Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Methyl 2,4-anhydro-5-azido-5,6-dideoxy-L-altronate

David J. Watkin,[a]* Stephen W. Johnson,[b] John H. Jones[b] and George W. J. Fleet[b]

[a]Department of Chemical Crystallography, Chemical Research Laboratory, Mansfield Road, Oxford OX1 3TA, England, and [b]Department of Organic Chemistry, Chemical Research Laboratory, Mansfield Road, Oxford OX1 3TA, England

Correspondence e-mail: david.watkin@chem.ox.ac.uk

Key indicators

Single-crystal X-ray study
T = 185 K
Mean σ(C–C) = 0.003 Å
R factor = 0.051
wR factor = 0.095
Data-to-parameter ratio = 10.8

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

Received 5 August 2004
Accepted 11 August 2004
Online 28 August 2004

The title compound, $C_7H_{11}N_3O_4$, was prepared from L-rhamnose as a conformationally restricted dipeptide isostere containing an oxetane ring. Its crystal structure was determined to confirm the synthetic product.

Comment

Sugar amino acids (SAA) are an important class of peptidomimetics (Schweizer, 2002; Gruner *et al.*, 2002). In particular, D-amino acid scaffolds derived from pyranoses (Kriek *et al.*, 2003; El Oualid *et al.*, 2002) and furanoses (van Well *et al.*, 2003; Chakraborty *et al.*, 2002) provide a well established series of conformationally fixed dipeptide isosteres. The azido ester described here, (I), prepared from L-rhamnose, is among the first examples of building blocks for dipeptide isosteres which contain an oxetane ring; it may be viewed as a conformationally restricted dipeptide isostere of L-ala-D-ser, (II).

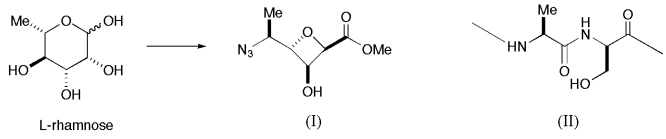

Fig. 1 shows the asymmetric unit (I). Its absolute structure (C4 *R* conformation, and C6 and C9 *S* conformation) was assumed based on the known absolute structure of the starting material.

The crystal packing for (I) consists of slightly pleated ribbons of molecules linked by weak hydrogen bonds, with the sheets stacked in van der Waals contact (Fig. 2).

Experimental

Compound (I) (Johnson *et al.*, 2004) was recrystallized from chloroform by solvent diffusion with hexane to give colourless plate-shaped crystals.

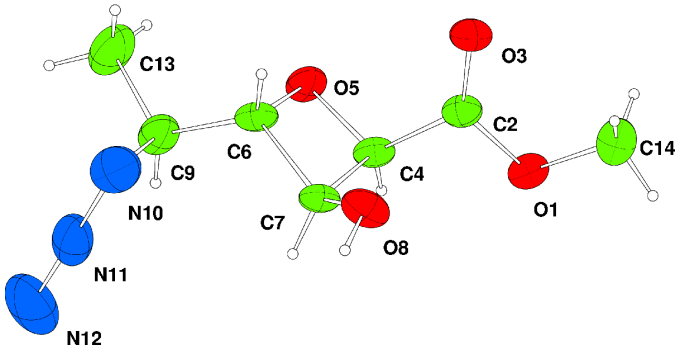

Figure 1
The asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level. H-atom radii are arbitrary.

Crystal data

$C_7H_{11}N_3O_4$
M_r = 201.18
Monoclinic, $P2_1$
a = 4.6318 (2) Å
b = 9.8575 (5) Å
c = 10.6310 (6) Å
β = 92.084 (2)°
V = 485.07 (4) Å^3
Z = 2
D_x = 1.377 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1439 reflections
θ = 5–32°
μ = 0.11 mm^{-1}
T = 185 K
Plate, colourless
0.50 × 0.40 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997)
T_{min} = 0.96, T_{max} = 0.98
4689 measured reflections
1733 independent reflections
1733 reflections with $I > -3\sigma(I)$
R_{int} = 0.021
θ_{max} = 32.0°
$h = -6 \rightarrow 6$
$k = -14 \rightarrow 8$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.095
S = 1.01
1733 reflections
160 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F) + (0.034P)^2 + 0.093P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.331 (2)	C6—C7	1.533 (2)
O1—C14	1.445 (3)	C6—C9	1.521 (3)
C2—O3	1.204 (2)	C7—O8	1.405 (2)
C2—C4	1.513 (3)	C9—N10	1.486 (3)
C4—O5	1.439 (2)	C9—C13	1.515 (3)
C4—C7	1.540 (2)	N10—N11	1.234 (3)
O5—C6	1.451 (2)	N11—N12	1.132 (4)
C2—O1—C14	116.48 (17)	C7—C6—C9	117.75 (15)
O1—C2—O3	124.83 (18)	C4—C7—C6	84.73 (13)
O1—C2—C4	110.25 (15)	C4—C7—O8	114.53 (15)
O3—C2—C4	124.92 (17)	C6—C7—O8	117.18 (15)
C2—C4—O5	111.04 (14)	C6—C9—N10	105.37 (17)
C2—C4—C7	114.58 (14)	C6—C9—C13	111.88 (19)
O5—C4—C7	91.58 (13)	N10—C9—C13	110.54 (19)
C4—O5—C6	91.52 (12)	C9—N10—N11	113.4 (2)
O5—C6—C7	91.38 (13)	N10—N11—N12	174.7 (3)
O5—C6—C9	110.23 (15)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O8—H5···O3^{i}	0.82 (4)	2.25 (3)	2.990 (2)	150 (3)
O8—H5···O5^{i}	0.82 (4)	2.32 (3)	2.962 (2)	135 (3)

