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Note

The crystal and molecular structure of methyl (1*R*)-1,2,3,5-tetra-*O*-acetyl-4-*O*-methyl-D-glucuronate methyl acetal*†

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The present study was undertaken as part of an investigation of the acetolysis reactions of methyl (methyl 4-*O*-methyl-β-D-glucopyranosid)uronate[1,2]. The reactions involve the formation of an intermediate product through cleavage of the pyranose ring and acetylation. This intermediate can have two possible configurations at C-1 which could not be distinguished by ^{1}H-n.m.r. spectroscopy. Therefore, the molecular structure was determined by X-ray crystallography and is reported herein.

TABLE I

CRYSTAL DATA AND X-RAY DIFFRACTION ANALYSIS DATA FOR METHYL (1*R*)-1,2,3,5-TETRA-*O*-ACETYL-4-*O*-METHYL-D-GLUCURONATE METHYL ACETAL

Crystal data
$C_{17}O_{12}H_{26}$; mol. wt. 422.39; m.p. 114–115°; Space group $P2_1$; $Z = 2$
Cell dimensions, $a = 7.704(2)$, $b = 17.007(1)$, $c = 8.717(1)$ Å
$\beta = 108.28(1)°$
Volume = 1084.6(5)Å^3
D_m = [1.293] gcm^{-3}
F(000) 448

Experimental and refinement data
Radiation (MoK_α) ($\lambda = 0.7093$ Å); μ 0.1 mm^{-1}
Temperature, 24 ±1°
2θ range 5–50°
Reflection measured (one quadrant) 2159
Reflections with Fo>3σ(Fo), 1600
Number of refined parameters, 262
Final refinement values: $R = 0.064$; $R_w = 0.057$
Diffractometer, Enraf–Nonius CAD4

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*Part III. Synthetic Studies on Oligosaccharides of a Glycolipid from the Spermatozoa of Bivalves. For Part II, see ref. 1.

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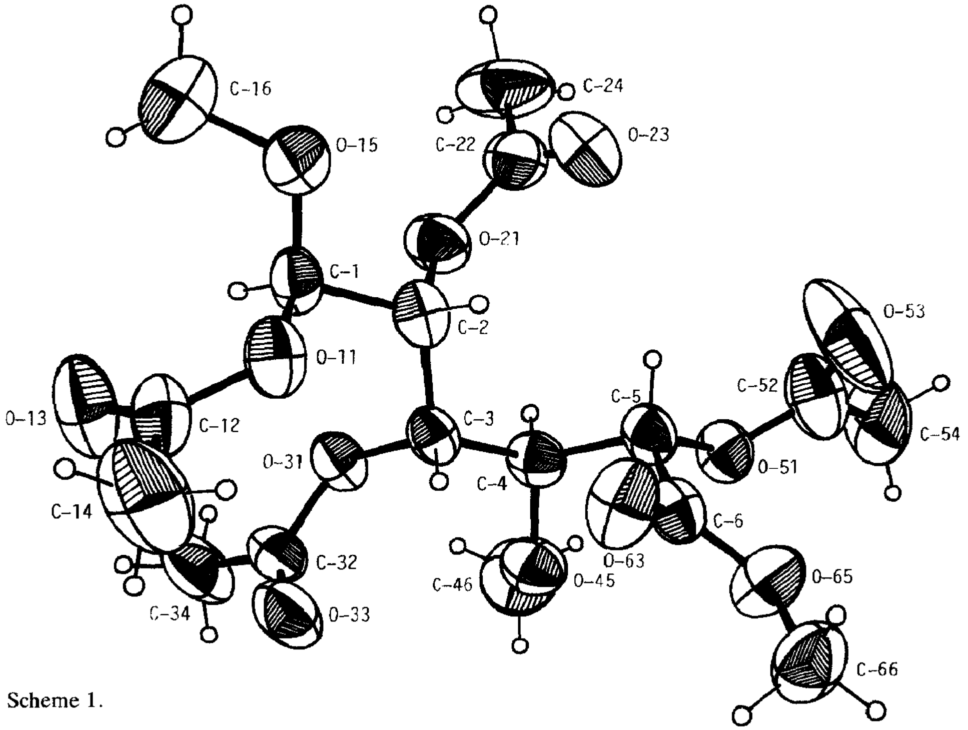

Scheme 1.

