

2,3,4-Tri-*O*-acetyl- β -L-arabinopyranosyl trichloroacetimidate

Zu-Li Sun

Science and Engineering College of Chemistry and Biology, Yantai University, Yantai 264005, People's Republic of China

Correspondence e-mail: zulisun10@126.com

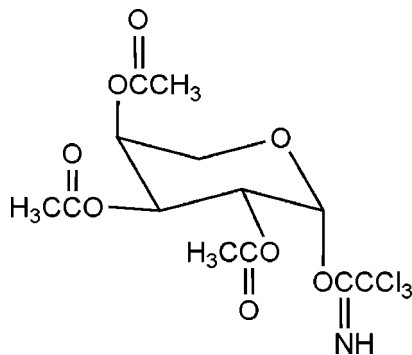
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.037; wR factor = 0.087; data-to-parameter ratio = 14.3.

In the title compound, $\text{C}_{13}\text{H}_{16}\text{Cl}_3\text{NO}_8$, the trichloroacetimidate group is located in an axial position on the anomeric carbon of the sugar ring.

Related literature

For applications of glycosyl trichloroacetimidate in glycosyl bond formation, see: Schmidt & Zhu (2008). For the preparation of the title compound, see: Schmidt & Stumpp (1983).



Experimental

Crystal data

$\text{C}_{13}\text{H}_{16}\text{Cl}_3\text{NO}_8$	$V = 1890.7$ (8) Å ³
$M_r = 420.62$	$Z = 4$
Monoclinic, $C2$	Mo $K\alpha$ radiation
$a = 21.384$ (5) Å	$\mu = 0.52$ mm ⁻¹
$b = 6.7994$ (16) Å	$T = 298$ K
$c = 13.096$ (3) Å	$0.49 \times 0.24 \times 0.08$ mm
$\beta = 96.796$ (3)°	

Data collection

Bruker SMART CCD area-detector diffractometer	4972 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2003)	3239 independent reflections
$T_{\min} = 0.784$, $T_{\max} = 0.959$	2933 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	H-atom parameters constrained
$wR(F^2) = 0.087$	$\Delta\rho_{\text{max}} = 0.23$ e Å ⁻³
$S = 1.06$	$\Delta\rho_{\text{min}} = -0.17$ e Å ⁻³
3239 reflections	Absolute structure: Flack (1983),
226 parameters	1334 Friedel pairs
1 restraint	Flack parameter: 0.04 (6)

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINTE* (Bruker, 2003); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JH2255).

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supplementary materials

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2,3,4-Tri-*O*-acetyl- β -L-arabinopyranosyl trichloroacetimidate

Z.-L. Sun

Comment

The title compound, a very useful glycosyl intermediate in glycosyl bond formation, was prepared from L-arabinose according to literature (Schmidt *et al.*, 1983) and its structure was further characterized by X-ray crystallographic techniques. The structure of 2,3,4-tri-*O*-acetyl- β -L-arabinopyranosyl trichloroacetimidate has monoclinic (C₂) symmetry. The structure reveals that the trichloroacetimidate group is located at axial position on anomeric carbon of sugar ring, as shown in Fig. 1. There is hydrogen bond interaction between N (1) and Cl (2) on the trichloroacetimidate group [N(1)···Cl(2) 3.009 (3) Å and N(1)—H(1)···Cl(2) 113.5 °].

Experimental

The title compound was prepared from L-arabinose by the following three steps: i) acetylation with Ac₂O in pyridine; ii) selective removal of acetyl group on anomeric carbon by ammonia methanol solution; iii) trichloroacetimidate formation with Cl₃CN/DBU in dichloromethane. Colorless single crystals were grown from a solution of petroleum ether/ethyl acetate (2:1).

Refinement

All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to anisotropically refined atoms were placed in geometrically idealized positions and included as riding atoms with C—H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.2 * U_{\text{eq}}(\text{C})$ (—CH); C—H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5 * U_{\text{eq}}(\text{C})$ (methyl); C—H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2 * U_{\text{eq}}(\text{C})$ (methylene); N—H = 0.88 Å and $U_{\text{iso}}(\text{H}) = 1.2 * U_{\text{eq}}(\text{N})$. The H atoms of one methyl is disordered over two closely spaced positions in 0.5/0.5 ratio.

