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Prop-2-yn-1-yl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside

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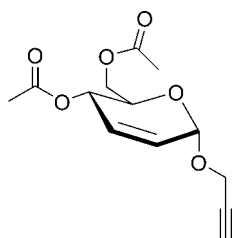
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.023; wR factor = 0.058; data-to-parameter ratio = 12.6.

The absolute structure of the title compound, $\text{C}_{13}\text{H}_{16}\text{O}_6$, was determined. The pyranosyl ring adopting an envelope conformation. The acetyl groups are located in equatorial positions. The crystal structure features weak $\text{C}-\text{H}\cdots\text{O}$ interactions.

Related literature

For details of the Ferrier arrangement, see: Ferrier & Prasad (1969) and for the synthesis of pseudoglycols utilizing the Ferrier arrangement, see: López *et al.* (1995); Yadav *et al.* (2001). For background to the synthetic methodology of glycosides, see: Kinfe *et al.* (2011); Breton (1997). For ring puckering analysis, see: Cremer & Pople (1975).



Experimental

Crystal data

 $\text{C}_{13}\text{H}_{16}\text{O}_6$ $M_r = 268.26$ Orthorhombic, $P2_12_12_1$ $a = 5.2277$ (2) Å $b = 14.8549$ (5) Å $c = 17.0509$ (5) Å $V = 1324.12$ (8) Å³ $Z = 4$ Cu $K\alpha$ radiation $\mu = 0.91$ mm⁻¹ $T = 100$ K $0.28 \times 0.06 \times 0.06$ mm

Data collection

Bruker APEX DUO 4K CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2008)
 $T_{\min} = 0.785$, $T_{\max} = 0.948$

12479 measured reflections
2184 independent reflections
2113 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.058$
 $S = 1.06$
2184 reflections
174 parameters
H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.1$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.12$ e Å⁻³
Absolute structure: Flack (1983),
872 Friedel pairs
Flack parameter: -0.05 (14)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C8}-\text{H8}\cdots\text{O4}^{\text{i}}$	0.95	2.37	3.2139 (17)	149
$\text{C11}-\text{H11B}\cdots\text{O6}^{\text{ii}}$	0.98	2.58	3.4869 (16)	154
$\text{C13}-\text{H13C}\cdots\text{O6}^{\text{iii}}$	0.98	2.38	3.3152 (19)	159

Symmetry codes: (i) $-x + \frac{3}{2}, -y, z - \frac{1}{2}$; (ii) $-x + \frac{1}{2}, -y, z - \frac{1}{2}$; (iii) $x + 1, y, z$.

Data collection: APEX2 (Bruker, 2011); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT and XPREP (Bruker, 2008); program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg & Putz, 2005); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NC2253).

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supporting information

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Prop-2-yn-1-yl 4,6-di-*O*-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside**Fanuel M. Mesfin, Henok H. Kinfé and Alfred Müller****S1. Comment**

Treatment of 3,4,6-tri-*O*-acetyl-D-glucal with a Lewis acid catalyst in the presence of alcohols and other C and S nucleophiles results to allylic rearrangement of the glucal and the reaction is called Ferrier rearrangement (Ferrier & Prasad, 1969; López *et al.*, 1995; Yadav *et al.*, 2001; Kinfé *et al.*, 2011). Recently, we reported the synthesis of the title compound by treating a glucal with NaHSO₄ supported on silica gel in the presence of propargyl alcohol (Kinfé *et al.*, 2011). Herein, we report the crystal structure of the pure diastereomer obtained by crystallization from the mixture of products.

In the crystal structure of the title compound the acetyl groups are in equatorial positions (see Fig. 1). The pyran ring adopts an envelope conformation with ring puckering parameters of $q_2 = 0.4180(14)$ Å, $q_3 = 0.3070(14)$ Å, $Q = 0.5186(13)$ Å and $\varphi_2 = 324.1(2)^\circ$ (see Cremer & Pople, 1975). Several weak C—H \cdots O interactions are noted and listed in Table 1.

