Crystal structure of 1-deoxy-1-(3-hydroxypropyl)-*O*-triphenylmethyl-β-D-lyxofuranose, $C_{27}H_{30}O_5$

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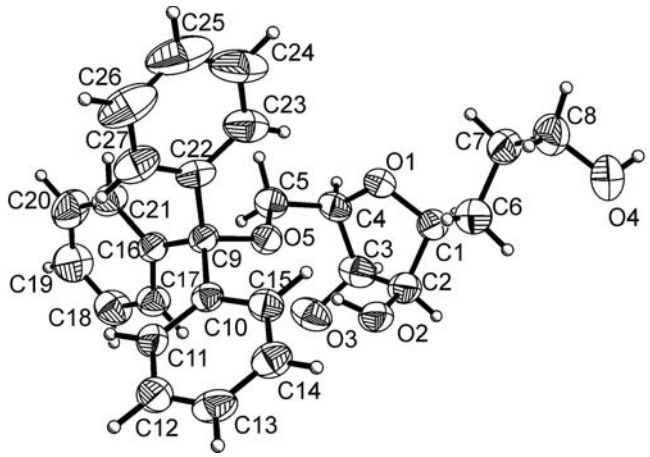

Abstract

$C_{27}H_{30}O_5$, monoclinic, $P12_11$ (no. 4), a = 9.4966(2) Å, b = 9.7936(2) Å, c = 12.8341(9) Å, β = 98.698(7)°, V = 1179.9 Å^3, Z = 2, $R_{gt}(F)$ = 0.041, $wR_{ref}(F^2)$ = 0.119, T = 292 K.

Source of material

The title compound is an intermediate for nucleoside synthesis. It was synthesized from the known 1-deoxy-1-(3-propenyl)-β-D-lyxofuranose, whose configuration was established in solution by NOE spectroscopy [1]. The absolute structure is certain from the synthetic route which does not affect stereogenic atoms: the starting compound was treated with Ph_3CCl in pyridine; the resulting alkene was converted t the title product by reaction with B_2H_6 and with H_2O_2 in NaOH. Crystals of the title compound were grown from ethylacetate. Thin layer chromatography shows no traces of the unreacted alkenes.

Experimental details

The refinement resulted in a crystal structure with a reasonable *R*-factor and bond lenghtes and angles; only the C7—C8 bond length is equal to 1.32 Å and elipsoids of C7 and C8 atoms are abnormally elongated. This disorder was resolved and refined using restrains on bond lengths of both chains and by making displacement parameters of C8 and C8A being exactly equal. The final refinement resulted in lower *R* factor and reasonable bond lengths and angles for both chains, with occupancies at 2:1 ratio. Displacement parameters of some neighboring carbon atoms were also restrained. All H atoms were positioned geometrically and refined using a riding model, with d(C—H) = 0.99 - 1.03 Å, U_{iso}(H) = 1.2 or 1.5 U_{eq}(C). Hydrogen atoms of the disordered propylene chain were placed at calculated positions with U_{iso}(H) = 1.2 U_{eq}(C). Analysis of the absolute structure by likelihood methods was performed using PLATON [4]. The results confirmed that the absolute structure had been correctly assigned: the probability that the structure is inverted is smaller than 10^{-33} with probability of racemic twinning at 10^{-3}. Because no atom heavier than O is present, Flack and Hooft parameters show relatively high standard deviations: –0.1(3) and 0.07(7); 1856 Bijvoet pairs.

