Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-*C*-Azidomethyl-2-deoxy-3,4-*O*-isopropylidene-D-ribono-1,5-lactone

Francesco Punzo,[a]*‡ David J. Watkin,[b] Sarah F. Jenkinson,[c] Filipa P. da Cruz[c] and George W. J. Fleet[c]

[a]Dipartimento di Scienze Chimiche, Facoltà di Farmacia, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy, [b]Department of Chemical Crystallography, Chemical Research Laboratory, Mansfield Road, Oxford OX1 3TA, England, and [c]Department of Organic Chemistry, Chemical Research Laboratory, Mansfield Road, Oxford OX1 3TA, England

‡ Visiting Scientist at the Department of Chemical Crystallography, Chemical Research Laboratory, Mansfield Road, Oxford OX1 3TA, England.

Correspondence e-mail: fpunzo@unict.it

Key indicators

Single-crystal X-ray study
T = 250 K
Mean σ(C–C) = 0.006 Å
R factor = 0.047
wR factor = 0.129
Data-to-parameter ratio = 11.3

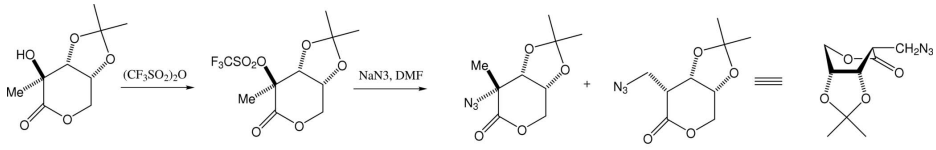
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 25 November 2005
Accepted 13 December 2005
Online 21 December 2005

X-ray crystallographic analysis firmly establishes the *ribo* stereochemistry and the unusual boat conformation of the title branched carbon chain lactone, $C_9H_{13}N_3O_4$, arising from an unexpected rearrangement in the nucleophilic substitution of a trifluoromethanesulfonate. There are two molecules in the asymmetric unit.

Comment

The Kiliani reaction of ketoses with cyanide (Hotchkiss *et al.*, 2004; Soengas *et al.*, 2005) provides access to a novel class of carbohydrate scaffold which contains a branched carbon chain. Such sugar building blocks have hitherto been rare and difficult to prepare in large quantities (Bols, 1996; Lichtenthaler & Peters, 2004). However, naturally occurring ketoses restrict the branched carbon chain to a hydroxymethyl group. A further class of branched carbohydrates is available from the Kiliani ascension on 1-deoxyketoses, themselves prepared by addition of organometallic reagents to sugar lactones. Thus, reaction of cyanide with a protected 1-deoxy-D-ribulose allowed the isolation of the isopropylidene derivative of arabinono-1,5-lactone, (1) (Hotchkiss *et al.*, 2006), shown to crystallize in a boat conformation (Punzo, Watkin, Jenkinson & Fleet, 2005).



(1) (2) (3) (4)

The value of protected sugar lactones such as (1) depends on being able to modify the tertiary alcohol functionality to other groups. Thus, the esterification of the free alcohol (1) with triflic anhydride in pyridine afforded the trifluoromethanesulfonate, (2), which on further reaction with sodium azide in dimethylformamide gave the *ribo*-azide, (3), as the major product in good yield, even though the overall reaction is a nucleophilic displacement at a very hindered position. It was possible that neighbouring group participation by an O atom might have been involved in the reaction but the X-ray crystal structure (Punzo, Watkin, Jenkinson, Cruz & Fleet, 2005) showed that the reaction proceeded with inversion of configuration to give the ribonolactone (3) in a boat conformation, with the C2-methyl group in a hindered flag-pole position. A small quantity of a second crystalline azide, the title compound, (4), was also isolated.

