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Carbohydrate Research 308 (1998) 431–433

Note

X-ray diffraction and high resolution NMR spectroscopy analysis of methyl β-D-glucofuranosidurono-6,3-lactone

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Received 24 March 1997; accepted in revised form 24 March 1998

Abstract

The X-ray diffraction and high resolution ^{1}H- and ^{13}C NMR spectral data are reported for the title compound.

Keywords: Methyl; β-D-Glucofuranosidurono-6,3-lactone; X-ray diffraction; ^{1}H NMR; ^{13}C NMR

Glycuronic acid lactones are of interest as synthons [1,2]. The synthesis of methyl β-D-glucofuranosidurono-6,3-lactone was carried out by Osman [1] and Philips [2], but the structure of the product was based only on its physical properties. For our studies of *O*-glycoside isomerization, we needed full characterization of this lactone. In order to confirm its structure, high resolution ^{1}H and ^{13}C NMR spectroscopy and X-ray diffraction analysis were carried out.

The high resolution ^{1}H NMR spectrum (500 MHz, CD_3OD) showed signals at δ (ppm) 4.95 (s, 1H, H-1), 4.94 (dd, 1H, $J_{4,5}$ 5.49 Hz, H-4), 4.83 (d, 1H, $J_{3,4}$ 4.88 Hz, H-3), 4.52 (d, 1H, $J_{4,5}$ 5.49 Hz, H-5), 4.20 (s, 1H, H-2). The ^{13}C NMR spectrum (125 MHz, CD_3OD) had signals at δ (ppm) 175.674 C-6, 110.590 C-1, 83.245 C-3, 77.593 C-2, 77.048 C-4, 69.055 C-5, 54.246 C-7 (OCH_3). In the crystal lattice,[1] the five-membered ring adopts a twist conformation $^{1}T_2$ (puckering parameters [3] $q = 0.355$, $\Phi = -125.1°$). The summary of crystallographic data, data collection and structure-refinement parameters are presented in Table 1. Torsion angles from X-ray analysis are tabulated in Table 2. The non-hydrogen atom coordinates and equivalent temperature factors are presented in Table 3 and Fig. 1.

The values of bond lengths and angles determined in this work for the title compound agree with the standard ones [4]. Each molecule forms two intermolecular hydrogen bonds (H-2A to O-1

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[1] Tables of atomic coordinates, bond lengths, and bond angles have been deposited with the Cambridge Crystallographic Data Centre. These tables may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 IEZ, UK.

0008-6215/98/$19.00
PII S0008-6215(98)00081-0

in the position 1-X, 0.5-Y, 0.5-Z provide H···O distance 1.937(0.035) H-2A-01 and O-H···O angle 140.18(2.42) O-2-H-2A-O-2.

Table 1
Crystal data and summary of intensity and structure refinement

Compound	DPAMA
Colour/shape	Colourless prisms
Empirical formula	$C_7H_{10}O_6$
Formula weight	180.15
F(000)	400
Space group	$P2_12_12_1$
Cell constants: a, Å	7.086(2)
b, Å	7.462(2)
c, Å	15.019(3)
α, °	90
β, °	90
γ, °	90
Cell volume, Å^3	794.1(1)
Formula units/unit cell	4
μ_{calc}, mm^{-1}	0.14
Density$_{calc}$, g/cm^3	1.590
Crystal size, mm	0.3×0.4×0.6
Diffractometer	Kuma KM4
Radiation	MoK_α
Scan mode	$\theta/2\theta$
Scan width	$1.4 + \mathrm{tg}\ \theta$
Standard reflections	222, 333, 224
Decay of standards	±2.04%
Reflections collected	1381
Independent reflections	1360
Reflections observed ($F > 2\sigma$(I))	1237
2θ range,°	1.8–60
Ranges of h	0→9
k	0→10
l	0→21
No. of parameters varied	157
Function minimized	$\Sigma\omega(F_o^2 - F_o^2)^2$
$\omega^{-1} = \sigma^2(F_o^2) + (\mathrm{axP})^2 + \mathrm{bxP}$	
where	
$P = (\mathrm{Max}(F_o^2, 0) + 2F_o^2)/3$	
a	0.0858
b	0.0000
Goodness of fit	1.107
R1	0.0367
$\omega R2$	0.1119
$\Delta\rho_{max}$, e/Å^3	0.33
$\Delta\rho_{min}$, e/Å^3	−0.19