Figures

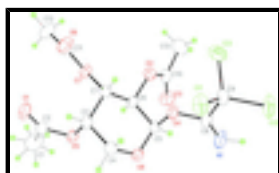


Fig. 1. Elipsoid plot.

2,3,4-tri-*O*-acetyl- β -L-arabinopyranosyl trichloroacetimidate

Crystal data

C₁₃H₁₆Cl₃NO₈

$M_r = 420.62$

$F(000) = 864$

$D_x = 1.478 \text{ Mg m}^{-3}$

supplementary materials

Monoclinic, $C2$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 21.384 (5) \text{ \AA}$	Cell parameters from 2245 reflections
$b = 6.7994 (16) \text{ \AA}$	$\theta = 2.6\text{--}23.4^\circ$
$c = 13.096 (3) \text{ \AA}$	$\mu = 0.52 \text{ mm}^{-1}$
$\beta = 96.796 (3)^\circ$	$T = 298 \text{ K}$
$V = 1890.7 (8) \text{ \AA}^3$	Plan, colourless
$Z = 4$	$0.49 \times 0.24 \times 0.08 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	3239 independent reflections
Radiation source: fine-focus sealed tube graphite	2933 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.021$
Absorption correction: multi-scan (SADABS; Bruker, 2003)	$\theta_{\text{max}} = 25.5^\circ$, $\theta_{\text{min}} = 1.9^\circ$
$T_{\text{min}} = 0.784$, $T_{\text{max}} = 0.959$	$h = -25 \rightarrow 21$
4972 measured reflections	$k = -8 \rightarrow 6$
	$l = -12 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.037$	H-atom parameters constrained
$wR(F^2) = 0.087$	$w = 1/[\sigma^2(F_o^2) + (0.0276P)^2 + 0.9525P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
3239 reflections	$(\Delta/\sigma)_{\text{max}} = 0.006$
226 parameters	$\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$
1 restraint	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1334 Friedel pairs
	Flack parameter: 0.04 (6)

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C2	0.61191 (15)	0.4264 (8)	0.4040 (2)	0.0721 (11)	
C3	0.71252 (13)	0.5071 (4)	0.3556 (2)	0.0431 (7)	
H3A	0.6937	0.6380	0.3448	0.052*	
C4	0.77597 (14)	0.5222 (4)	0.4187 (2)	0.0479 (7)	
H4A	0.8017	0.6154	0.3862	0.057*	
H4B	0.7704	0.5729	0.4863	0.057*	
C5	0.81676 (12)	0.2479 (4)	0.33786 (19)	0.0385 (6)	
H5A	0.8369	0.1197	0.3519	0.046*	
C6	0.75450 (12)	0.2193 (4)	0.27061 (18)	0.0354 (6)	
H6A	0.7285	0.1266	0.3044	0.042*	