X-ray crystal-structure analysis of (4) firmly establishes that the relative configuration of the azidomethyl branch at C2 is in

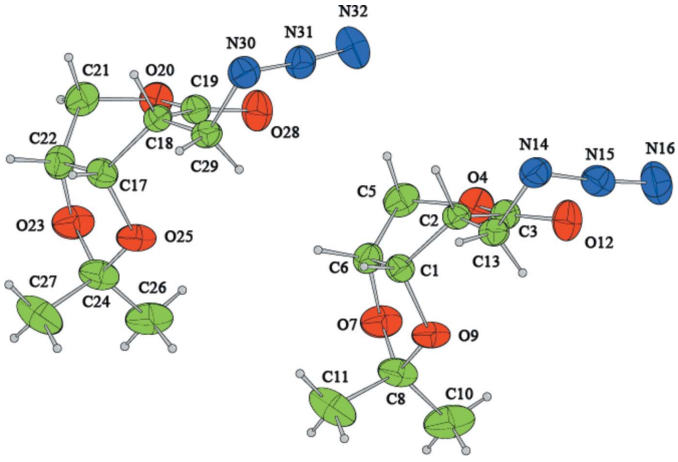


Figure 1
The asymmetric unit of (4), containing two molecules, with displacement ellipsoids drawn at the 50% probability level. H-atom radii are arbitrary.

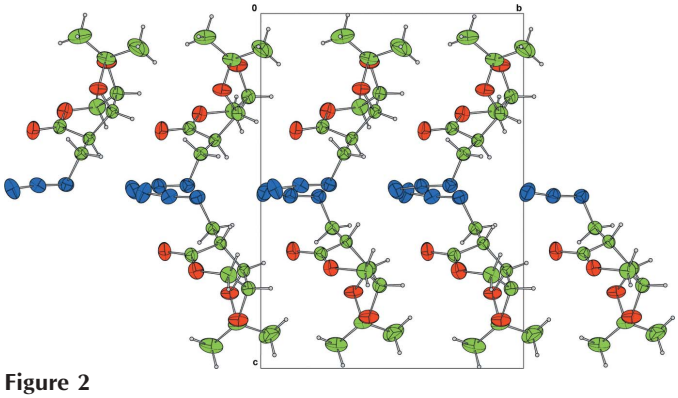


Figure 2
A packing diagram of (4), viewed down the *a* axis.

a bowsprit conformation. The absolute configuration of (4) was determined by the use of D-erythronolactone as the starting material for the synthesis. Azides (3) and (4) are likely to be useful building blocks for the synthesis of novel branched prolines and pipecolic acids, respectively.

In Fig. 2, a pseudo-translational operator of the form (0.48 + *x*, 0.48 + *y*, +*z*) is clearly detectable.

Experimental

The title lactone, (4) {m.p. 365–367 K; $[\alpha]_D^{23}$ −168.2% (*c* 1.0 in MeCN)}, was crystallized by dissolving it in ethyl acetate, adding cyclohexane and allowing slow competitive evaporation of the two solvents until clear colourless crystals formed. The multi-scan technique was used to correct for changes in the illuminated volume.

Crystal data

$C_9H_{13}N_3O_4$
M_r = 227.22
Monoclinic, $P2_1$
a = 6.6145 (2) Å
b = 11.1194 (4) Å
c = 15.0252 (8) Å
β = 91.6306 (13)°
V = 1104.65 (8) Å^3
Z = 4
D_x = 1.366 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 2605 reflections
θ = 5–30°
μ = 0.11 mm^{-1}
T = 250 K
Plate, colourless
0.30 × 0.20 × 0.10 mm

Data collection

Bruker Nonius KappaCCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.98, T_{max} = 0.99
5623 measured reflections
3275 independent reflections
1944 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 29.9°
h = −9 → 9
k = −15 → 15
l = −21 → 21

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.129
S = 1.08
3275 reflections
290 parameters
H-atom parameters constrained
$w = [1 - (F_o - F_c)^2/36\sigma^2(F)]^2/[38.7T_0(x) + 61.9T_1(x) + 38.9T_2(x)]$ where T_i are Chebychev polynomials and $x = F_c/F_{max}$ (Prince, 1982; Watkin, 1994)
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}
Extinction correction: Larson (1970), eq. 22
Extinction coefficient: 1.0 (2) × 10^2

Table 1
Selected geometric parameters (Å, °).