S2. Experimental

To a solution of a tri-*O*-acetyl-D-glucal (100 mg, 0.36 mmol) and propargyl alcohol (0.042 ml, 0.72 mmol) in CH₃CN (1 ml) NaHSO₄-SiO₂ (2.5 mg, 3.0 mmol NaHSO₄/g) was added (see Breton, 1997). The resulting mixture was stirred at 80 °C for 5 min. After adding silica gel to the reaction mixture at room temperature, the solvent was evaporated *in vacuo* without heating until a free-flowing solid was obtained. The resulting solid was column chromatographed using 1:9 ethyl acetate:hexane eluent to afford α : β (6:1) mixture of 2,3-unsaturated glycosides in 90% yield as a white solid.

Recrystallization from a mixture of DCM and hexane afforded the title compound in 50% yield as colorless crystals.

S3. Refinement

All hydrogen atoms were positioned in geometrically idealized positions with C—H = 1.00 Å (methine), 0.99 Å (methylene), 0.98 Å (methyl) and 0.95 Å (aromatic and acetylenic). All hydrogen atoms were allowed to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}$, except for the methyl where $U_{iso}(H) = 1.5U_{eq}$ was utilized. The initial positions of methyl hydrogen atoms were located from a Fourier difference map and refined as fixed rotor. The D enantiomer was determined on the basis of 872 Friedel pairs with the final Flack parameter refined to -0.05 (14). The highest residual electron density of 0.10 e.Å⁻³ is 0.63 Å from H6A representing no physical meaning.

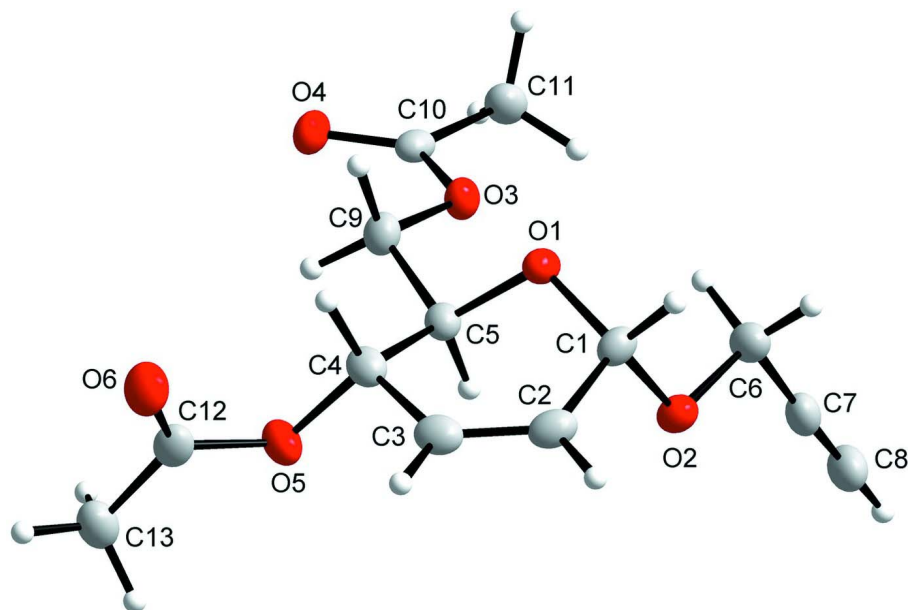


Figure 1

Crystal structure of the title compound with labelling and displacement ellipsoids drawn at the 50% probability level.

Prop-2-yn-1-yl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside

Crystal data

$C_{13}H_{16}O_6$

$M_r = 268.26$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 5.2277(2) \text{ \AA}$

$b = 14.8549(5) \text{ \AA}$

$c = 17.0509(5) \text{ \AA}$

$V = 1324.12(8) \text{ \AA}^3$

$Z = 4$

$F(000) = 568$

$D_x = 1.346 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$

Cell parameters from 7170 reflections

$\theta = 6.0\text{--}64.2^\circ$

$\mu = 0.91 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Needle, colourless

$0.28 \times 0.06 \times 0.06 \text{ mm}$

Data collection

Bruker APEX DUO 4K CCD
diffractometer

Radiation source: Incoatec $I\mu S$ microfocus X-
ray source

Incoatec Quazar Multilayer Mirror
monochromator

Detector resolution: $8.4 \text{ pixels mm}^{-1}$

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2008)

