Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1109). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A 1′-C-Branched Uracil Nucleoside

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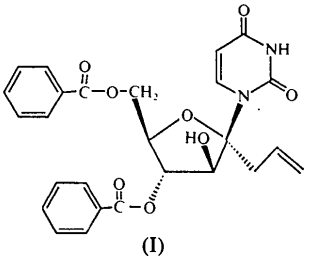
Abstract

The structure of the 1′-C-branched uracil nucleoside, 1-(1′-allyl-3′,5′-di-*O*-benzoyl-β-D-arabinofuranosyl)-2,4(1*H*,3*H*)-pyrimidinedione, $C_{26}H_{24}N_2O_8$, has been determined. The uracil nucleobase has the β orientation in this molecule.

Comment

Isolation of the nucleoside antibiotic 9-(β-D-psicofuranosyl)adenine, psicofuranine (Yüntsen, Ohkuma, Ishii & Yonehara, 1956), stimulated the synthesis of nucleosides having a carbon substituent at the anomeric position. Synthetic methods so far available for this class of compounds involve inital preparation of sugar components which are then condensed with nucleobases, forming a mixture of both α- and β-anomers in most cases [for a recent example see Faiver-Buet, Grouiller & Descotes (1992)]. Quite recently, a new stereospecific method for the synthesis of a variety of 1′-C-branched uracil nucleosides from a 1′,2′-unsaturated derivative has been reported (Haraguchi, Itoh, Tanaka, Yamaguchi & Miyasaka, 1994). The title compound (I) was obtained from 1-[1′-allyl-2′-bromo-3′,5′-bis-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-β-D-arabinofuranosyl]-uracil, which was synthesized by the Haraguchi *et al.* (1994) method, through hydrolysis of the O^2,2′-anhydro intermediate.



(I)

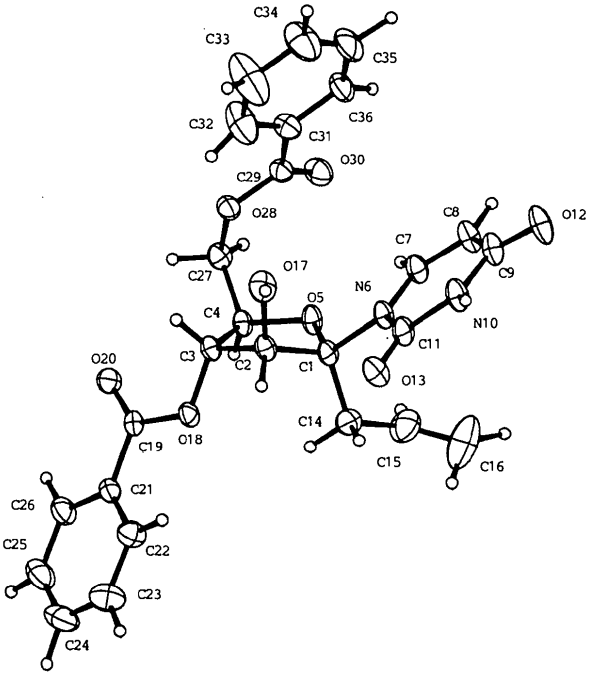


Fig. 1. Displacement ellipsoid plot of the title compound with ellipsoids drawn at the 50% probability level. Isotropic H-atom displacement parameters are represented by spheres of arbitrary size.

Experimental

Crystal data

$C_{26}H_{24}N_2O_8$
M_r = 492.48

Cu $K\alpha$ radiation
λ = 1.5418 Å

Orthorhombic
$P2_12_12_1$
a = 10.618 (1) Å
b = 21.954 (1) Å
c = 10.611 (1) Å
V = 2473.6 (2) Å^3
Z = 4
D_x = 1.322 Mg m^{-3}

Cell parameters from 20 reflections
θ = 28.0–31.5°
μ = 0.781 mm^{-1}
T = 297 K
Prism
0.30 × 0.18 × 0.50 mm
Clear

Data collection

Rigaku AFC-5 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2691 measured reflections
2623 independent reflections
2329 observed reflections [$F > 3\sigma(F)$]