C5—C6	1.497 (6)	C21—C22	1.498 (6)
C2—C1—C6	111.9 (3)	C18—C17—O25	107.6 (3)
C2—C1—O9	107.8 (3)	C22—C17—O25	104.5 (3)
O9—C8—C11	111.4 (4)	O20—C21—C22	110.4 (3)
C18—C17—C22	112.1 (3)		

In the absence of significant anomalous dispersion effects, Friedel pairs were merged before refinement. H atoms were seen in difference Fourier maps. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry [C—H in the range 0.93–98 Å and U_{iso}(H) in the range 1.2–1.5 times U_{eq} of the parent atom], after which their positions were refined with riding constraints.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997)'; data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

Financial support (to FPC) provided by the Fundacao para a Ciencia e a Tecnologia, Portugal, is gratefully acknowledged.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, C. K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Bols, M. (1996). *Carbohydrate Building Blocks*. New York: John Wiley & Sons, Inc.
Hotchkiss, D. J., Jenkinson, S. F., Storer, R., Heinz, T. & Fleet, G. W. J. (2006). *Tetrahedron Lett.* **47**, 315–318.
Hotchkiss, D., Soengas, R., Simone, M. I., van Ameijde, J., Hunter, S., Cowley, A. R. & Fleet, G. W. J. (2004). *Tetrahedron Lett.* **45**, 9461–9464.
Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
Lichtenthaler, F. W. & Peters, S. (2004). *C. R. Chim.* **7**, 65–90.
Nonius (2001). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Prince, E. (1982). *Mathematical Techniques in Crystallography and Materials Science*. New York: Springer-Verlag.
Punzo, F., Watkin, D. J., Jenkinson, S. F., Cruz, F. P. & Fleet, G. W. J. (2005). *Acta Cryst.* E**61**, o511–o512.
Punzo, F., Watkin, D. J., Jenkinson, S. F. & Fleet, G. W. J. (2005). *Acta Cryst.* E**61**, o127–129.
Soengas, R., Izumori, K., Simone, M. I., Watkin, D. J., Skytte, U. P., Soetaert, W. & Fleet, G. W. J. (2005). *Tetrahedron Lett.* **46**, 5755–5759.
Watkin, D. J. (1994). *Acta Cryst.* A**50**, 411–437.
Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.

supporting information

Acta Cryst. (2006). E**62**, o321–o323 [doi:10.1107/S1600536805041632]

2-*C*-Azidomethyl-2-deoxy-3,4-*O*-isopropylidene-D-ribono-1,5-lactone

Francesco Punzo, David J. Watkin, Sarah F. Jenkinson, Filipa P. da Cruz and George W. J. Fleet

S1. Comment

The Kiliani reaction of ketoses with cyanide (Hotchkiss *et al.*, 2004; Soengas *et al.*, 2005) provides access to a novel class of carbohydrate scaffold which contains a branched carbon chain. Such sugar building blocks have hitherto been rare and difficult to prepare in large quantities (Bols, 1996; Lichtenthaler & Peters, 2004). However, naturally occurring ketoses restrict the branched carbon chain to a hydroxymethyl group. A further class of branched carbohydrates is available from the Kiliani ascension on 1-deoxyketoses, themselves prepared by addition of organometallic reagents to sugar lactones. Thus, reaction of cyanide with a protected 1-deoxy-*D*-ribulose allowed the isolation of the isopropylidene derivative of arabinono-1,5-lactone, (1) (Hotchkiss *et al.*, 2006), shown to crystallize in a boat conformation (Punzo, Watkin, Jenkinson & Fleet, 2005).

The value of protected sugar lactones such as (1) depends on being able to modify the tertiary alcohol functionality to other groups. Thus, the esterification of the free alcohol (1) with triflic anhydride in pyridine afforded the trifluoromethanesulfonate, (2), which on further reaction with sodium azide in dimethylformamide gave the *ribo*-azide, (3), as the major product in good yield, even though the overall reaction is a nucleophilic displacement at a very hindered position. It was possible that neighbouring group participation by an O atom might have been involved in the reaction but the X-ray crystal structure (Punzo, Watkin, Jenkinson, Cruz & Fleet, 2005) showed that the reaction proceeded with inversion of configuration to give the ribonolactone (3) in a boat conformation, with the C2-methyl group in a hindered flag-pole position. A small quantity of a second crystalline azide, the title compound, (4), was also isolated.

X-ray crystal analysis of (4) firmly establishes that the relative configuration of the azidomethyl branch at C2 is in a bow–sprit conformation. The absolute configuration of (4) was determined by the use of *D*-erythronolactone as the starting material for the synthesis. Azides (3) and (4) are likely to be useful building blocks for the synthesis of novel branched prolines and pipecolic acids, respectively.