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

Because the intensity data were collected with molybdenum radiation, there were no measurable anomalous differences, as a consequence of which it was admissible to merge Freidel pairs of reflections. The absolute structure of (I) was assumed to correlate with the known absolute structure of the L-rhamnose starting material. All H atoms were found in difference-density syntheses. They were initially refined with soft restraints on the bonds to regularize their geometry (bond lengths to accepted values, angles either set by symmetry or to accepted values, and U_{iso} dependent upon the adjacent bonded atom), after which they were refined with riding constraints only.

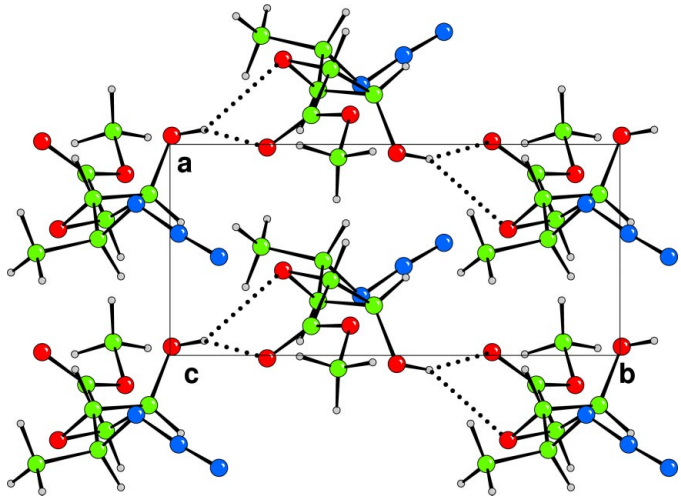

Figure 2
Packing diagram of (I), viewed down the c axis. The weakly hydrogen-bonded pleated ribons in the bc plane are simply stacked along the a axis. Hydrogen bonds are shown as dashed lines.

Data collection: *COLLECT* (Nonius, 1997–2001); cell refinement: *DENZO*/*SCALEPACK*; data reduction: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*92 (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*.

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, K., Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Chakraborty, T. K., Ghosh, S. & Jayaprakash, S. (2002). *Curr. Med. Chem.* **9**, 421–435.
El Oualid, F., Bruining, L., Leroy, I. M., Cohen, L. H., van Boom, J. H., van der Marel, G. A., Overkleeft, H. S. & Overhand, M. (2002). *Helv. Chim. Acta*, **85**, 3455–3472.
Gruner, S. A. W., Locardi, E., Lohof, E. & Kessler, H. (2002). *Chem. Rev.* **102**, 491–514.
Johnson, S. W., Jenkinson, S. F., Angus, D., Jones, J. H., Watkin, D. J. & Fleet, G. W. J. (2004). *Tetrahedron: Asymmetry*, **15**. In the press.
Kriek, N. M. A. J., van der Hout, E., Kelly, P., van Meijgaarden, K. E., Geluk, A., Ottenhoff, T. H. M., van der Marel, G. A., Overhand, M., van Boom, J. H., Valentijn, A. R. P. M. & Overkleeft, H. S. (2003). *Eur. J. Org. Chem.* pp. 2418–2427.
Nonius (1997–2001). *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 and R. M. Sweet, pp. 307–326. New York: Academic Press.
Schweizer, F. (2002) *Angew. Chem. Int. Ed.* **41**, 230–253.
Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.
Well, R. M. van, Marinelli, L., Altona, C., Erkelens, K., Siegal, G., van Raaij, M., Llamas-Saiz, A. L., Kessler, H., Novellino, E., Lavecchia, A., van Boom, J. H. & Overhand, M. (2003). *J. Am. Chem. Soc.* **125**, 10822–10829.

