°]. The molecule is folded about the O1—C1 bond with a torsion angle C5′—O1—C1—N1 of 159.9 (4)°. An intramolecular hydrogen bond involving the hydroxy O8′ and carbonyl O2 atoms helps fix the molecule in an extended arrangement (see Table 1). The bond distances and angles in the molecule are normal within experimental error. The absolute configuration of the molecule was assigned with

respect to the starting material, D-arabinose, used for the synthesis.

In the crystal, the molecules are packed in pairs in a tail-to-tail arrangement. The base-linker moieties are separated by an average distance of *ca* 3.53 Å (for example, between atoms C8 and C5 of symmetry-related molecules).

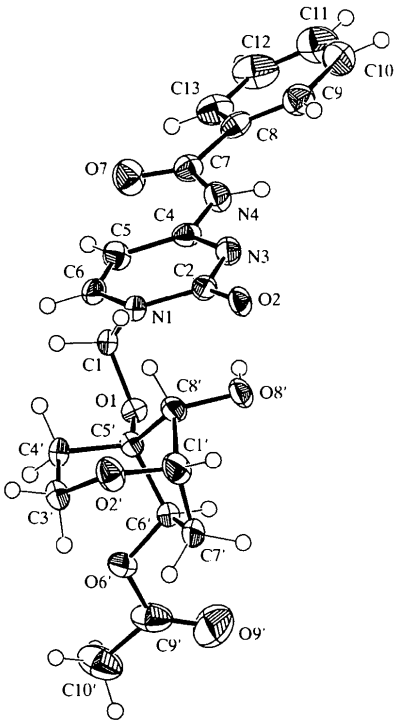


Fig. 1. A perspective view of (2), showing the numbering scheme used (displacement ellipsoids are at the 50% probability level).

Experimental

The title nucleoside (2) (Epple, 1997) was prepared in four steps from (1*S*,5*S*,6*R*,8*S*)-5,6-dihydroxy-8-(*tert*-butyldimethylsilyloxy)-2-oxabicyclo[3.2.1]octane (Egger *et al.*, 1998). After selective esterification of the secondary hydroxy group at C6′ with acetic anhydride, the remaining bridgehead hydroxy group at C5′ was transformed into the corresponding methoxymethylene ether function by treatment with NaI and methoxymethyl chloride in dimethoxyethane. This acetal was subsequently converted into the corresponding nucleoside by reaction with N^4-Bz-cytosine under standard Vorbrüggen conditions (Vorbrüggen & Bennua, 1981). In the final step, the nucleoside analogue was desilylated with ^{n}Bu$_4$NF in THF and crystallized from an MeOH–$MeCl_2$ (1:1) mixture by slow evaporation.

Crystal data

$C_{21}H_{23}N_3O_7$
M_r = 429.42
Monoclinic
$P2_1$
a = 10.564 (5) Å
b = 6.268 (2) Å
c = 15.878 (6) Å
β = 107.94 (2)°
V = 1000.2 (7) Å^3
Z = 2
D_x = 1.426 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 27 reflections
θ = 10.55–14.25°
μ = 0.108 mm^{-1}
T = 193 (2) K
Plate
0.54 × 0.23 × 0.15 mm
Colourless

Data collection

Stoe AED-2 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3898 measured reflections
1949 independent reflections
1511 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 25°
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 7$
$l = -18 \rightarrow 18$
2 standard reflections
frequency: 60 min
intensity decay: 5.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.146
S = 0.91
1949 reflections
283 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0945P)^2 + 0.5453P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.027
$\Delta\rho_{max}$ = 0.209 e Å^{-3}
$\Delta\rho_{min}$ = −0.211 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.012 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å) and hydrogen-bonding geometry (Å, °)*

O1—C1	1.416 (5)	C4—N4	1.379 (6)
O1—C5′	1.424 (6)	N4—C7	1.379 (7)
C1—N1	1.452 (6)	C1′—O2′	1.439 (7)
N1—C6	1.356 (6)	O2′—C3′	1.449 (6)
N1—C2	1.405 (6)	C6′—O6′	1.437 (6)
C2—O2	1.239 (6)	C8′—O8′	1.419 (6)
C2—N3	1.362 (6)	O6′—C9′	1.350 (7)
N3—C4	1.327 (7)	O9′—C9′	1.213 (9)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8′—H8′···O2	0.84	1.93	2.762 (5)	172.3

Data collection: *STADI*4 (Stoe & Cie, 1997*a*). Cell refinement: *STADI*4. Data reduction: *X-RED* (Stoe & Cie, 1997*b*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *Xtal_GX* (Hall & du Boulay, 1997). Software used to prepare material for publication: *SHELXL*97.