From Fig. 2, it seems evident that a pseudo-translational operator of the form (0.48 + *x*, 0.48 + *y*, +*z*) is clearly detectable.

S2. Experimental

The title lactone, (4) {m.p. 365–367 K; $[\alpha]_D^{23}$ −168.2 (*c* 1.0 in MeCN)}, was crystallized by dissolving it in ethyl acetate, adding cyclohexane and allowing slow competitive evaporation of the two solvents until clear colourless crystals formed. The multi-scan technique was used to correct for changes in the illuminated volume.

S3. Refinement

In the absence of significant anomalous dispersion effects, Friedel pairs were merged before refinement. H atoms were seen in a difference Fourier maps. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry [C—H in the range 0.93–98 Å and U_{iso}(H) in the range 1.2–1.5 times U_{eq} of the adjacent

atom], after which their positions were refined with riding constraints.

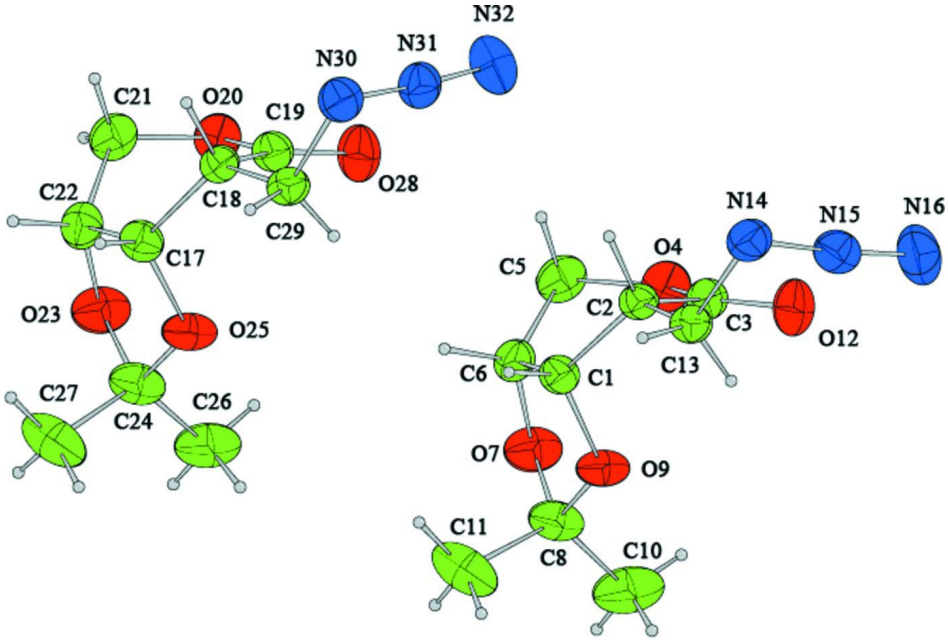


Figure 1

The asymmetric unit of (4), containing two molecules, with displacement ellipsoids drawn at the 50% probability level. H-atom radii are arbitrary.

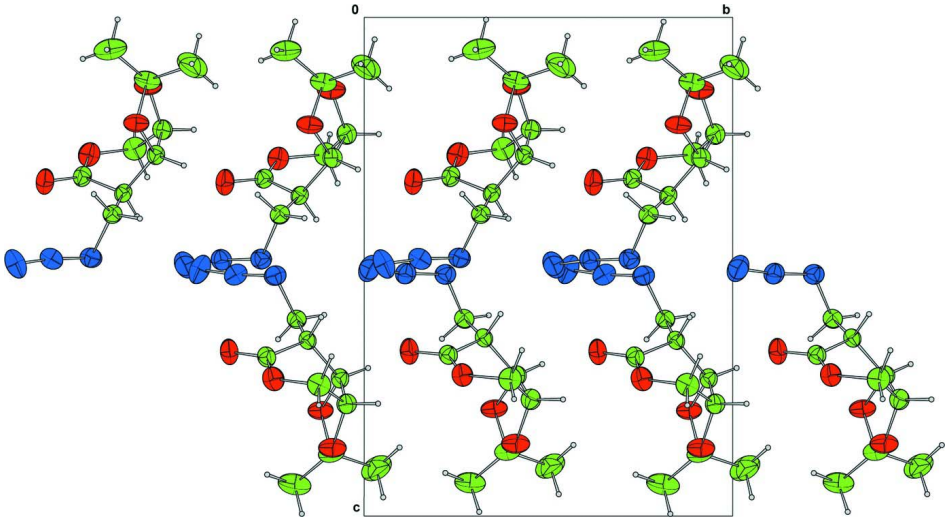


Figure 2

A packing diagram of (4), viewed down the *a* axis.