$T_{\min} = 0.785$, $T_{\max} = 0.948$

12479 measured reflections

2184 independent reflections

2113 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 64.6^\circ$, $\theta_{\min} = 6.0^\circ$

$h = -6 \rightarrow 5$

$k = -17 \rightarrow 17$

$l = -19 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.058$

$S = 1.06$

2184 reflections

174 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0281P)^2 + 0.1772P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.1 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.12 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack (1983), 872 Friedel pairs

$$\text{Absolute structure parameter: } -0.05 (14)$$

Special details

Experimental. The intensity data was collected on a Bruker Apex DUO 4 K CCD diffractometer using an exposure time of 5 s/frame. A total of 2276 frames were collected with a frame width of 1° covering up to $\theta = 64.63^\circ$ with 98.1% completeness accomplished.

Analytical data: ¹H NMR (CDCl₃, 300 MHz): δ 5.90 (d, $J = 10.4$ Hz, 1H), 5.82 (td, $J = 2.4$ and 10.0 Hz, 1H), 5.32 (dd, $J = 1.2$ and 9.6 Hz, 1H), 5.21 (s, 1H), 4.40–4.03 (m, 5H), 2.44 (t, $J = 2.4$ Hz, 1H), 2.08 (s, 3H), 2.07 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz): δ 170.8, 170.2, 129.8, 127.2, 92.8, 79.0, 74.8, 67.2, 65.1, 62.7, 55.0, 20.9, 20.8

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	−0.1501 (2)	0.08128 (8)	0.42326 (7)	0.0220 (3)
H1	−0.2982	0.0577	0.3924	0.026*
C2	−0.2436 (3)	0.15417 (9)	0.47693 (8)	0.0249 (3)
H2	−0.3473	0.201	0.4562	0.03*
C3	−0.1854 (3)	0.15485 (9)	0.55205 (8)	0.0255 (3)
H3	−0.2594	0.1994	0.585	0.031*
C4	−0.0052 (2)	0.08713 (9)	0.58703 (7)	0.0229 (3)
H4	−0.1016	0.0424	0.6194	0.028*
C5	0.1419 (3)	0.03970 (8)	0.52242 (7)	0.0204 (3)
H5	0.2635	0.083	0.4974	0.024*
C6	0.1114 (3)	0.05767 (9)	0.31257 (7)	0.0268 (3)
H6A	−0.0353	0.0393	0.2795	0.032*
H6B	0.1814	0.0032	0.3383	0.032*
C7	0.3070 (3)	0.09936 (8)	0.26419 (7)	0.0256 (3)
C8	0.4705 (3)	0.12937 (9)	0.22357 (8)	0.0312 (3)
H8	0.6014	0.1534	0.1911	0.037*
C9	0.2870 (3)	−0.04105 (9)	0.55155 (7)	0.0229 (3)
H9A	0.4102	−0.0229	0.5927	0.028*
H9B	0.1674	−0.0857	0.5742	0.028*
C10	0.6141 (2)	−0.13598 (8)	0.50283 (7)	0.0201 (3)
C11	0.7222 (3)	−0.17820 (9)	0.43096 (8)	0.0269 (3)
H11A	0.9074	−0.1854	0.4371	0.04*
H11B	0.6871	−0.1397	0.3856	0.04*