Discussion

In the title crystal structure, all bond lengths and bond angles have standard dimensions. Puckering parameters of furanose five-member ring are Q(2) = 0.403(3) Å, φ = 59.6(4)° which corresponds to a twisted (half-chair) conformation around atoms C1 and C2, visibly shifted towards an envelope one with C2 atom in a corner. C1 atom is positioned at –0.25 Å below the O1–C3–C4 plane; C2 is at 0.41 Å above. All non-hydrogen substituents are placed above the average plane of the five-membered ring; all hydrogens are located below. There is only one furanose molecule known with such orientation of substituents [2]. A hydrogen bond connects O2 and O5 atoms (d(O2–H2···O5) = 2.79 Å, ∠O2–H2···O5 = 161°). Two remaining OH groups make intermolecular hydrogen bonds (d(O3–H3···O4) = 2.89 Å, ∠O3–H3···O4 = 157°, and d(O4–H4···O2) = 2.75 Å, ∠O4–H4···O2 = 166°) forming an infinite two-dimensional network in a plane perpendicular to [001]. Two short C–H···O contacts were detected that possibly stabilize the existing conformation of the molecule: an intramolecular contact d(C23–H23···O5) = 2.79 Å; and an intermolecular contact d(C13–H13···O1) = 3.30 Å.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.20 × 0.20 × 0.20 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	6.72 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID imaging plate, ω
$2\theta_{max}$:	136.42°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11380, 4103
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3298
$N(param)_{refined}$:	322
Programs:	SHELXS-97, SHELXL-97, SHELXTL [3], PLATON [4]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(2)	2*a*		0.636(4)	0.733(1)	0.102(3)	0.104
H(3)	2*a*		0.310(5)	0.860(2)	0.013(4)	0.132
H(1)	2*a*		0.720(4)	1.059(3)	–0.002(2)	0.089
H(2A)	2*a*		0.6341(4)	0.8632(4)	–0.084(3)	0.086
H(3A)	2*a*		0.462(1)	0.991(3)	–0.031(2)	0.088
H(4A)	2*a*		0.497(2)	1.083(3)	0.1258(2)	0.074
H(5A)	2*a*		0.5284(6)	0.976(1)	0.289(1)	0.072
H(5B)	2*a*		0.389(2)	0.9065(4)	0.2111(3)	0.072
H(11A)	2*a*		0.439(3)	0.4497(3)	0.348(1)	0.072
H(12A)	2*a*		0.540(2)	0.236(3)	0.3132(7)	0.085
H(13A)	2*a*		0.749(2)	0.223(3)	0.2417(6)	0.086
H(14A)	2*a*		0.869(3)	0.4199(4)	0.204(1)	0.079
H(15A)	2*a*		0.781(2)	0.638(3)	0.2399(5)	0.067
H(17A)	2*a*		0.321(1)	0.621(1)	0.192(2)	0.076
H(18A)	2*a*		0.0819	0.6305	0.2018	0.096
H(19A)	2*a*		0.0018	0.7318	0.3442	0.112
H(20A)	2*a*		0.162(1)	0.821(2)	0.485(3)	0.107
H(21A)	2*a*		0.411(2)	0.806(1)	0.478(2)	0.081
H(23A)	2*a*		0.7429	0.9088	0.3558	0.098

Table 2. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(24A)	2*a*		0.9032	0.9625	0.5071	0.138
H(25A)	2*a*		0.9061	0.8370	0.6580	0.155
H(26A)	2*a*		0.7536	0.6571	0.6605	0.138
H(27A)	2*a*		0.5902	0.6051	0.5147	0.098
H(6A)	2*a*	0.668	0.9196	0.9085	–0.0060	0.123
H(6B)	2*a*	0.668	0.9111	0.8727	0.1127	0.123
H(7A)	2*a*	0.668	0.9498	1.1480	0.0408	0.088
H(7B)	2*a*	0.668	0.9426	1.1115	0.1594	0.088
H(8A)	2*a*	0.668	1.1860	1.1186	0.1466	0.104
H(8B)	2*a*	0.668	1.1496	0.9620	0.1537	0.104
H(4)	2*a*	0.668	1.2023	1.0929	–0.0109	0.179
H(6C)	2*a*	0.332	0.9223	0.9586	–0.0090	0.123
H(6D)	2*a*	0.332	0.8957	0.8453	0.0701	0.123
H(2C)	2*a*	0.332	0.9676	1.0557	0.1973	0.112
H(2D)	2*a*	0.332	1.0733	0.9373	0.1770	0.112
H(8C)	2*a*	0.332	1.0183	1.1641	0.0355	0.104
H(8D)	2*a*	0.332	1.1526	1.1623	0.1238	0.104
H(4D)	2*a*	0.332	1.1961	1.0741	–0.0338	0.179