2-*C*-Azidomethyl-2-deoxy-3,4-*O*-isopropylidene-D-ribono-1,5-lactone

Crystal data

$C_9H_{13}N_3O_4$	a = 6.6145 (2) Å
M_r = 227.22	b = 11.1194 (4) Å
Monoclinic, $P2_1$	c = 15.0252 (8) Å
Hall symbol: P 2yb	β = 91.6306 (13)°

V = 1104.65 (8) Å^3
Z = 4
F(000) = 480
D_x = 1.366 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2605 reflections

θ = 5–30°
μ = 0.11 mm^{-1}
T = 250 K
Plate, colourless
0.30 × 0.20 × 0.10 mm

Data collection

Bruker Nonius KappaCCD area-detector diffractometer
Graphite monochromator
ω scans
Absorption correction: multi-scan *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997)
T_{min} = 0.98, T_{max} = 0.99

5623 measured reflections
3275 independent reflections
1944 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 29.9°, θ_{min} = 5.2°
h = −9→9
k = −15→15
l = −21→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.129
S = 1.08
3275 reflections
290 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

Method, part 1, Chebychev polynomial (Watkin, 1994; *P*rince, 1982) $w = 1/[A_0T_0(x) + A_1T_1(x) \cdots + A_{n-1}T_{n-1}(x)]$ where A_i are the Chebychev coefficients listed below and x = F/F_{max} Method = Robust Weighting (*P*rince, 1982) W = $w[1-(\delta F/6\sigma F)^2]^2$, A_i are 38.7 61.9 38.9 16.8 3.80
$(\Delta/\sigma)_{max}$ = 0.000084
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}
Extinction correction: Larson (1970), eq. 22
Extinction coefficient: 100 (20)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.1434 (5)	0.4343 (3)	0.2760 (2)	0.0325
C2	0.1712 (5)	0.3460 (3)	0.3525 (2)	0.0297
C3	0.2760 (5)	0.2350 (4)	0.3191 (3)	0.0353
O4	0.4472 (4)	0.2535 (3)	0.27514 (19)	0.0442
C5	0.5095 (6)	0.3773 (4)	0.2633 (3)	0.0444
C6	0.3404 (5)	0.4523 (3)	0.2251 (3)	0.0368
O7	0.2914 (4)	0.4136 (3)	0.13657 (17)	0.0499
C8	0.0759 (6)	0.4113 (4)	0.1262 (3)	0.0456
O9	0.0077 (4)	0.3815 (3)	0.21194 (17)	0.0411
C10	0.0181 (8)	0.3108 (6)	0.0639 (4)	0.0696
C11	−0.0025 (9)	0.5331 (6)	0.0961 (4)	0.0788
O12	0.2165 (5)	0.1336 (3)	0.3293 (2)	0.0505
C13	−0.0290 (5)	0.3168 (4)	0.3946 (2)	0.0331
N14	0.0038 (5)	0.2581 (3)	0.4822 (2)	0.0415
N15	−0.0430 (5)	0.1513 (3)	0.4842 (2)	0.0406
N16	−0.0843 (6)	0.0537 (4)	0.4944 (3)	0.0618
C17	0.5920 (5)	0.9137 (3)	0.2819 (2)	0.0355
C18	0.6377 (5)	0.8247 (3)	0.3572 (2)	0.0294