C7	0.71942 (11)	0.4112 (4)	0.25338 (17)	0.0354 (5)	
H7A	0.7423	0.4991	0.2115	0.042*	
C8	0.91695 (12)	0.3220 (4)	0.2839 (2)	0.0449 (7)	
C9	0.94598 (13)	0.4576 (5)	0.2087 (2)	0.0518 (7)	
C10	0.77615 (13)	-0.0517 (4)	0.1675 (2)	0.0453 (7)	
C11	0.62909 (13)	0.5066 (5)	0.1420 (2)	0.0461 (7)	
C12	0.56681 (14)	0.4375 (7)	0.0926 (3)	0.0725 (10)	
H12A	0.5464	0.5418	0.0519	0.109*	
H12B	0.5412	0.3995	0.1447	0.109*	
H12C	0.5726	0.3267	0.0493	0.109*	
C13	0.78124 (19)	-0.1138 (5)	0.0615 (3)	0.0723 (10)	
H13A	0.7903	-0.2520	0.0604	0.109*	
H13B	0.8145	-0.0419	0.0353	0.109*	
H13C	0.7422	-0.0881	0.0195	0.109*	
Cl1	0.93304 (4)	0.70622 (13)	0.24083 (7)	0.0688 (3)	
Cl2	1.02723 (4)	0.41909 (16)	0.21284 (8)	0.0838 (3)	
Cl3	0.90994 (5)	0.40977 (19)	0.08308 (6)	0.0833 (3)	
O1	0.58775 (12)	0.5583 (6)	0.3561 (2)	0.0997 (11)	
O2	0.76398 (9)	0.1433 (2)	0.17167 (13)	0.0429 (4)	
O3	0.78190 (11)	-0.1520 (3)	0.24214 (18)	0.0617 (6)	
O4	0.85537 (8)	0.3662 (3)	0.27922 (14)	0.0441 (4)	
O5	0.67371 (8)	0.3848 (3)	0.41230 (13)	0.0521 (5)	
O6	0.65015 (10)	0.6661 (3)	0.13335 (17)	0.0622 (6)	
O7	0.65915 (8)	0.3634 (3)	0.19901 (13)	0.0436 (5)	
O8	0.80828 (8)	0.3379 (3)	0.43005 (13)	0.0445 (5)	
N1	0.94316 (12)	0.1918 (5)	0.3390 (2)	0.0720 (9)	
H1	0.9834	0.1736	0.3329	0.108*	
C1	0.57884 (18)	0.2786 (11)	0.4638 (3)	0.125 (2)	
H1A	0.5975	0.2786	0.5342	0.187*	0.50
H1B	0.5828	0.1502	0.4349	0.187*	0.50
H1C	0.5351	0.3126	0.4607	0.187*	0.50
H1'1	0.5638	0.3421	0.5217	0.187*	0.50
H1'2	0.6077	0.1757	0.4877	0.187*	0.50
H1'3	0.5439	0.2236	0.4204	0.187*	0.50

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C2	0.0401 (16)	0.130 (4)	0.0470 (16)	0.021 (2)	0.0094 (13)	0.009 (2)
C3	0.0419 (15)	0.0449 (17)	0.0431 (14)	0.0097 (12)	0.0079 (11)	0.0031 (12)
C4	0.0467 (17)	0.0527 (19)	0.0437 (15)	0.0000 (14)	0.0027 (12)	-0.0069 (13)
C5	0.0312 (13)	0.0394 (16)	0.0447 (15)	0.0055 (11)	0.0040 (11)	0.0105 (12)
C6	0.0375 (13)	0.0336 (14)	0.0359 (13)	0.0016 (11)	0.0078 (10)	0.0053 (11)
C7	0.0317 (12)	0.0351 (14)	0.0394 (12)	0.0002 (12)	0.0043 (10)	0.0052 (12)
C8	0.0304 (13)	0.0492 (18)	0.0543 (16)	0.0029 (13)	0.0022 (12)	0.0009 (14)
C9	0.0375 (15)	0.0553 (19)	0.0639 (17)	0.0045 (14)	0.0122 (13)	0.0024 (15)
C10	0.0404 (14)	0.0346 (16)	0.0615 (17)	-0.0002 (12)	0.0087 (13)	-0.0024 (14)
C11	0.0378 (15)	0.062 (2)	0.0380 (14)	0.0087 (14)	0.0025 (11)	0.0069 (13)