supporting information

Acta Cryst. (2004). E**60**, o1609–o1610 [https://doi.org/10.1107/S1600536804019968]

Methyl 2,4-anhydro-5-azido-5,6-dideoxy-L-altronate

David J. Watkin, Stephen W. Johnson, John H. Jones and George W. J. Fleet

Methyl 2,4-anhydro-5-azido-5,6-dideoxy-*L*-altronate

Crystal data

$C_7H_{11}N_3O_4$
$M_r = 201.18$
Monoclinic, $P2_1$
Hall symbol: P 2yb
$a = 4.6318$ (2) Å
$b = 9.8575$ (5) Å
$c = 10.6310$ (6) Å
$\beta = 92.084$ (2)°
$V = 485.07$ (4) Å^3
$Z = 2$
$F(000) = 212$
$D_x = 1.377$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1439 reflections
$\theta = 5$–32°
$\mu = 0.11$ mm^{-1}
$T = 185$ K
Plate, colourless
0.50 × 0.40 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
Graphite monochromator
ω scans
Absorption correction: multi-scan DENZO/SCALEPACK (Otwinowski & Minor, 1997)
$T_{min} = 0.96$, $T_{max} = 0.98$
4689 measured reflections
1733 independent reflections
1733 reflections with $I > -3\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 32.0°$, $\theta_{min} = 5.3°$
$h = -6 \rightarrow 6$
$k = -14 \rightarrow 8$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.095$
$S = 1.01$
1733 reflections
160 parameters
35 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: difference Fourier map
Only H-atom coordinates refined
$w = 1/[\sigma^2(F) + (0.034P)^2 + 0.093P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.000205$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.1410 (3)	0.40054 (18)	0.21529 (13)	0.0400
C2	0.1392 (4)	0.3140 (2)	0.31133 (17)	0.0307
O3	−0.0147 (3)	0.21590 (17)	0.31663 (13)	0.0401
C4	0.3567 (4)	0.3571 (2)	0.41317 (18)	0.0299
O5	0.4021 (3)	0.25130 (15)	0.50505 (13)	0.0355

C6	0.2570 (4)	0.32935 (18)	0.59975 (18)	0.0320
C7	0.2362 (3)	0.45325 (19)	0.51267 (17)	0.0282
O8	−0.0413 (3)	0.50394 (17)	0.48281 (16)	0.0405
C9	0.4480 (5)	0.3407 (2)	0.71873 (19)	0.0401
N10	0.2816 (5)	0.4247 (2)	0.80673 (19)	0.0545
N11	0.4227 (5)	0.5193 (3)	0.85376 (19)	0.0564
N12	0.5334 (7)	0.6089 (3)	0.9016 (3)	0.0819
C13	0.5152 (8)	0.2029 (3)	0.7759 (3)	0.0665
C14	−0.0618 (5)	0.3739 (3)	0.1117 (2)	0.0501
H41	0.534 (3)	0.390 (2)	0.3796 (16)	0.0374*
H61	0.067 (4)	0.2891 (19)	0.6166 (16)	0.0383*
H71	0.370 (3)	0.5239 (17)	0.5357 (17)	0.0350*
H91	0.626 (4)	0.391 (2)	0.7011 (18)	0.0519*
H131	0.645 (5)	0.216 (3)	0.851 (2)	0.0843*
H132	0.324 (5)	0.168 (3)	0.796 (2)	0.0843*
H133	0.608 (5)	0.147 (3)	0.711 (2)	0.0843*
H141	−0.034 (5)	0.450 (2)	0.056 (2)	0.0677*
H142	−0.261 (4)	0.370 (3)	0.141 (2)	0.0677*
H143	−0.005 (6)	0.289 (2)	0.076 (3)	0.0677*
H5	−0.069 (6)	0.576 (4)	0.519 (3)	0.0610*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0484 (8)	0.0328 (7)	0.0388 (7)	−0.0058 (6)	0.0007 (6)	0.0063 (6)
C2	0.0334 (8)	0.0237 (8)	0.0353 (8)	0.0013 (7)	0.0067 (6)	−0.0004 (7)
O3	0.0482 (7)	0.0302 (7)	0.0419 (7)	−0.0118 (6)	0.0023 (6)	0.0011 (6)
C4	0.0287 (7)	0.0207 (7)	0.0406 (9)	0.0018 (6)	0.0052 (7)	0.0018 (6)
O5	0.0472 (8)	0.0217 (6)	0.0377 (7)	0.0108 (6)	0.0033 (6)	0.0009 (5)
C6	0.0369 (9)	0.0187 (7)	0.0409 (9)	0.0007 (7)	0.0085 (7)	0.0000 (7)
C7	0.0260 (7)	0.0174 (7)	0.0413 (9)	0.0006 (6)	0.0013 (6)	−0.0010 (7)
O8	0.0322 (7)	0.0285 (7)	0.0603 (9)	0.0099 (5)	−0.0043 (6)	−0.0116 (7)
C9	0.0530 (11)	0.0316 (10)	0.0361 (9)	0.0099 (9)	0.0057 (8)	0.0008 (8)
N10	0.0712 (13)	0.0455 (11)	0.0482 (11)	0.0071 (10)	0.0211 (9)	−0.0051 (9)
N11	0.0815 (15)	0.0483 (12)	0.0388 (9)	0.0201 (11)	−0.0043 (9)	−0.0065 (9)
N12	0.101 (2)	0.0691 (18)	0.0741 (17)	0.0172 (16)	−0.0171 (15)	−0.0326 (15)
C13	0.106 (2)	0.0445 (14)	0.0483 (13)	0.0222 (16)	−0.0035 (14)	0.0082 (11)
C14	0.0574 (13)	0.0535 (15)	0.0389 (11)	−0.0018 (12)	−0.0035 (9)	0.0058 (10)