Table 2
Torsion angles obtained from X-ray diffraction analysis

No.	Dihedral angle	[°]
1	C-7–O-1–C-1–O-4	−72.3
2	C-7–O-1–C-1–C-2	172.4
3	C-4–O-4–C-1–O-1	−85.4
4	C-4–O-4–C-1–C-2	32.1
5	O-1–C-1–C-2–O-2	−163.4
6	O-4–C-1–C-2–O-2	76.1
7	O-1–C-1–C-2–C-3	83.0
8	O-4–C-1–C-2–C-3	−37.4
9	C-6–O-3–C-3–C-4	3.9
10	O-2–C-2–C-3–O-3	160.4
11	C-1–C-2–C-3–O-3	−84.3
12	O-2–C-2–C-3–C-4	−86.4
13	C-1–C-2–C-3–C-4	28.9
14	C-1–O-4-C-4–C-5	100.0
15	C-1–O-4-C-4–C-3	−13.0
16	O-3–C-3-C-4–O-4	103.2
17	C-2–C-3–C-4–O-4	−11.2
18	O-3–C-3–C-4-C-5	−16.2
19	C-2–C-3–C-4–C-5	−130.6
20	O-4–C-4–C-5–O-5	27.8
21	C-3–C-4–C-5–O-5	142.5
22	O-4–C-4–C-5–C-6	−93.2
23	C-3–C-4–C-5–C-6	21.5
24	C-3–O-3–C-6–O-3	−170.5
25	C-3–O-3–C-6–C-5	10.6
26	O-5–C-5–C-6–O-6	35.5
27	C-4–C-5–C-6–O-6	160.7
28	O-5–C-5–C-6–O-3	−145.8
29	C-4–C-5–C-6–O-3	−20.5

Table 3
Non-hydrogen fractional atomic coordinates and equivalent temperature factors with esd's in parentheses

Atom	x/a	y/b	z/c	U_{eq}
O-1	0.2478(2)	0.0938(2)	0.22181(10)	0.0337(3)
O-2	0.6580(2)	0.3386(2)	0.14735(10)	0.0334(3)
O-3	0.5172(2)	−0.1272(2)	0.12924(9)	0.0309(3)
O-4	0.2897(2)	0.2326(2)	0.08222(10)	0.0335(3)
O-5	0.1007(2)	−0.0609(2)	0.00950(12)	0.0431(4)
O-6	0.2791(2)	−0.3235(2)	0.11850(11)	0.0388(4)
C-1	0.3426(3)	0.2286(2)	0.17340(12)	0.0257(3)
C-2	0.5526(2)	0.1842(2)	0.17234(11)	0.0245(3)
C-3	0.5641(3)	0.0505(2)	0.09523(12)	0.0269(3)
C-4	0.4016(3)	0.1064(2)	0.03326(11)	0.0281(4)
C-5	0.2980(3)	−0.0704(3)	0.01488(12)	0.0302(4)
C-6	0.3555(3)	−0.1904(2)	0.09202(12)	0.0279(4)
C-7	0.0541(4)	0.1326(4)	0.2370(4)	0.0765(13)

esds-estimated standard deviations.

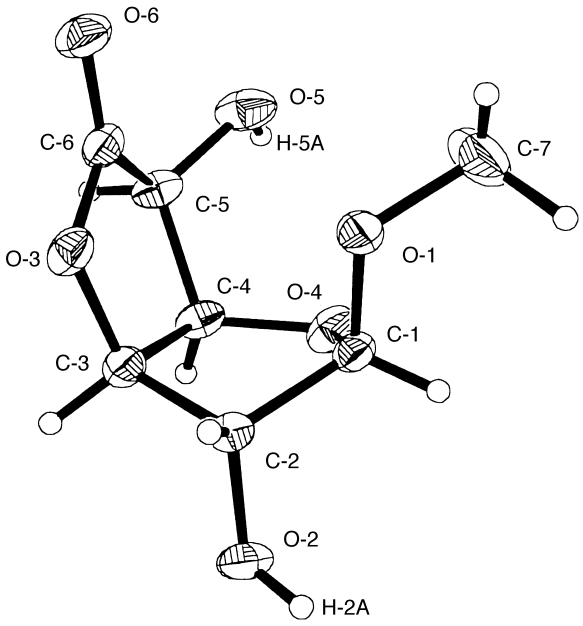

Fig. 1. The X-ray structure of methyl β-D-glucofuranosiduronono-6,3-lactone.

Acknowledgement

This work was partially supported by the Polish Research Council (KBN) under grant BW-8000-5-0233-6.

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