R_{int} = 0.031
θ_{max} = 60°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 26$
$l = 0 \rightarrow 12$
3 standard reflections monitored every 150 reflections
intensity variation: <3%

Refinement

Refinement on F
R = 0.048
wR = 0.047
S = 1.50
2329 reflections
421 parameters
All H-atom parameters refined

Calculated weights $w = 1/[\sigma^2(F) + 0.005F^2]$
$(\Delta/\sigma)_{max}$ = 0.16
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	U_{eq}
C1	−1.0569 (3)	−0.3166 (1)	−0.6919 (3)	0.036 (1)
C2	−0.9157 (3)	−0.3179 (1)	−0.6522 (3)	0.038 (1)
C3	−0.9247 (3)	−0.3114 (1)	−0.5087 (3)	0.036 (1)
C4	−1.0515 (3)	−0.2799 (1)	−0.4836 (3)	0.035 (1)
O5	−1.1168 (2)	−0.2786 (1)	−0.6025 (2)	0.041 (1)
N6	−1.0756 (3)	−0.2860 (1)	−0.8158 (2)	0.038 (1)
C7	−1.1604 (4)	−0.2395 (1)	−0.8296 (3)	0.045 (1)
C8	−1.1845 (4)	−0.2129 (2)	−0.9406 (4)	0.053 (1)
C9	−1.1214 (4)	−0.2335 (2)	−1.0513 (3)	0.052 (1)
N10	−1.0367 (3)	−0.2800 (1)	−1.0309 (3)	0.051 (1)
C11	−1.0110 (3)	−0.3094 (1)	−0.9178 (3)	0.043 (1)
O12	−1.1361 (3)	−0.2141 (1)	−1.1595 (2)	0.070 (1)
O13	−0.9367 (3)	−0.3511 (1)	−0.9108 (2)	0.053 (1)
C14	−1.1178 (4)	−0.3793 (2)	−0.6931 (4)	0.049 (1)
C15	−1.2564 (5)	−0.3766 (3)	−0.7200 (6)	0.076 (2)
C16	−1.3110 (11)	−0.3941 (7)	−0.8202 (12)	0.162 (6)
O17	−0.8501 (3)	−0.2673 (1)	−0.6994 (2)	0.054 (1)
O18	−0.9218 (2)	−0.3723 (1)	−0.4564 (2)	0.040 (1)
C19	−0.9078 (3)	−0.3755 (1)	−0.3302 (3)	0.037 (1)
O20	−0.9145 (2)	−0.3312 (1)	−0.2632 (2)	0.045 (1)
C21	−0.8894 (3)	−0.4388 (1)	−0.2857 (3)	0.040 (1)
C22	−0.8553 (5)	−0.4851 (2)	−0.3672 (4)	0.055 (1)
C23	−0.8365 (6)	−0.5431 (2)	−0.3220 (6)	0.075 (2)
C24	−0.8523 (6)	−0.5554 (2)	−0.1956 (6)	0.075 (2)
C25	−0.8870 (5)	−0.5092 (2)	−0.1137 (5)	0.068 (1)
C26	−0.9034 (4)	−0.4510 (2)	−0.1579 (4)	0.052 (1)
C27	−1.0432 (4)	−0.2161 (1)	−0.4338 (3)	0.044 (1)
O28	−0.9705 (2)	−0.1781 (1)	−0.5167 (2)	0.046 (1)
C29	−1.0335 (4)	−0.1420 (1)	−0.5968 (4)	0.044 (1)
O30	−1.1463 (2)	−0.1370 (1)	−0.5966 (3)	0.059 (1)
C31	−0.9481 (4)	−0.1084 (1)	−0.6832 (4)	0.053 (1)
C32	−0.8221 (5)	−0.1116 (4)	−0.6736 (9)	0.122 (3)
C33	−0.7469 (8)	−0.0787 (5)	−0.7539 (12)	0.179 (6)
C34	−0.7973 (9)	−0.0450 (3)	−0.8471 (9)	0.118 (3)
C35	−0.9215 (9)	−0.0419 (3)	−0.8593 (7)	0.101 (3)
C36	−0.9995 (6)	−0.0729 (2)	−0.7771 (6)	0.075 (2)

