Carbohydrate Research, 241 (1993) 261–266
Elsevier Science Publishers B.V., Amsterdam

Note

The X-ray crystallographic structures of methyl 2-*O*-methyl-α-D-glucopyranoside and methyl 4,6-*O*-(*S*)-benzylidene-2-*O*-methyl-α-D-galactopyranoside

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(Received November 28th, 1991; accepted August 15th, 1992)

As part of a programme involving X-ray crystallographic studies[1] of *cis*- and *trans*-fused hexopyranosides, we now report on the crystal structures of methyl 2-*O*-methyl-α-D-glucopyranoside[2] (**1**), which was obtained by debenzylidenation of methyl 4,6-*O*-benzylidene-2-*O*-methyl-3-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside[3] followed by detosylation, and methyl 4,6-*O*-benzylidene-2-*O*-methyl-α-D-galactopyranoside (**2**), which was prepared[4] by selective tosylation of methyl 4,6-*O*-benzylidene-α-D-galactopyranoside followed by Purdie methylation and detosylation.

Perspective views of **1** and **2** are depicted in Figs. 1 and 2, respectively. The final atomic co-ordinates for **1**, with their standard deviations in parentheses, are listed in Tables I and II, and the corresponding parameters for **2** are given in Tables III and IV.

For **1**, the C–C bond lengths in the sugar ring have a mean value of 1.52 Å, in agreement with values observed for other carbohydrates, and there is a $^4C_1$ conformation with C-2, C-3, C-5, and O-5 coplanar (C-4 and C-1, respectively, lie 0.67 Å above and 0.69 Å below this plane). There are intermolecular hydrogen bonds involving O-2 and O-4, O-3 and O-6, and O-3 and O-4. The hydrogen atoms attached to O-3, O-4, and O-6 were not located. All other hydrogen atoms were attached in calculated positions with fixed thermal parameters.

In the crystal structure of **2**, there is the expected[5] double-chair conformation with the phenyl group equatorial. For **2**, C-5 lies 0.637 Å below and C-7 lies 0.66 Å above plane 1 (C-6, O-6, C-4, and O-4), and C-4 lies 0.65 Å above, and C-1 lies 0.69 Å below plane 2 (C-2, C-3, C-5, and O-5 of the pyranose ring). Plane 2 of the pyranose ring lies at an angle of 76.82° to plane 1. The phenyl ring is oriented at an angle of 75.97° to plane 1. There is an intermolecular hydrogen bond involving O-3 and O-6 (2.83 Å).

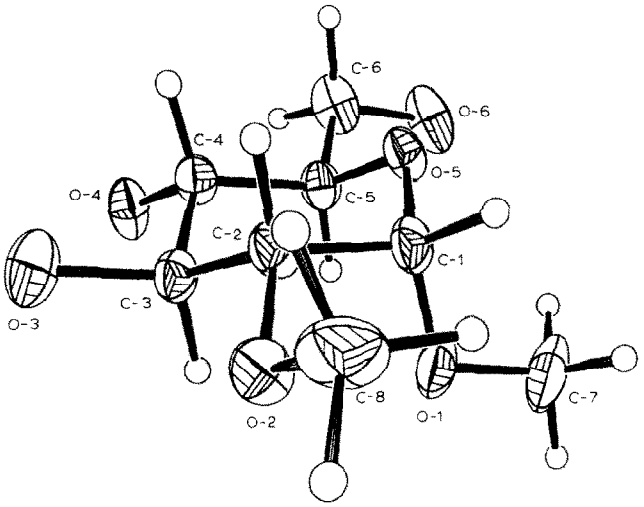

Fig. 1. ORTEP[11] drawing of methyl 2-*O*-methyl-α-D-glucopyranoside (**1**) and the numbering scheme.

EXPERIMENTAL

Compounds **1** and **2** were prepared as described[2–4]. The crystallographic data * are given in Table V. The structures were solved by direct methods, SHELX-86[6], and refined by full-matrix least squares using SHELX 76[7]. The data were corrected for Lorentz and polarisation effects, but not for absorption. For **1**, hydrogen

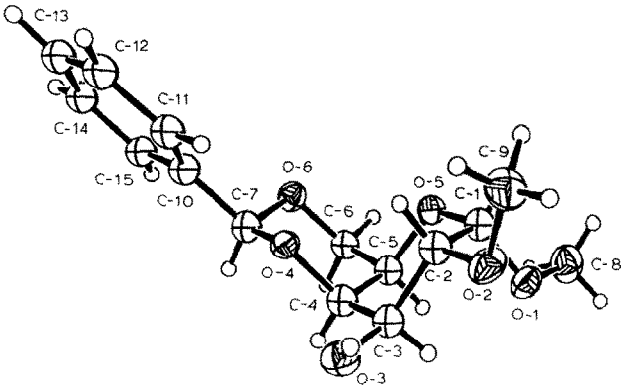

Fig. 2. ORTEP[11] drawing of methyl 4,6-*O*-benzylidene-2-*O*-methyl-α-D-galactopyranoside (**2**) and the numbering scheme.

