Crystal structure of 5,6-dideoxy-1,2:3,4-di-*O*-isopropylidene-β-*D*-arabino-5-hexenose, $C_{12}H_{20}O_5$

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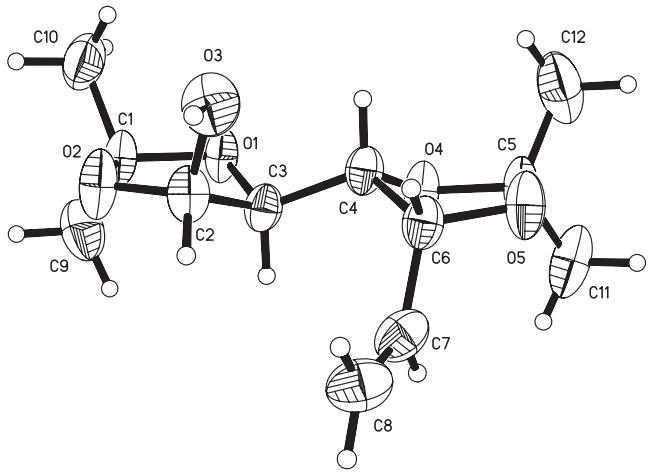

Abstract

$C_{12}H_{20}O_5$, orthorhombic, $P2_12_12$ (no. 18), a = 11.629(2) Å, b = 19.558(2) Å, c = 5.774(1) Å, V = 1313.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.068, $wR_{ref}(F^2)$ = 0.157, T = 293 K.

Source of material

The title compound was obtained as the major product by fragmentation of 6-deoxy-6-iodo-1,2:3,4-di-*O*-isopropylidene-*a*-*L*-galactose with zinc, ammonium chloride and vitamin B_{12} in methanol [1-5]. Isolation by column chromatography (ethyl acetate/petroleum ether) followed by crystallization of the anomeric mixture from ethyl acetate gave the title 5-hexenose compound in the form of colourless crystals [1] (m.p. 352-354 K); $[\alpha]_D^{20}$ = +19 (c = 1.025, CH_2Cl_2). When crystals of this anomer are dissolved, the optical rotation changes (mutarotation); the anomer mixture with β/α = 63 : 37 in the *L*-series (obtained from *D*-galactose) shows $[\alpha]_D^{20}$ = +33 (c = 1.11, $CHCl_3$).

Experimental details

H atoms were located in difference fourier map, but refined with fixed individual displacement parameters using a riding model with d(C—H) ranging from 0.93 to 0.98 Å, except H3A of the hydroxy group which is refined free, because of its relevance for the intermolecular hydrogen bond. In addition, the methyl groups were allowed to rotate but not to tip.

Discussion

The alkenyl bond of the side-chain C7=C8 is verified by the distance of 1.316(6) Å. Both dioxolane rings show an envelope conformation with C3 and C4 out-of-plane. This results in a *cis* configuration of the hydrogen. An intermolecular hydrogen bond is present between the hydroxy group O3–H3A as donor and the oxygen O1 of a dioxalane moiety as acceptor. This interaction is nearly linear indicated by an angle ∠O3–H3A···O1 of 175(4)° and d(H3A···O1) = 1.86(5) Å.

Table 1. Data collection and handling.

Crystal:	colourless plates, size 0.2 × 0.8 × 1.0 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	7.96 cm^{-1}
Diffractometer, scan mode:	Siemens P4, ω
$2\theta_{max}$:	134.86°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2438, 2062
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1803
$N(param)_{refined}$:	163
Programs:	SHELXS-97 [6], SHELXL-97 [7], SHELXTL-Plus [8]