This work has been supported by the Swiss National Science Foundation.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1178). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1143–1144

(1α,3α,5α)-1,3,5-Trimethyl-1,3,5-cyclohexanetricarboxylic Acid Acetonitrile Solvate

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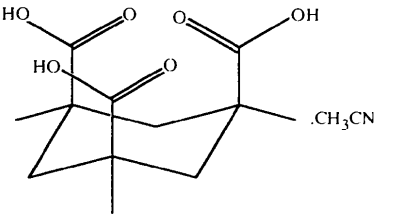
(*Received 30 September 1997; accepted 15 January 1998*)

Abstract

In the title compound, $C_{12}H_{18}O_6.CH_3CN$, both components have crystallographically imposed C_3 symmetry. The hydrogen bonds between the three carboxylic acid groups of (1α,3α,5α)-1,3,5-trimethyl-1,3,5-cyclohexanetricarboxylic acid (Kemp's triacid) and three other triacid moieties make a three-dimensional hydrogen-bonding network, producing large intermolecular cavities.

Comment

During a chemical study on the interactions between metal ions and several kinds of (1α,3α,5α)-1,3,5-trimethyl-1,3,5-cyclohexanetricarboxylic acid (Kemp's triacid) (Hirose *et al.*, 1995; Baldwin *et al.*, 1996), the crystal structures of the acid and an adduct were determined. The structure determined for the acid was disordered [trigonal, a = 25.152 (2), c = 12.592 (2) Å, Z = 18, $R\bar{3}$] and is yet to be published. This paper reports the acetonitrile adduct, (I), with the cyclohexane ring having a chair conformation. There is a hydrogen-bonding system between O11 and a neighbouring O10 atom at $(1-x, 1-y, -z)$ [O···O = 2.651 (3) Å and O11—H11···O10 = 175.4 (3)°]. There are no links between the acetonitrile and the triacid.



(I)

For the compound under investigation, each carboxylic acid group of each Kemp's triacid formed intermolecular hydrogen bonds with a centrosymmetrically related neighbour. A three-dimensional interconnecting network (Fig. 2), formed by hydrogen bonds, links neighbouring acid groups to give six-membered sets of Kemp's acids, in alternating hydrogen-bond links above and below the *ab* plane around the lattice points (0,0,0), $(\frac{2}{3},\frac{1}{3},\frac{1}{3})$ and $(\frac{1}{3},\frac{2}{3},\frac{2}{3})$. The acetonitrile lies outside this framework, in a void of 172 Å^3. Corey–Pauling–Kendrew (CPK) space-filling model studies showed that large intermolecular cavities would be formed within the crystal structure if this compound kept its C_3 symmetry. The introduction of acetonitrile is a stabilizing influence, as it would fill this void. The structure of the disodium tetrahydrate has also been determined (Bencini *et al.*, 1994).

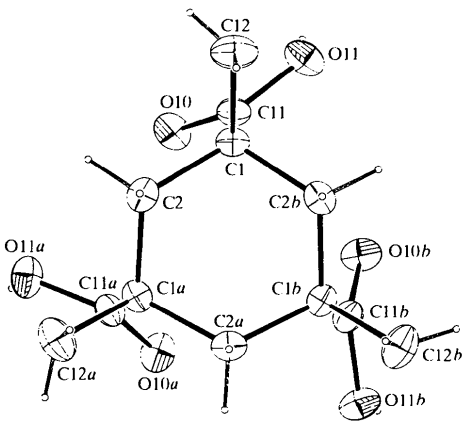


Fig. 1. *PLATON*96 (Spek, 1996) view of the (1α,3α,5α)-1,3,5-trimethyl-1,3,5-cyclohexanetricarboxylic acid of the title compound, with displacement ellipsoids at the 20% probability level. [Symmetry codes: (*a*) $1-y, x-y, z$; (*b*) $1-x+y, 1-x, z$.]

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