Geometric parameters (Å, º)

O1—C2	1.331 (2)	O8—H5	0.82 (4)
O1—C14	1.445 (3)	C9—N10	1.486 (3)
C2—O3	1.204 (2)	C9—C13	1.515 (3)
C2—C4	1.513 (3)	C9—H91	0.985 (16)
C4—O5	1.439 (2)	N10—N11	1.234 (3)
C4—C7	1.540 (2)	N11—N12	1.132 (4)
C4—H41	0.964 (15)	C13—H131	0.993 (17)

O5—C6	1.451 (2)	C13—H132	0.981 (18)
C6—C7	1.533 (2)	C13—H133	0.996 (18)
C6—C9	1.521 (3)	C14—H141	0.969 (17)
C6—H61	0.986 (15)	C14—H142	0.983 (17)
C7—O8	1.405 (2)	C14—H143	0.962 (17)
C7—H71	0.958 (16)		

C2—O1—C14	116.48 (17)	O8—C7—H71	112.1 (10)
O1—C2—O3	124.83 (18)	C7—O8—H5	111 (2)
O1—C2—C4	110.25 (15)	C6—C9—N10	105.37 (17)
O3—C2—C4	124.92 (17)	C6—C9—C13	111.88 (19)
C2—C4—O5	111.04 (14)	N10—C9—C13	110.54 (19)
C2—C4—C7	114.58 (14)	C6—C9—H91	110.1 (11)
O5—C4—C7	91.58 (13)	N10—C9—H91	107.2 (12)
C2—C4—H41	112.6 (10)	C13—C9—H91	111.5 (12)
O5—C4—H41	113.1 (11)	C9—N10—N11	113.4 (2)
C7—C4—H41	112.3 (11)	N10—N11—N12	174.7 (3)
C4—O5—C6	91.52 (12)	C9—C13—H131	108.5 (19)
O5—C6—C7	91.38 (13)	C9—C13—H132	103 (2)
O5—C6—C9	110.23 (15)	H131—C13—H132	113.6 (16)
C7—C6—C9	117.75 (15)	C9—C13—H133	107.9 (18)
O5—C6—H61	110.5 (11)	H131—C13—H133	111.6 (16)
C7—C6—H61	113.2 (11)	H132—C13—H133	111.7 (16)
C9—C6—H61	111.9 (10)	O1—C14—H141	103.0 (17)
C4—C7—C6	84.73 (13)	O1—C14—H142	110.9 (16)
C4—C7—O8	114.53 (15)	H141—C14—H142	111.6 (16)
C6—C7—O8	117.18 (15)	O1—C14—H143	106.2 (17)
C4—C7—H71	112.1 (11)	H141—C14—H143	113.4 (15)
C6—C7—H71	113.5 (11)	H142—C14—H143	111.4 (16)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8—H5···O3^{i}	0.82 (4)	2.25 (3)	2.990 (2)	150 (3)
O8—H5···O5^{i}	0.82 (4)	2.32 (3)	2.962 (2)	135 (3)

Symmetry code: (i) −*x*, *y*+1/2, −*z*+1.