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	2*a*		0.6916(2)	1.0073(2)	0.1405(2)	0.075(2)	0.051(1)	0.067(1)	–0.011(1)	0.016(1)	–0.0064(9)
O(2)	2*a*		0.6676(3)	0.7365(2)	0.0411(2)	0.096(2)	0.051(1)	0.062(1)	–0.007(1)	0.019(1)	–0.0057(9)
O(3)	2*a*		0.3892(3)	0.8226(2)	0.0182(2)	0.094(2)	0.076(2)	0.086(2)	–0.018(1)	–0.017(2)	0.005(1)
O(5)	2*a*		0.5675(2)	0.7887(2)	0.2309(1)	0.067(1)	0.0401(9)	0.058(1)	0.0039(9)	0.0143(9)	0.0018(8)
C(1)	2*a*		0.7365(5)	0.9769(3)	0.0416(3)	0.107(3)	0.060(2)	0.061(2)	–0.023(2)	0.030(2)	–0.005(2)
C(2)	2*a*		0.6356(4)	0.8678(3)	–0.0056(2)	0.104(3)	0.061(2)	0.049(2)	–0.013(2)	0.011(2)	0.003(1)
C(3)	2*a*		0.4956(4)	0.9230(3)	0.0194(3)	0.095(3)	0.056(2)	0.062(2)	–0.006(2)	–0.009(2)	0.011(2)
C(4)	2*a*		0.5393(3)	0.9927(3)	0.1286(2)	0.072(2)	0.040(1)	0.073(2)	–0.002(1)	0.007(2)	0.004(1)
C(5)	2*a*		0.4982(3)	0.9194(3)	0.2211(2)	0.069(2)	0.043(2)	0.070(2)	0.009(1)	0.012(1)	0.003(1)
C(9)	2*a*		0.5469(3)	0.7053(3)	0.3213(2)	0.059(2)	0.044(1)	0.042(1)	0.001(1)	0.007(1)	–0.002(1)
C(10)	2*a*		0.6000(3)	0.5631(3)	0.2937(2)	0.056(2)	0.045(1)	0.040(1)	0.005(1)	0.003(1)	0.000(1)
C(11)	2*a*		0.5315(4)	0.4444(3)	0.3165(2)	0.080(2)	0.052(2)	0.052(2)	–0.002(2)	0.017(1)	0.002(1)
C(12)	2*a*		0.5887(4)	0.3184(3)	0.2970(2)	0.100(3)	0.049(2)	0.065(2)	–0.001(2)	0.020(2)	0.002(1)
C(13)	2*a*		0.7121(4)	0.3089(3)	0.2554(2)	0.102(3)	0.048(2)	0.064(2)	0.018(2)	0.008(2)	–0.007(1)
C(14)	2*a*		0.7817(4)	0.4260(3)	0.2337(2)	0.073(2)	0.063(2)	0.061(2)	0.014(2)	0.008(2)	–0.004(2)
C(15)	2*a*		0.7274(3)	0.5524(3)	0.2541(2)	0.057(2)	0.051(2)	0.059(2)	0.001(1)	0.006(1)	–0.001(1)
C(16)	2*a*		0.3914(3)	0.7082(3)	0.3329(2)	0.058(2)	0.049(1)	0.048(1)	0.003(1)	0.008(1)	0.000(1)
C(17)	2*a*		0.2908(3)	0.6593(3)	0.2517(2)	0.059(2)	0.069(2)	0.060(2)	–0.005(2)	0.003(1)	–0.008(2)
C(18)	2*a*		0.1469(4)	0.6663(4)	0.2565(3)	0.062(2)	0.090(2)	0.084(2)	–0.009(2)	–0.004(2)	–0.002(2)
C(19)	2*a*		0.0989(4)	0.7259(5)	0.3414(3)	0.062(2)	0.109(3)	0.109(3)	0.002(2)	0.014(2)	–0.013(3)