Methyl (1*R*)-1,2,3,5-tetra-*O*-acetyl-4-*O*-methyl-D-glucuronate methyl acetal crystallized in the monoclinic space-group $P2_1$. Further crystallographic data are given in Table I. The structure was solved by the direct method and refined by full-matrix, least-square techniques*.

A perspective view of the acetal molecule with the thermal ellipsoids of 50% probability (except hydrogen atoms) and the atomic labeling is shown in Scheme 1. The final positional coordinates with the estimated standard deviations and the isotropic equivalent temperature factors for the non-hydrogen atoms are given in Table II. The four established configurations[1] at C-2 to C-5 confirmed that the enantiomeric attribution is correct for the entire molecular structure. Therefore, the configuration at C-1 is undoubtedly determined as *R*, as shown in Scheme 1.

The solid state structure of this molecule is, to our knowledge, the first example of an open-chain derivative of uronic acid, and is described as follows. Two sets of chain skeletons of O-15 to O-45, and O-31 to C-52 make a planar, zigzag arrangement, respectively, and the two zigzag planes cross the C-3–C-4 bond as a common junction line. Since the relative torsional angle of C-2–C-3–C-4–C-5 is about 58° (ref. 3), namely *cis*, the conformation of the O-15-to-C-52 chain can be

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*Programs of the Enraf–Nonius's SDP package were used. The package includes modified versions of Main, Hull, Lessinger, Germain, Declercq, Woolfson's Multan, and Johnson's Ortep II, and LSFM for full-matrix least-squares refinement.

TABLE II

ATOMIC POSITIONAL PARAMETERS AND TEMPERATURE FACTORS

Atoms	x	y	z	B_{eq}
O-15	0.2558(6)	0.250	0.7193(5)	5.4(1)
O-11	0.2603(6)	0.3252(3)	0.5012(6)	4.5(1)
O-13	0.5092(7)	0.4002(3)	0.6017(7)	7.2(2)
O-21	0.3779(6)	0.1221(3)	0.5947(5)	4.8(1)
O-23	0.0969(8)	0.0716(4)	0.5563(7)	8.5(2)
O-31	0.5701(5)	0.2156(3)	0.4185(5)	4.0(1)
O-33	0.5222(7)	0.3195(3)	0.2526(6)	5.7(1)
O-41	0.4536(6)	0.1292(3)	0.1413(5)	4.7(1)
O-51	0.2096(6)	0.0082(2)	0.1223(5)	4.3(1)
O-53	−0.0485(9)	−0.0343(4)	0.148(1)	11.8(2)
O-63	0.0122(7)	0.1986(3)	0.1013(6)	5.6(1)
O-65	0.0061(7)	0.1067(3)	−0.0819(5)	5.3(1)
C-1	0.3436(8)	0.2600(4)	0.6051(8)	3.9(1)
C-12	0.3573(9)	0.3925(4)	0.5139(9)	5.1(2)
C-14	0.246(1)	0.4535(5)	0.404(1)	8.2(3)
C-16	0.332(1)	0.2935(6)	0.864(1)	7.5(3)
C-2	0.2999(8)	0.1883(4)	0.4921(8)	4.1(1)
C-22	0.253(1)	0.0721(4)	0.6252(8)	5.7(2)
C-24	0.351(1)	0.0152(5)	0.757(1)	9.1(3)
C-3	0.3799(8)	0.1925(3)	0.3552(7)	3.4(1)
C-32	0.6271(9)	0.2785(4)	0.3507(8)	4.3(1)
C-34	0.825(1)	0.2904(6)	0.420(1)	7.2(2)
C-4	0.3768(8)	0.1161(4)	0.2634(7)	3.8(1)
C-46	0.619(1)	0.0866(7)	0.159(1)	7.6(2)
C-5	0.1840(8)	0.0825(4)	0.1902(7)	3.8(1)
C-52	0.085(1)	−0.0460(5)	0.112(1)	6.6(2)
C-54	0.127(1)	−0.1204(5)	0.042(1)	8.0(3)
C-6	0.0612(8)	0.1363(4)	0.0652(7)	4.0(1)
C-66	−0.122(1)	0.1549(5)	−0.204(1)	6.3(2)