Table 2. *Selected geometric parameters* (Å, °)

C1—O5	1.415 (4)	C9—O12	1.235 (5)
C1—N6	1.490 (4)	C9—N10	1.377 (6)
C1—C14	1.520 (6)	N10—C11	1.389 (5)
C1—C2	1.557 (5)	C11—O13	1.211 (5)
C2—O17	1.404 (5)	C14—C15	1.501 (7)
C2—C3	1.532 (5)	C15—C16	1.271 (14)
C3—O18	1.449 (4)	O18—C19	1.348 (4)
C3—C4	1.536 (5)	C19—O20	1.206 (4)
C4—O5	1.440 (4)	C19—C21	1.480 (5)
C4—C27	1.500 (5)	C27—O28	1.437 (5)
N6—C7	1.369 (5)	O28—C29	1.342 (5)
N6—C11	1.381 (4)	C29—O30	1.203 (5)
C7—C8	1.339 (6)	C29—C31	1.486 (6)
C8—C9	1.426 (6)		
O5—C1—N6	105.5 (2)	C7—C8—C9	119.8 (4)
O5—C1—C14	110.4 (3)	O12—C9—N10	119.0 (4)
O5—C1—C2	105.2 (2)	O12—C9—C8	126.6 (4)
N6—C1—C14	110.1 (3)	N10—C9—C8	114.4 (3)
N6—C1—C2	112.0 (3)	C9—N10—C11	127.4 (3)
C14—C1—C2	113.2 (3)	O13—C11—N6	123.8 (3)
O17—C2—C3	108.2 (3)	O13—C11—N10	122.1 (3)
O17—C2—C1	111.5 (3)	N6—C11—N10	114.0 (3)
C3—C2—C1	101.9 (2)	C15—C14—C1	112.5 (4)
O18—C3—C2	107.0 (3)	C16—C15—C14	126.4 (7)
O18—C3—C4	111.5 (3)	C19—O18—C3	115.5 (2)
C2—C3—C4	105.6 (2)	O20—C19—O18	122.5 (3)
O5—C4—C27	108.5 (3)	O20—C19—C21	125.1 (3)
O5—C4—C3	106.2 (2)	O18—C19—C21	112.3 (3)
C27—C4—C3	115.4 (3)	O28—C27—C4	111.0 (3)
C1—O5—C4	111.0 (2)	C29—O28—C27	117.6 (3)
C7—N6—C11	121.4 (3)	O30—C29—O28	123.3 (3)
C7—N6—C1	121.2 (3)	O30—C29—C31	124.3 (4)
C11—N6—C1	117.3 (3)	O28—C29—C31	112.4 (3)
C8—C7—N6	123.0 (3)		

Initial structure analysis was performed, with a continuous process connected to the data collection, using the fully automatic *FASE* procedure (Yamaguchi, 1993). The structure was solved by direct methods (*SAPI*85; Yao *et al.*, 1985), which is included in *FASE*. Data collection and cell refinement were performed with *AFD* (Rigaku Corporation, 1985*a*); *FASE* was used for data reduction. Program(s) used to refine structure: *RCRYSTAN* (Rigaku Corporation, 1985*b*). Molecular graphics: *ACV* (Stardent Computer Inc., 1990). Software used to prepare material for publication: *XPACK* (Yamaguchi, 1987).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1095). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Three 1,3,4-Trisubstituted β-Lactam Antibiotics

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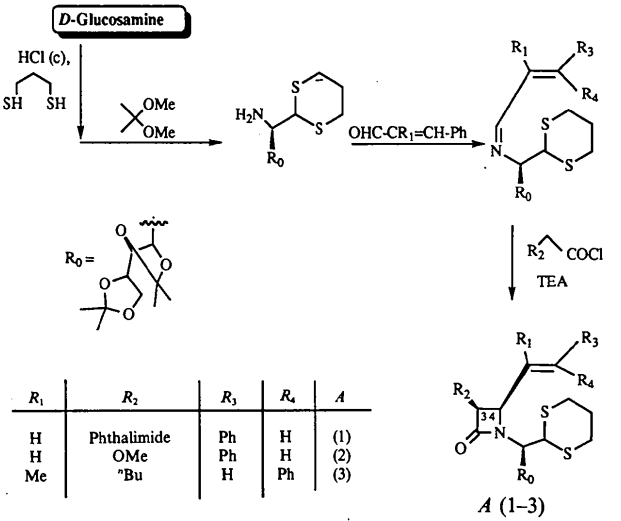
Abstract