H11C	0.6432	-0.2373	0.4229	0.04*
C12	0.1406 (3)	0.13903 (8)	0.71258 (7)	0.0235 (3)
C13	0.3572 (3)	0.18527 (9)	0.75213 (8)	0.0292 (3)
H13A	0.3149	0.195	0.8075	0.044*
H13B	0.3885	0.2434	0.7267	0.044*
H13C	0.5111	0.1479	0.7483	0.044*
O1	-0.03843 (18)	0.00939 (5)	0.46538 (5)	0.0208 (2)
O2	0.02791 (19)	0.12087 (6)	0.37098 (5)	0.0234 (2)
O3	0.42076 (17)	-0.07942 (6)	0.48563 (5)	0.0217 (2)
O4	0.68222 (18)	-0.15169 (6)	0.56925 (5)	0.0254 (2)
O5	0.18437 (19)	0.13295 (6)	0.63443 (5)	0.0272 (2)
O6	-0.0477 (2)	0.10886 (6)	0.74305 (5)	0.0322 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0193 (7)	0.0225 (6)	0.0240 (6)	0.0010 (6)	-0.0010 (5)	0.0055 (5)
C2	0.0188 (7)	0.0219 (6)	0.0339 (7)	0.0009 (5)	0.0051 (6)	0.0042 (6)
C3	0.0203 (7)	0.0245 (7)	0.0318 (7)	-0.0026 (6)	0.0075 (6)	-0.0021 (5)
C4	0.0200 (7)	0.0265 (7)	0.0223 (6)	-0.0051 (6)	0.0034 (5)	-0.0019 (5)
C5	0.0194 (7)	0.0227 (6)	0.0191 (6)	-0.0035 (5)	0.0003 (5)	0.0003 (5)
C6	0.0343 (8)	0.0235 (7)	0.0226 (6)	-0.0009 (6)	0.0030 (6)	-0.0016 (5)
C7	0.0319 (8)	0.0258 (7)	0.0191 (6)	0.0024 (6)	-0.0035 (6)	-0.0030 (5)
C8	0.0379 (9)	0.0341 (7)	0.0217 (6)	-0.0062 (7)	0.0024 (6)	-0.0026 (6)
C9	0.0220 (7)	0.0276 (7)	0.0192 (6)	-0.0005 (5)	0.0015 (5)	0.0016 (5)
C10	0.0183 (7)	0.0172 (6)	0.0248 (7)	-0.0032 (5)	-0.0028 (5)	0.0028 (5)
C11	0.0307 (8)	0.0226 (6)	0.0273 (7)	0.0037 (6)	-0.0025 (6)	-0.0012 (5)
C12	0.0249 (8)	0.0231 (6)	0.0225 (6)	0.0075 (5)	0.0029 (6)	-0.0013 (5)
C13	0.0300 (9)	0.0310 (7)	0.0266 (7)	0.0057 (6)	-0.0026 (6)	-0.0050 (5)
O1	0.0210 (5)	0.0191 (4)	0.0223 (4)	-0.0017 (4)	-0.0029 (4)	0.0018 (3)
O2	0.0266 (5)	0.0209 (4)	0.0227 (4)	0.0002 (4)	0.0046 (4)	0.0021 (3)
O3	0.0220 (5)	0.0246 (4)	0.0184 (4)	0.0029 (4)	-0.0016 (4)	0.0003 (3)
O4	0.0262 (5)	0.0279 (5)	0.0221 (5)	0.0007 (4)	-0.0051 (4)	0.0053 (4)
O5	0.0267 (5)	0.0342 (5)	0.0207 (4)	-0.0084 (4)	0.0034 (4)	-0.0048 (4)
O6	0.0293 (6)	0.0422 (6)	0.0252 (5)	0.0008 (5)	0.0070 (4)	-0.0011 (4)

Geometric parameters (Å, °)

C1—O1	1.4130 (14)	C7—C8	1.187 (2)
C1—O2	1.4165 (15)	C8—H8	0.95
C1—C2	1.4996 (18)	C9—O3	1.4412 (15)
C1—H1	1	C9—H9A	0.99
C2—C3	1.3164 (19)	C9—H9B	0.99
C2—H2	0.95	C10—O4	1.2100 (15)
C3—C4	1.5018 (18)	C10—O3	1.3465 (15)
C3—H3	0.95	C10—C11	1.4881 (18)
C4—O5	1.4487 (15)	C11—H11A	0.98
C4—C5	1.5170 (17)	C11—H11B	0.98