C19	0.7776 (5)	0.7281 (4)	0.3233 (2)	0.0334
O20	0.9443 (4)	0.7664 (3)	0.28289 (19)	0.0415
C21	0.9716 (6)	0.8956 (4)	0.2745 (3)	0.0433
C22	0.7852 (6)	0.9522 (4)	0.2340 (3)	0.0406
O23	0.7530 (4)	0.9107 (3)	0.14513 (18)	0.0523
C24	0.5423 (6)	0.8893 (4)	0.1302 (3)	0.0463
O25	0.4735 (4)	0.8523 (3)	0.21528 (18)	0.0441
C26	0.5129 (8)	0.7871 (5)	0.0669 (3)	0.0634
C27	0.4363 (9)	1.0045 (5)	0.1004 (4)	0.0761
O28	0.7494 (4)	0.6221 (3)	0.3305 (2)	0.0491
C29	0.4482 (5)	0.7715 (4)	0.3955 (2)	0.0340
N30	0.4865 (5)	0.7200 (3)	0.4847 (2)	0.0400
N31	0.5298 (5)	0.6122 (3)	0.4864 (2)	0.0410
N32	0.5691 (6)	0.5142 (4)	0.4964 (3)	0.0617
H11	0.0921	0.5106	0.2969	0.0389*
H21	0.2632	0.3832	0.3987	0.0360*
H51	0.5554	0.4115	0.3202	0.0528*
H52	0.6189	0.3770	0.2223	0.0525*
H61	0.3811	0.5377	0.2254	0.0434*
H101	−0.1295	0.3018	0.0648	0.1027*
H102	0.0567	0.3308	0.0043	0.1030*
H103	0.0836	0.2367	0.0832	0.1026*
H111	−0.1471	0.5321	0.0933	0.1182*
H112	0.0425	0.5963	0.1375	0.1186*
H113	0.0480	0.5518	0.0375	0.1189*
H131	−0.1006	0.3913	0.4034	0.0398*
H132	−0.1105	0.2663	0.3545	0.0404*
H171	0.5167	0.9832	0.3048	0.0421*
H181	0.7078	0.8701	0.4052	0.0353*
H211	1.0078	0.9279	0.3326	0.0514*
H212	1.0822	0.9070	0.2346	0.0509*
H221	0.7977	1.0397	0.2340	0.0486*
H261	0.3729	0.7631	0.0651	0.0936*
H262	0.5505	0.8124	0.0085	0.0939*
H263	0.5920	0.7202	0.0865	0.0938*
H271	0.2935	0.9907	0.0935	0.1132*
H272	0.4590	1.0679	0.1426	0.1141*
H273	0.4915	1.0282	0.0441	0.1135*
H291	0.3491	0.8380	0.4026	0.0408*
H292	0.3931	0.7112	0.3556	0.0413*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0320 (17)	0.0298 (19)	0.036 (2)	0.0043 (15)	−0.0033 (14)	−0.0005 (15)
C2	0.0285 (16)	0.0282 (18)	0.0323 (19)	0.0048 (14)	−0.0041 (14)	−0.0033 (15)
C3	0.0356 (18)	0.031 (2)	0.039 (2)	0.0035 (16)	−0.0028 (16)	−0.0030 (16)
O4	0.0340 (13)	0.0451 (17)	0.0540 (18)	0.0085 (13)	0.0078 (12)	−0.0046 (14)