* *Supplementary material.*—Lists of anisotropic and isotropic thermal parameters bond lengths, and bond angles have been deposited with, and can be obtained from, Elsevier Science Publishers, B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, Netherlands. Reference should be made to No. BBA/DD/519/*Carbohydr. Res.*, 241 (1993) 261–266.

TABLE I

Fractional atomic co-ordinates for **1**

Atom	*x*	*y*	*z*
O-1	0.0510 (3)	−0.6041 (3)	−0.9152 (2)
O-2	−0.0263 (3)	−0.8195 (2)	−1.0472 (2)
O-3	−0.0936 (3)	−0.6869 (2)	−1.2532 (2)
O-4	−0.1010 (3)	−0.4052 (2)	−1.2372 (2)
O-5	−0.1918 (3)	−0.5050 (2)	−0.9465 (2)
O-6	−0.2012 (4)	−0.2264 (2)	−0.9244 (2)
C-1	−0.1062 (4)	−0.6264 (3)	−0.9373 (3)
C-2	−0.1203 (4)	−0.7050 (3)	−1.0481 (3)
C-3	−0.0670 (4)	−0.6206 (3)	−1.1480 (2)
C-4	−0.1563 (4)	−0.4913 (3)	−1.1496 (2)
C-5	−0.1360 (4)	−0.4194 (3)	−1.0359 (3)
C-6	−0.2307 (5)	−0.2927 (3)	−1.0280 (3)
C-7	0.0798 (6)	−0.5470 (5)	−0.8070 (3)
C-8	−0.0834 (5)	−0.9226 (4)	−0.9778 (4)

atoms were included in calculated positions with fixed thermal parameters. All atoms were refined anisotropically. For **2**, all of the hydrogen atoms were observed in difference maps and were refined with isotropic thermal parameters, except those on the phenyl ring and the OH group which were included in the calculated positions. The oxygen atoms and the carbons of the methyl groups were refined anisotropically. The thermal parameters were terms U_{ij} of $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

The atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from

TABLE II

Fractional atomic co-ordinates for the hydrogen atoms (1)

Atom	*x*	*y*	*z*
H-1	−0.156	−0.682	−0.867
H-2	−0.242	−0.733	−1.056
H-3	0.057	−0.603	−1.138
H-4	−0.278	−0.515	−1.165
H-5	−0.013	−0.395	−1.028
H-6	−0.353	−0.317	−1.033
H-7	−0.199	−0.228	−1.098
H-8	0.204	−0.533	−0.796
H-9	0.037	−0.612	−0.742
H-10	0.021	−0.453	−0.801
H-11	−0.005	−1.006	−0.982
H-12	−0.198	−0.952	−1.007
H-13	−0.092	−0.888	−0.891