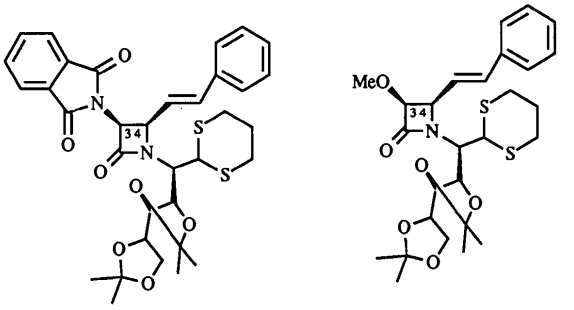
Monobactams (2-azetidinones) are four-membered cyclic amides which exhibit very important antibacterial properties, as well as β-lactamase- and elastase-inhibitory activities. A stereoselective asymmetric synthesis of 1,3,4-trisubstituted and 3,4-disubstituted 2-azetidinones was performed using D-glucosamine as the chiral auxiliary *via* a Staudinger [2+2] cycloaddition. The absolute stereochemistries at C3 and C4 of three of these potential therapeutic substances: 2-[1-{(1,3-dithian-2-yl)[2,2,2′,2′-tetramethyl-4,4′-bi(1,3-dioxolanyl)-5-yl]methyl}-2-oxo-4-(*E*)-styrylazetidin-3-yl]isoindol-1,3-dione, (1), 1-{(1,3-dithian-2-yl)[2,2,2′,2′-tetramethyl-4,4′-bi(1,3-dioxolanyl)-5-yl]methyl}-3-methoxy-4-(*E*)-styrylazetidin-2-one, (2), and 3-butyl-1-{(1,3-dithian-2-yl)[2,2,2′,2′-tetramethyl-4,4′-bi(1,3-dioxolanyl)-5-yl]methyl}-4-[1-methyl-(*Z*)-styryl]azetidin-2-one, (3), have been established by X-ray diffraction analyses. The four-membered ring is quite planar in compounds (1) and (3), but slightly bent in (2). The arrangement of the substituents in the vicinity of the lactam ring is similar in (1) and (3), but in (2) the dithiane ring is rotated around the N1—C2′ bond by approximately 120°.

Comment

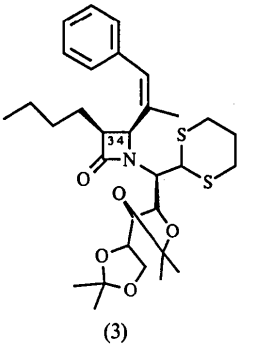
Monobactams (2-azetidinones) are four-membered cyclic amides. They exhibit very important antibacterial properties, as well as β-lactamase- and elastase-inhibitory activities (Mascaretti, Roveri & Danelon, 1993; Firestone, Barker, Pisano, Ashe & Dahlgren, 1990; Maillard *et al.*, 1990; Hagmann *et al.*, 1991, 1992). They have also been reported as potential hypocholesterolemic agents (Burnett *et al.*, 1991) and trombin inhibitors (Han, 1990). Recently, we published (Barton *et al.*, 1990; Adonias *et al.*, 1993) an asymmetric synthesis of 1,3,4-trisubstituted and 3,4-disubstituted 2-azetidinones, using D-glucosamine as chiral auxiliary, *via* a Staudinger [2+2] cycloaddition. The compounds (1), (2) and (3) were prepared in good overall yields according to the scheme below. Complete diastereospecificity was observed for compounds (1) and (3), while a 2:1 mixture of two *cis*-monobactams was obtained in the synthesis of (2). The *cis* orientation of the substituents



R_1	R_2	R_3	R_4	*A*
H	Phthalimide	Ph	H	(1)
H	OMe	Ph	H	(2)
Me	^{t}Bu	H	Ph	(3)



(1) (2)



(3)