C5	0.0307 (18)	0.053 (3)	0.050 (3)	−0.0055 (18)	0.0035 (16)	−0.002 (2)
C6	0.0354 (19)	0.037 (2)	0.038 (2)	−0.0065 (16)	0.0005 (16)	0.0010 (16)
O7	0.0409 (14)	0.074 (2)	0.0348 (15)	−0.0044 (15)	0.0046 (11)	−0.0005 (15)
C8	0.0377 (19)	0.066 (3)	0.033 (2)	0.001 (2)	−0.0015 (16)	0.009 (2)
O9	0.0299 (12)	0.062 (2)	0.0315 (15)	−0.0020 (12)	−0.0035 (10)	0.0011 (14)
C10	0.060 (3)	0.104 (4)	0.044 (3)	−0.006 (3)	−0.005 (2)	−0.012 (3)
C11	0.091 (4)	0.084 (4)	0.061 (3)	0.020 (3)	−0.011 (3)	0.025 (3)
O12	0.0572 (17)	0.0309 (16)	0.0637 (19)	0.0017 (13)	0.0062 (14)	−0.0032 (13)
C13	0.0315 (17)	0.0350 (19)	0.033 (2)	0.0017 (15)	−0.0021 (14)	−0.0009 (16)
N14	0.0417 (17)	0.046 (2)	0.037 (2)	−0.0091 (16)	−0.0016 (14)	0.0020 (16)
N15	0.0290 (17)	0.050 (2)	0.043 (2)	−0.0014 (15)	0.0016 (13)	0.0071 (17)
N16	0.061 (2)	0.045 (2)	0.079 (3)	−0.005 (2)	0.003 (2)	0.019 (2)
C17	0.0334 (17)	0.036 (2)	0.037 (2)	0.0059 (17)	0.0009 (15)	0.0000 (17)
C18	0.0270 (16)	0.0290 (18)	0.0321 (19)	0.0017 (14)	−0.0008 (14)	−0.0032 (15)
C19	0.0329 (18)	0.032 (2)	0.035 (2)	0.0035 (16)	−0.0009 (15)	−0.0017 (16)
O20	0.0325 (12)	0.0422 (16)	0.0500 (17)	0.0036 (12)	0.0049 (12)	−0.0021 (14)
C21	0.0299 (18)	0.050 (3)	0.050 (2)	−0.0060 (18)	0.0037 (16)	0.001 (2)
C22	0.044 (2)	0.037 (2)	0.041 (2)	−0.0047 (17)	0.0037 (16)	0.0006 (17)
O23	0.0446 (15)	0.077 (2)	0.0355 (16)	−0.0063 (16)	0.0059 (12)	0.0007 (16)
C24	0.041 (2)	0.066 (3)	0.033 (2)	0.004 (2)	0.0007 (16)	0.006 (2)
O25	0.0344 (13)	0.067 (2)	0.0306 (15)	−0.0025 (14)	−0.0033 (11)	0.0039 (14)
C26	0.059 (3)	0.091 (4)	0.040 (3)	−0.001 (3)	−0.007 (2)	−0.005 (3)
C27	0.090 (4)	0.080 (4)	0.058 (3)	0.021 (3)	−0.009 (3)	0.022 (3)
O28	0.0510 (17)	0.0323 (16)	0.0645 (19)	0.0053 (13)	0.0083 (14)	−0.0022 (13)
C29	0.0303 (16)	0.037 (2)	0.035 (2)	0.0009 (16)	−0.0028 (14)	−0.0018 (17)
N30	0.0403 (17)	0.042 (2)	0.038 (2)	−0.0027 (16)	0.0026 (14)	0.0006 (15)
N31	0.0418 (19)	0.040 (2)	0.041 (2)	−0.0056 (16)	0.0027 (14)	0.0025 (16)
N32	0.073 (3)	0.046 (2)	0.066 (3)	0.005 (2)	0.003 (2)	0.013 (2)

Geometric parameters (Å, º)

C1—C2	1.519 (5)	C17—C18	1.526 (5)
C1—C6	1.543 (5)	C17—C22	1.545 (5)
C1—O9	1.424 (4)	C17—O25	1.427 (5)
C1—H11	0.969	C17—H171	0.987
C2—C3	1.508 (5)	C18—C19	1.515 (5)
C2—C13	1.518 (5)	C18—C29	1.514 (5)
C2—H21	0.999	C18—H181	0.986
C3—O4	1.343 (4)	C19—O20	1.343 (4)
C3—O12	1.206 (5)	C19—O28	1.198 (5)
O4—C5	1.449 (5)	O20—C21	1.453 (5)
C5—C6	1.497 (6)	C21—C22	1.498 (6)
C5—H51	0.976	C21—H211	0.968
C5—H52	0.964	C21—H212	0.968
C6—O7	1.426 (5)	C22—O23	1.423 (5)
C6—H61	0.986	C22—H221	0.976
O7—C8	1.430 (4)	O23—C24	1.426 (5)
C8—O9	1.416 (5)	C24—O25	1.430 (5)