expressed as a *trans–trans–cis–trans–trans* arrangement. On this main chain arrangement, the OAc-1 and OAc-2 groups are in *trans* conformation. The carbon skeleton of the molecule shows a *trans–cis–cis* conformation from C-1 to C-6. Intramolecular, nonbonded contacts are seen between the OAc-1 and OAc-3 groups. The smallest of these contacts, which measures 3.19 Å, is between C-12 and O-33. Another close, intramolecular nonbonded contact between C-5 and O-23 (3.47 Å) and the quasicircular conformation of seven atoms bonded to the two atoms enclosing hydrogen atoms are noteworthy. The torsional angles, listed in Table III, help in understanding the entire molecular conformation.

The intermolecular atomic distances show no unusual contact smaller than 3.25 Å, which is observed between O-51 and O-13′ where the prime indicates a symmetry-related position*. The skeletal C–C bond-length of 1.52 Å (average of 5

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*Lists of individual bond lengths, bond angles, hydrogen atomic positions, anisotropic thermal parameters for non-hydrogen atoms, and structure amplitudes (F_o and F_c) have been deposited with, and can be obtained from Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/000/*Carbohydr. Res.*, 000 (1989) 000–000.

TABLE III

TORSION ANGLES

Atoms	*Angle*[a]
O-15–C-1–C-2–C-3	177.31
O-11–C-1–C-2–O-21	−178.50
O-21–C-2–C-3–O-31	−69.75
C-1–C-2–C-3–C-4	166.94
O-31–C-3–C-4–C-5	179.05
C-2–C-3–C-4–O-45	179.70
C-2–C-3–C-4–C-5	57.92
O-45–C-4–C-5–C-6	−58.55
C-3–C-4–C-5–O-51	−174.96

[a] In degrees.

values) is slightly shorter than the ideal value[4] of 1.541 Å but is in good agreement with the values observed for D-arabinose oxime in the acyclic form[5]. The C–C–C bond angle of 113.9° (average of 4 values) for the carbon skeleton is greater than the value for the tetrahedral angle. This distortion of the C–C–C bond angles is probably due to a mixed steric effect of a long carbon-chain associated with bulky substituents. A similar opening of the C–C–C bond angles has been observed for another long carbon-chain system[6] and for some particular locations in the carbon chain of carbohydrates[7].

EXPERIMENTAL

Acetolysis of methyl (methyl 4-*O*-methyl-β-D-glucopyranosid)uronate with trifluoroborate etherate in acetic anhydride provided a mixture of the *R* and *S* acetal isomers (81% yield) in a 4:5 ratio[8]. Colorless plate crystals of the (*R*)-acetal were obtained by crystallization from 2-propanol.

REFERENCES

1 O. KANIE, T. TAKEDA, AND Y. OGIHARA, *Carbohydr. Res.*, 190 (1989) 53–64.

2 P. KOVÁČ, R. BREZNY, V. MIHALOV, AND R. PALOVCIK, *J. Carbohydr. Nucleosides Nucleotides*, 2 (1975) 445–458.

3 G. A. JEFFREY AND H. S. KIM, *Carbohydr. Res.*, 14 (1970) 207–216.

4 *International Tables for X-Ray Crystallography*, Vol. III, Kynoch Press, Birmingham, U.K., 1962, p. 276.

5 A. MOSTAD, *Acta Chem. Scand., Ser. B*, 32 (1978) 733–742.

6 M. GOTO AND E. ASADA, *Bull. Chem. Soc. Jpn.*, 53 (1980) 2111–2113.

7 T. B. GRINDLEY, S. KUSUMA, T. S. CAMERON, AND A. KUMARI, *Carbohydr. Res.*, 159 (1987) 171–183.

8 O. KANIE, S. FUJISAWA, T. TAKEDA, Y. OGIHARA, AND M. SUGITA, *Abstr. Pap. 11th Jpn. Carbohydr. Symp.*, (1988) 25; O. KANIE, T. TAKEDA, AND Y. OGIHARA, *Carbohydr. Res.*, in press.