C(20)	2*a*		0.1965(4)	0.7768(5)	0.4223(3)	0.074(2)	0.109(3)	0.089(2)	0.010(2)	0.029(2)	–0.016(2)
C(21)	2*a*		0.3414(3)	0.7682(3)	0.4181(2)	0.060(2)	0.078(2)	0.065(2)	0.005(2)	0.012(2)	–0.014(2)
C(22)	2*a*		0.6496(3)	0.7510(3)	0.4197(2)	0.062(2)	0.057(2)	0.057(2)	0.008(1)	–0.001(1)	–0.020(1)
C(23)	2*a*		0.7435(4)	0.8582(4)	0.4171(3)	0.067(2)	0.076(2)	0.100(2)	0.002(2)	0.004(2)	–0.031(2)
C(24)	2*a*		0.8402(4)	0.8900(5)	0.5082(5)	0.069(3)	0.124(4)	0.144(4)	–0.007(2)	–0.011(3)	–0.070(3)
C(25)	2*a*		0.8423(5)	0.8153(7)	0.5980(4)	0.094(3)	0.173(5)	0.106(3)	0.033(3)	–0.030(3)	–0.074(3)
C(26)	2*a*		0.7507(5)	0.7090(6)	0.5995(3)	0.122(4)	0.151(4)	0.061(2)	0.040(3)	–0.024(2)	–0.024(2)
C(27)	2*a*		0.6535(4)	0.6770(4)	0.5118(2)	0.092(3)	0.092(2)	0.055(2)	0.017(2)	–0.006(2)	–0.008(2)
C(6)	2*a*	0.668(5)	0.8907(7)	0.9422(7)	0.0587(5)	0.102(3)	0.106(3)	0.109(3)	–0.035(3)	0.045(2)	–0.041(3)
C(7)	2*a*	0.668	0.9711(5)	1.0783(6)	0.0945(5)	0.082(4)	0.069(3)	0.073(3)	–0.003(3)	0.025(3)	–0.004(3)
C(8)	2*a*	0.668	1.1308(6)	1.0440(8)	0.1114(4)	0.091(4)	0.104(5)	0.067(3)	–0.019(3)	0.017(3)	0.009(3)
O(4)	2*a*	0.668	1.1652(3)	1.0236(4)	0.0084(2)	0.118(2)	0.142(3)	0.110(2)	–0.047(2)	0.060(2)	–0.018(2)
C(6A)	2*a*	0.332	0.8904(3)	0.9431(4)	0.0584(2)	0.102(3)	0.106(3)	0.109(3)	–0.035(3)	0.045(2)	–0.041(3)
C(7A)	2*a*	0.332	1.009(1)	1.007(2)	0.1437(8)	0.078(7)	0.10(1)	0.11(1)	–0.022(7)	0.041(6)	–0.021(7)
C(8A)	2*a*	0.332	1.087(2)	1.105(1)	0.0777(9)	0.091(4)	0.104(5)	0.067(3)	–0.019(3)	0.017(3)	0.009(3)
O(4A)	2*a*	0.332	1.1652(3)	1.0236(4)	0.0084(2)	0.118(2)	0.142(3)	0.110(2)	–0.047(2)	0.060(2)	–0.018(2)

References

1. Doboszewski, B.: Easy synthesis of 1-allyl-1-deoxy-β- and α-D-lyxofuranoses. J. Carbohydr. Chem. **21** (2002) 79-88.
2. Hürzeler, M.; Bernet, B.; Mäder, T.; Vasella, A.: Glyconothio-*O*-lactones. Cycloaddition to dienes, diazomethane, and carbenoids. Helv. Chim. Acta **76** (1993) 1779-1801.
3. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
4. Spek, A. L.: Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **36** (2003) 7-13.