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C12	0.0437 (17)	0.095 (3)	0.074 (2)	0.0004 (19)	-0.0150 (15)	0.017 (2)
C13	0.096 (3)	0.048 (2)	0.076 (2)	0.0055 (19)	0.0225 (19)	-0.0130 (18)
C11	0.0594 (5)	0.0493 (5)	0.1014 (7)	0.0004 (4)	0.0246 (4)	0.0029 (5)
C12	0.0401 (4)	0.0873 (7)	0.1296 (8)	0.0112 (4)	0.0332 (5)	0.0213 (6)
C13	0.0909 (7)	0.1090 (8)	0.0525 (4)	-0.0057 (6)	0.0185 (4)	0.0003 (5)
O1	0.0543 (15)	0.161 (3)	0.0849 (18)	0.0531 (18)	0.0137 (13)	0.026 (2)
O2	0.0549 (12)	0.0344 (11)	0.0407 (10)	0.0050 (8)	0.0117 (8)	0.0045 (8)
O3	0.0771 (15)	0.0365 (12)	0.0708 (14)	0.0036 (11)	0.0056 (11)	0.0099 (11)
O4	0.0290 (9)	0.0485 (12)	0.0558 (10)	0.0062 (8)	0.0093 (7)	0.0142 (9)
O5	0.0339 (9)	0.0780 (15)	0.0454 (10)	0.0122 (10)	0.0086 (8)	0.0120 (11)
O6	0.0526 (13)	0.0589 (16)	0.0721 (14)	0.0066 (11)	-0.0053 (10)	0.0246 (12)
O7	0.0336 (9)	0.0472 (12)	0.0479 (10)	0.0013 (9)	-0.0038 (7)	0.0051 (9)
O8	0.0382 (10)	0.0553 (12)	0.0389 (9)	0.0044 (9)	0.0000 (8)	0.0068 (9)
N1	0.0384 (14)	0.083 (2)	0.095 (2)	0.0141 (15)	0.0109 (13)	0.0363 (19)
C1	0.045 (2)	0.251 (7)	0.080 (3)	-0.011 (3)	0.0175 (19)	0.045 (4)

Geometric parameters (Å, °)

C2—O1	1.178 (5)	C9—C12	1.752 (3)
C2—O5	1.343 (4)	C9—C13	1.763 (3)
C2—C1	1.502 (6)	C9—C11	1.771 (3)
C3—O5	1.442 (3)	C10—O3	1.187 (3)
C3—C4	1.506 (4)	C10—O2	1.353 (3)
C3—C7	1.512 (4)	C10—C13	1.467 (4)
C3—H3A	0.9800	C11—O6	1.185 (4)
C4—O8	1.430 (3)	C11—O7	1.344 (3)
C4—H4A	0.9700	C11—C12	1.486 (4)
C4—H4B	0.9700	C12—H12A	0.9600
C5—O8	1.385 (3)	C12—H12B	0.9600
C5—O4	1.438 (3)	C12—H12C	0.9600
C5—C6	1.519 (3)	C13—H13A	0.9600
C5—H5A	0.9800	C13—H13B	0.9600
C6—O2	1.432 (3)	C13—H13C	0.9600
C6—C7	1.508 (4)	N1—H1	0.8820
C6—H6A	0.9800	C1—H1A	0.9600
C7—O7	1.434 (3)	C1—H1B	0.9600
C7—H7A	0.9800	C1—H1C	0.9600
C8—N1	1.234 (4)	C1—H1'1	0.9600
C8—O4	1.345 (3)	C1—H1'2	0.9600
C8—C9	1.533 (4)	C1—H1'3	0.9600
O1—C2—O5	124.7 (4)	O2—C10—C13	110.9 (3)
O1—C2—C1	125.7 (3)	O6—C11—O7	123.6 (3)
O5—C2—C1	109.6 (4)	O6—C11—C12	125.4 (3)
O5—C3—C4	107.0 (2)	O7—C11—C12	111.0 (3)
O5—C3—C7	109.2 (2)	C11—C12—H12A	109.5
C4—C3—C7	109.8 (2)	C11—C12—H12B	109.5
O5—C3—H3A	110.2	H12A—C12—H12B	109.5
C4—C3—H3A	110.2	C11—C12—H12C	109.5
C7—C3—H3A	110.2	H12A—C12—H12C	109.5