C4—H4	1	C11—H11C	0.98
C5—O1	1.4272 (15)	C12—O6	1.1999 (17)
C5—C9	1.5038 (18)	C12—O5	1.3550 (15)
C5—H5	1	C12—C13	1.486 (2)
C6—O2	1.4366 (15)	C13—H13A	0.98
C6—C7	1.453 (2)	C13—H13B	0.98
C6—H6A	0.99	C13—H13C	0.98
C6—H6B	0.99		
O1—C1—O2	111.24 (10)	C8—C7—C6	176.82 (14)
O1—C1—C2	111.73 (10)	C7—C8—H8	180
O2—C1—C2	107.36 (10)	O3—C9—C5	107.62 (10)
O1—C1—H1	108.8	O3—C9—H9A	110.2
O2—C1—H1	108.8	C5—C9—H9A	110.2
C2—C1—H1	108.8	O3—C9—H9B	110.2
C3—C2—C1	121.60 (12)	C5—C9—H9B	110.2
C3—C2—H2	119.2	H9A—C9—H9B	108.5
C1—C2—H2	119.2	O4—C10—O3	123.03 (11)
C2—C3—C4	121.74 (12)	O4—C10—C11	125.29 (12)
C2—C3—H3	119.1	O3—C10—C11	111.64 (10)
C4—C3—H3	119.1	C10—C11—H11A	109.5
O5—C4—C3	109.64 (10)	C10—C11—H11B	109.5
O5—C4—C5	106.06 (10)	H11A—C11—H11B	109.5
C3—C4—C5	109.91 (10)	C10—C11—H11C	109.5
O5—C4—H4	110.4	H11A—C11—H11C	109.5
C3—C4—H4	110.4	H11B—C11—H11C	109.5
C5—C4—H4	110.4	O6—C12—O5	122.65 (12)
O1—C5—C9	107.86 (10)	O6—C12—C13	126.95 (12)
O1—C5—C4	107.87 (10)	O5—C12—C13	110.39 (12)
C9—C5—C4	112.72 (10)	C12—C13—H13A	109.5
O1—C5—H5	109.4	C12—C13—H13B	109.5
C9—C5—H5	109.4	H13A—C13—H13B	109.5
C4—C5—H5	109.4	C12—C13—H13C	109.5
O2—C6—C7	109.20 (11)	H13A—C13—H13C	109.5
O2—C6—H6A	109.8	H13B—C13—H13C	109.5
C7—C6—H6A	109.8	C1—O1—C5	112.37 (9)
O2—C6—H6B	109.8	C1—O2—C6	111.37 (10)
C7—C6—H6B	109.8	C10—O3—C9	116.18 (9)
H6A—C6—H6B	108.3	C12—O5—C4	117.67 (10)
O1—C1—C2—C3	10.49 (18)	C9—C5—O1—C1	-168.46 (10)
O2—C1—C2—C3	-111.74 (14)	C4—C5—O1—C1	69.51 (12)
C1—C2—C3—C4	5.0 (2)	O1—C1—O2—C6	62.63 (13)
C2—C3—C4—O5	131.20 (13)	C2—C1—O2—C6	-174.84 (10)
C2—C3—C4—C5	14.99 (17)	C7—C6—O2—C1	-175.81 (11)
O5—C4—C5—O1	-168.20 (9)	O4—C10—O3—C9	-3.13 (16)
C3—C4—C5—O1	-49.76 (13)	C11—C10—O3—C9	174.60 (11)
O5—C4—C5—C9	72.84 (13)	C5—C9—O3—C10	162.29 (10)

C3—C4—C5—C9	-168.72 (11)	O6—C12—O5—C4	-0.61 (17)
O1—C5—C9—O3	61.81 (13)	C13—C12—O5—C4	178.21 (10)
C4—C5—C9—O3	-179.22 (10)	C3—C4—O5—C12	95.77 (13)
O2—C1—O1—C5	71.48 (13)	C5—C4—O5—C12	-145.60 (10)
C2—C1—O1—C5	-48.49 (14)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C8—H8 \cdots O4 ⁱ	0.95	2.37	3.2139 (17)	149
C11—H11B \cdots O6 ⁱⁱ	0.98	2.58	3.4869 (16)	154
C13—H13C \cdots O6 ⁱⁱⁱ	0.98	2.38	3.3152 (19)	159

Symmetry codes: (i) $-x+3/2, -y, z-1/2$; (ii) $-x+1/2, -y, z-1/2$; (iii) $x+1, y, z$.