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

Atom	Site	x	y	z	U_{iso}
H(2)	4*c*	0.3506	0.8477	0.2388	0.049
H(3A)	4*c*	0.198(4)	0.840(2)	0.040(9)	0.07(1)
H(3)	4*c*	0.3771	0.8053	0.5970	0.042
H(4)	4*c*	0.1605	0.7438	0.5024	0.042
H(6)	4*c*	0.2593	0.7027	0.1966	0.046
H(7)	4*c*	0.4715	0.6923	0.4447	0.057
H(8A)	4*c*	0.4278	0.7375	0.0017	0.066
H(8B)	4*c*	0.5525	0.7306	0.1206	0.066
H(9A)	4*c*	0.3526	0.9991	0.7511	0.094
H(9B)	4*c*	0.4131	0.9280	0.7788	0.094
H(9C)	4*c*	0.3237	0.9526	0.9642	0.094
H(10A)	4*c*	0.0777	0.9325	0.6026	0.094
H(10B)	4*c*	0.1393	1.0014	0.6655	0.094
H(10C)	4*c*	0.1099	0.9485	0.8607	0.094
H(11A)	4*c*	0.4134	0.6056	0.7660	0.102
H(11B)	4*c*	0.3327	0.5415	0.7542	0.102
H(11C)	4*c*	0.3245	0.5919	0.9648	0.102
H(12A)	4*c*	0.1188	0.5593	0.6753	0.119
H(12B)	4*c*	0.0742	0.6339	0.6330	0.119
H(12C)	4*c*	0.1103	0.6108	0.8827	0.119

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

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4*c*	0.2367(2)	0.8487(1)	0.7280(4)	0.065(2)	0.023(1)	0.032(1)	0.002(1)	0.008(1)	0.0004(9)
C(1)	4*c*	0.2486(4)	0.9199(2)	0.6680(6)	0.066(3)	0.022(2)	0.035(2)	0.001(2)	0.000(2)	0.002(1)
O(2)	4*c*	0.2804(3)	0.9207(1)	0.4288(5)	0.097(3)	0.028(1)	0.038(2)	0.002(1)	0.006(2)	0.003(1)
C(2)	4*c*	0.2837(4)	0.8536(2)	0.3400(6)	0.060(3)	0.033(2)	0.030(2)	–0.002(2)	–0.000(2)	–0.001(1)
O(3)	4*c*	0.1827(3)	0.8375(2)	0.2212(5)	0.071(2)	0.061(2)	0.040(2)	–0.003(2)	–0.014(2)	0.007(1)
C(3)	4*c*	0.2957(4)	0.8095(2)	0.5554(6)	0.047(2)	0.028(2)	0.031(2)	0.003(2)	0.003(2)	–0.002(1)
O(4)	4*c*	0.2632(3)	0.7007(1)	0.7371(4)	0.076(2)	0.026(1)	0.027(1)	0.001(1)	–0.002(1)	0.0000(9)
C(4)	4*c*	0.2433(4)	0.7397(2)	0.5303(6)	0.048(2)	0.028(2)	0.029(2)	0.002(2)	–0.002(2)	0.001(1)
O(5)	4*c*	0.2702(3)	0.6272(1)	0.4297(5)	0.087(2)	0.029(1)	0.037(1)	–0.003(1)	–0.002(2)	–0.005(1)
C(5)	4*c*	0.2495(4)	0.6299(2)	0.6737(7)	0.074(3)	0.023(2)	0.040(2)	–0.001(2)	0.001(2)	–0.001(1)
C(6)	4*c*	0.2973(4)	0.6948(2)	0.3457(6)	0.052(2)	0.031(2)	0.031(2)	0.002(2)	–0.003(2)	–0.004(1)
C(7)	4*c*	0.4245(4)	0.7035(2)	0.3199(7)	0.051(3)	0.050(2)	0.042(2)	0.013(2)	–0.005(2)	–0.008(2)
C(8)	4*c*	0.4730(4)	0.7261(3)	0.1287(7)	0.049(3)	0.071(3)	0.045(2)	0.009(2)	0.002(2)	–0.009(2)
C(9)	4*c*	0.3429(4)	0.9528(2)	0.8025(9)	0.082(4)	0.045(2)	0.060(3)	–0.019(2)	–0.010(3)	–0.002(2)
C(10)	4*c*	0.1335(4)	0.9536(2)	0.702(1)	0.069(3)	0.039(2)	0.080(3)	0.012(2)	0.012(3)	0.007(2)
C(11)	4*c*	0.3380(5)	0.5885(2)	0.8012(8)	0.118(5)	0.037(2)	0.051(3)	0.019(2)	–0.008(3)	–0.001(2)
C(12)	4*c*	0.1269(5)	0.6063(3)	0.721(1)	0.103(4)	0.048(3)	0.087(4)	–0.024(3)	0.018(4)	–0.004(3)

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