O8—C4—C3	113.0 (2)	H12B—C12—H12C	109.5
O8—C4—H4A	109.0	C10—C13—H13A	109.5
C3—C4—H4A	109.0	C10—C13—H13B	109.5
O8—C4—H4B	109.0	H13A—C13—H13B	109.5
C3—C4—H4B	109.0	C10—C13—H13C	109.5
H4A—C4—H4B	107.8	H13A—C13—H13C	109.5
O8—C5—O4	111.1 (2)	H13B—C13—H13C	109.5
O8—C5—C6	111.5 (2)	C10—O2—C6	116.1 (2)
O4—C5—C6	106.32 (19)	C8—O4—C5	118.1 (2)
O8—C5—H5A	109.3	C2—O5—C3	117.2 (3)
O4—C5—H5A	109.3	C11—O7—C7	117.0 (2)
C6—C5—H5A	109.3	C5—O8—C4	114.1 (2)
O2—C6—C7	107.34 (19)	C8—N1—H1	115.3
O2—C6—C5	111.3 (2)	C2—C1—H1A	109.5
C7—C6—C5	111.2 (2)	C2—C1—H1B	109.5
O2—C6—H6A	109.0	H1A—C1—H1B	109.5
C7—C6—H6A	109.0	C2—C1—H1C	109.5
C5—C6—H6A	109.0	H1A—C1—H1C	109.5
O7—C7—C6	106.3 (2)	H1B—C1—H1C	109.5
O7—C7—C3	111.17 (19)	C2—C1—H1'1	109.5
C6—C7—C3	109.9 (2)	H1A—C1—H1'1	51.8
O7—C7—H7A	109.8	H1B—C1—H1'1	140.8
C6—C7—H7A	109.8	H1C—C1—H1'1	60.7
C3—C7—H7A	109.8	C2—C1—H1'2	109.5
N1—C8—O4	124.2 (3)	H1A—C1—H1'2	60.7
N1—C8—C9	128.1 (3)	H1B—C1—H1'2	51.8
O4—C8—C9	107.8 (2)	H1C—C1—H1'2	140.8
C8—C9—C12	111.5 (2)	H1'1—C1—H1'2	109.5
C8—C9—C13	108.8 (2)	C2—C1—H1'3	109.5
C12—C9—C13	108.89 (17)	H1A—C1—H1'3	140.8
C8—C9—C11	109.6 (2)	H1B—C1—H1'3	60.7
C12—C9—C11	108.52 (17)	H1C—C1—H1'3	51.8
C13—C9—C11	109.53 (17)	H1'1—C1—H1'3	109.5
O3—C10—O2	122.1 (3)	H1'2—C1—H1'3	109.5
O3—C10—C13	127.0 (3)		
O5—C3—C4—O8	64.9 (3)	O3—C10—O2—C6	-3.8 (4)
C7—C3—C4—O8	-53.5 (3)	C13—C10—O2—C6	176.7 (2)
O8—C5—C6—O2	174.5 (2)	C7—C6—O2—C10	-159.8 (2)
O4—C5—C6—O2	53.3 (3)	C5—C6—O2—C10	78.3 (3)
O8—C5—C6—C7	54.9 (3)	N1—C8—O4—C5	-3.4 (4)
O4—C5—C6—C7	-66.4 (2)	C9—C8—O4—C5	175.5 (2)
O2—C6—C7—O7	64.1 (2)	O8—C5—O4—C8	98.2 (3)
C5—C6—C7—O7	-173.92 (18)	C6—C5—O4—C8	-140.3 (2)
O2—C6—C7—C3	-175.5 (2)	O1—C2—O5—C3	-2.1 (5)
C5—C6—C7—C3	-53.6 (3)	C1—C2—O5—C3	177.3 (3)
O5—C3—C7—O7	52.8 (3)	C4—C3—O5—C2	146.6 (3)
C4—C3—C7—O7	169.9 (2)	C7—C3—O5—C2	-94.6 (3)
O5—C3—C7—C6	-64.5 (3)	O6—C11—O7—C7	1.3 (4)
C4—C3—C7—C6	52.5 (3)	C12—C11—O7—C7	-178.5 (2)

supplementary materials

N1—C8—C9—C12	-3.6 (4)	C6—C7—O7—C11	-155.7 (2)
O4—C8—C9—C12	177.5 (2)	C3—C7—O7—C11	84.8 (3)
N1—C8—C9—C13	116.5 (3)	O4—C5—O8—C4	62.6 (3)
O4—C8—C9—C13	-62.4 (3)	C6—C5—O8—C4	-55.8 (3)
N1—C8—C9—C11	-123.8 (3)	C3—C4—O8—C5	56.4 (3)
O4—C8—C9—C11	57.3 (3)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1···C12	0.88	2.55	3.009 (3)	114

Fig. 1