TABLE III

Fractional atomic co-ordinates (Å) for **2**

Atom	*x*	*y*	*z*
O-1	0.1648 (5)	−0.2485 (2)	−0.4241 (1)
O-2	0.0618 (5)	−0.0349 (2)	−0.4068 (1)
O-3	0.3757 (5)	−0.0254 (2)	−0.3020 (1)
O-4	0.0263 (4)	−0.1605 (1)	−0.2384 (1)
O-5	−0.0963 (5)	−0.2907 (2)	−0.3411 (1)
O-6	−0.1355 (5)	−0.3268 (2)	−0.2153 (1)
C-8	0.1098 (11)	−0.3424 (3)	−0.4552 (2)
C-9	−0.1824 (9)	0.0185 (3)	−0.4228 (2)
C-1	−0.0521 (7)	−0.2181 (2)	−0.3873 (1)
H-1	−0.2251 (73)	−0.2186 (23)	−0.4086 (12)
C-2	0.0185 (7)	−0.1106 (2)	−0.3620 (1)
H-5	−0.1350 (80)	−0.0846 (24)	−0.3343 (13)
C-3	0.2814 (7)	−0.1205 (2)	−0.3258 (1)
H-10	0.4323 (95)	−0.1484 (26)	−0.3582 (16)
C-4	0.2341 (7)	−0.1998 (2)	−0.2783 (1)
H-11	0.3985 (97)	−0.2088 (31)	−0.2561 (16)
C-5	0.1409 (7)	−0.3031 (2)	−0.3036 (1)
H-20	0.3046 (95)	−0.3338 (31)	−0.3248 (17)
C-6	0.0547 (8)	−0.3764 (3)	−0.2550 (2)
H-18	0.2120 (95)	−0.3960 (31)	−0.2270 (15)
H-19	−0.0495 (86)	−0.4329 (29)	−0.2726 (14)
C-7	−0.0242 (7)	−0.2314 (2)	−0.1931 (1)
H-12	0.1649 (83)	−0.2471 (25)	−0.1750 (13)
H-2	−0.0397 (96)	−0.3322 (31)	−0.4816 (17)
H-3	0.1193 (92)	−0.3990 (33)	−0.4244 (19)
H-4	0.2751 (87)	−0.3594 (34)	−0.4871 (20)
H-6	−0.2386 (96)	0.0629 (31)	−0.3914 (17)
H-7	−0.3403 (88)	−0.0325 (30)	−0.4296 (17)
H-8	−0.1028 (69)	0.0619 (58)	−0.4548 (28)
C-10	−0.2351 (7)	−0.1874 (2)	−0.1514 (1)
C-11	−0.3646 (8)	−0.0925 (3)	−0.1610 (1)
C-14	−0.5588 (9)	−0.0545 (3)	−0.1207 (2)
C-1	−0.6223 (10)	−0.1119 (3)	−0.0721 (2)
C-14	−0.4965 (9)	−0.2062 (3)	−0.0627 (2)
C-15	−0.3032 (8)	−0.2447 (3)	−0.1013 (1)

TABLE IV

Fractional atomic co-ordinates (Å) for hydrogen atoms (calculated positions) (**2**)

Atom	*x*	*y*	*z*
H-9	0.311	0.034	−0.318
H-13	−0.322	−0.053	−0.195
H-14	−0.646	0.011	−0.127
H-15	−0.754	−0.086	−0.045
H-16	−0.543	−0.246	−0.029
H-17	−0.216	−0.310	−0.094

TABLE V

Crystal data for **1** and **2**

	1	**2**
Crystal size (mm)	0.3×0.21×0.38	0.31×0.24×0.30
Formula	$C_8H_{16}O_6$	$C_{15}H_{20}O_6$
M (amu)	208.211	296.319
Orthorhombic		
Space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	8.554 (2)	4.826 (1)
b (Å)	10.087 (2)	12.834 (2)
c (Å)	11.780 (2)	22.862 (5)
U (Å^3)	1016.33	1416.03
Z	4	4
D_c (g·cm^{-3})	1.36	1.39
μ (cm^{-1})	0.76	0.66
F_{000}	448.0	632
Radiation Mo-$K\alpha$		
Graphite monochromator	$\lambda = 0.71069$ Å	$\lambda = 0.71069$ Å
Diffractometer	Enraf–Nonius CAD4F	Enraf–Nonius CAD4F
Orienting reflections range	$25,13 < \theta < 20°$	$25,13 < \theta < 20°$
Temperature (°C)	22	22
Scan method	ω-2θ	ω-2θ
Data collection range	$2 < 2\theta < 50°$	$2 < 2\theta < 48°$
No. of unique data	1370	1768
Total $I > 3\sigma I$	1210	1573
No. of parameters fitted	129	184
R^a, R_w^b	5.0%, 5.13%	5.12%, 5.91%
Largest shift/esd, final cycle	< 0.001	< 0.001
Largest positive peak (e/Å^3)	0.16	0.21
Largest negative peak (e/Å^3)	−0.07	−0.09

[a] $R = [\Sigma \| F_o | - | F_c \|] / \Sigma | F_o |$.

[b] $R_w = [[\Sigma w(|F_o - F_c|)^2] / [\Sigma w(|F_o|)^2]]^{1/2}$; $w = 1/[(\sigma F_o)^2\ 0.00031 \cdot F_o^2]$ for **1**; $w = 1/[(\sigma F_o)^2\ 0.00015 \cdot F_o^2]$ for **2**.

the literature[8–10]. All calculations were performed on a VAX 8700 computer. The ORTEP program[11] was used to obtain the drawings.

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