C8—C10	1.500 (7)	C24—C26	1.492 (7)
C8—C11	1.516 (7)	C24—C27	1.521 (7)
C10—H101	0.982	C26—H261	0.963
C10—H102	0.963	C26—H262	0.961
C10—H103	0.972	C26—H263	0.951
C11—H111	0.956	C27—H271	0.960
C11—H112	0.979	C27—H272	0.958
C11—H113	0.974	C27—H273	0.967
C13—N14	1.480 (5)	C29—N30	1.473 (5)
C13—H131	0.965	C29—H291	0.996
C13—H132	0.975	C29—H292	0.964
N14—N15	1.228 (5)	N30—N31	1.233 (5)
N15—N16	1.131 (5)	N31—N32	1.130 (5)
C2—C1—C6	111.9 (3)	C18—C17—C22	112.1 (3)
C2—C1—O9	107.8 (3)	C18—C17—O25	107.6 (3)
C6—C1—O9	104.1 (3)	C22—C17—O25	104.5 (3)
C2—C1—H11	110.9	C18—C17—H171	109.9
C6—C1—H11	110.8	C22—C17—H171	112.2
O9—C1—H11	111.1	O25—C17—H171	110.3
C1—C2—C3	108.9 (3)	C17—C18—C19	108.7 (3)
C1—C2—C13	111.4 (3)	C17—C18—C29	112.7 (3)
C3—C2—C13	112.2 (3)	C19—C18—C29	111.8 (3)
C1—C2—H21	108.4	C17—C18—H181	106.8
C3—C2—H21	107.0	C19—C18—H181	109.2
C13—C2—H21	108.7	C29—C18—H181	107.4
C2—C3—O4	116.1 (3)	C18—C19—O20	116.3 (3)
C2—C3—O12	124.7 (3)	C18—C19—O28	124.7 (3)
O4—C3—O12	119.2 (3)	O20—C19—O28	119.0 (3)
C3—O4—C5	116.9 (3)	C19—O20—C21	117.3 (3)
O4—C5—C6	111.4 (3)	O20—C21—C22	110.4 (3)
O4—C5—H51	110.2	O20—C21—H211	108.5
C6—C5—H51	109.2	C22—C21—H211	112.9
O4—C5—H52	107.2	O20—C21—H212	106.4
C6—C5—H52	108.8	C22—C21—H212	108.7
H51—C5—H52	109.9	H211—C21—H212	109.7
C1—C6—C5	111.7 (3)	C17—C22—C21	112.1 (3)
C1—C6—O7	104.5 (3)	C17—C22—O23	104.1 (3)
C5—C6—O7	109.7 (3)	C21—C22—O23	110.2 (3)
C1—C6—H61	110.9	C17—C22—H221	110.3
C5—C6—H61	109.5	C21—C22—H221	110.5
O7—C6—H61	110.5	O23—C22—H221	109.4
C6—O7—C8	107.8 (3)	C22—O23—C24	108.8 (3)
O7—C8—O9	104.4 (3)	O23—C24—O25	104.0 (3)
O7—C8—C10	108.5 (4)	O23—C24—C26	109.7 (4)
O9—C8—C10	108.2 (4)	O25—C24—C26	108.2 (4)
O7—C8—C11	110.4 (4)	O23—C24—C27	110.2 (4)
O9—C8—C11	111.4 (4)	O25—C24—C27	110.5 (4)

C10—C8—C11	113.6 (4)	C26—C24—C27	113.8 (4)
C1—O9—C8	107.9 (3)	C24—O25—C17	107.9 (3)
C8—C10—H101	107.7	C24—C26—H261	109.7
C8—C10—H102	109.8	C24—C26—H262	109.0
H101—C10—H102	109.1	H261—C26—H262	109.2
C8—C10—H103	109.9	C24—C26—H263	109.8
H101—C10—H103	110.1	H261—C26—H263	108.2
H102—C10—H103	110.2	H262—C26—H263	111.0
C8—C11—H111	109.6	C24—C27—H271	109.9
C8—C11—H112	110.9	C24—C27—H272	111.2
H111—C11—H112	108.8	H271—C27—H272	108.9
C8—C11—H113	109.7	C24—C27—H273	107.8
H111—C11—H113	109.3	H271—C27—H273	110.2
H112—C11—H113	108.5	H272—C27—H273	108.9
C2—C13—N14	110.9 (3)	C18—C29—N30	112.0 (3)
C2—C13—H131	108.2	C18—C29—H291	107.8
N14—C13—H131	108.4	N30—C29—H291	106.8
C2—C13—H132	109.8	C18—C29—H292	109.7
N14—C13—H132	111.1	N30—C29—H292	110.3
H131—C13—H132	108.3	H291—C29—H292	110.1
C13—N14—N15	114.7 (3)	C29—N30—N31	115.5 (3)
N14—N15—N16	173.6 (5)	N30—N31—N32	173.5 (5)