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CRYSTAL AND MOLECULAR STRUCTURES OF SUBSTITUTED β-D-GLUCOFURANOSIDURONO-6,3-LACTONES

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ABSTRACT

The crystal and molecular structures of methyl β-D-glucofuranosidurono-6,3-lactone (**1**), 5-*O*-pivaloyl-β-D-glucofuranurono-6,3-lactone (**2**), and methyl 2-*O*-acetyl-5-*O*-pivaloyl-β-D-glucofuranosidurono-6,3-lactone (**3**) were determined by X-ray analysis. Crystals of compound **1** are orthorhombic, space group $P2_12_12_1$ with the unit cell $a = 7.074(1)$, $b = 7.448(1)$, $c = 14.995(2)$ Å, $Z = 4$. Crystals of **2** and **3** are monoclinic, space group $P2_1$. The unit-cell parameters are $a = 6.315(1)$, $b = 9.307(2)$, $c = 10.612(2)$ Å, $\beta = 98.68(1)°$, $Z = 2$ for **2**; and $a = 13.337(1)$, $b = 10.296(1)$, $c = 13.544(1)$ Å, $\beta = 118.24(1)°$, $Z = 4$ for **3**. The structures were solved by MULTAN-80 and refined by a full-matrix procedure to final values of $R = 0.042(1)$, 0.048(2), and 0.093(3). The furanoid rings in **1**, **2**, and conformer B of **3** appear in twisted, ${}^1T_2$ conformation, and the lactone rings adopt conformations between *T* and *E*. The lactone ring of conformer A of **3** adopts a *T* conformation and that of the furanoid ring is E_2. The molecular packing is through the hydrogen bonds involving hydroxyl groups HO-2 · · · · O-1 [2.812(2) Å] in **1**. A hydrogen bond between a hydroxyl group and the pivaloyl carbonyl group, HO-1 · · · · O-7 [2.855(3) Å], connects the molecules of **2**. There are no free hydroxyl groups in **3** and molecular packing reflects van der Waals interactions only.

INTRODUCTION

The pivaloyl group is a useful protecting group since it shows no tendency to migrate, and it can be easily detected by ^{1}H-n.m.r. spectroscopy. Pivaloyl chloride is highly selective in its reactions with nucleosides[1], partially protected D-mannitol[2], sucrose[3], and methyl β-D-glucopyranoside[4]. Selective acylations of D-glucofuranurono-6,3-lactone and its derivatives have also been reported[5], and a series of partially protected compounds was prepared. The chemical shifts of the signals of

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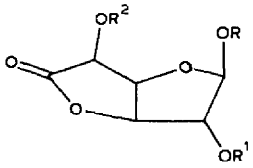
the pivaloyl groups in the ^{1}H-n.m.r. spectra of these compounds were used to assign the position of the substituents. Three representatives (**1–3**) of a series have been subjected to X-ray analysis.



1 R = Me, R^1 = R^2 = H
2 R = R^1 = H, R^2 = Me_3CCO
3 R = Me, R^1 = Ac, R^2 = Me_3CCO

EXPERIMENTAL

Crystals of **1** suitable for X-ray diffraction were obtained from aqueous 96% ethanol, and those of **2** and **3** were obtained from 2-propanol. Preliminary cell dimensions and the space groups were determined from oscillation and Weissenberg photographs recorded with Cu$K\alpha$ radiation. Final cell parameters were refined from diffractometer measurements of 15 reflections for each compound.

Crystal data: **1** ($C_7H_{10}O_6$), M_r = 190.96, orthorhombic, space group $P2_12_12_1$, a = 7.074(1), b = 7.448(1), c = 14.995(2) Å, V = 790.04 Å^3, Z = 4, D_c = 1.605 M.gm^{-3}, μ(Mo$K\alpha$) = 1.34 cm^{-1}, F(000) = 400 electrons; **2** ($C_{11}H_{16}O_7$), M_r = 260.25, monoclinic, space group $P2_1$, a = 6.315(1), b = 9.307(1), c = 10.612(2) Å, β = 98.68(1)°, V = 615.56 Å^3, Z = 2, D_c = 1.401 Mg.m^{-3}, μ(Mo$K\alpha$) = 1.10 cm^{-1}, F(000) = 276 electrons; **3** ($C_{14}H_{20}O_8$), M_r = 316.31, monoclinic, space group $P2_1$, a = 13.337(1), b = 10.296(1), c = 13.544(1) Å, β = 118.24(1)°, V = 1638.46 Å^3, Z = 4, D_c = 1.282 Mg.m^{-3}, μ(Mo$K\alpha$) = 0.99 cm^{-1}, F(000) = 672 electrons.

TABLE I

FINAL ATOMIC CO-ORDINATES (× 10^4) AND ISOTROPIC THERMAL PARAMETERS (× 100) FOR NON-HYDROGEN ATOMS FOR **1**

Atom	*x*	*y*	*z*	*U* (Å^2)
O-4	7104(2)	2677(2)	5822(1)	3.3(1)
O-1	7520(2)	4070(2)	7216(1)	3.3(1)
O-2	3419(2)	1615(2)	6471(1)	3.4(1)
O-3	4835(2)	6278(2)	6293(1)	3.1(1)
O-5	8995(2)	5601(2)	5094(1)	4.3(1)
O-6	7211(2)	8231(2)	6185(1)	3.9(1)
C-1	6576(3)	2709(2)	6734(1)	2.6(1)
C-2	4475(3)	3158(3)	6725(1)	2.5(1)
C-3	4359(3)	4496(3)	5952(1)	2.7(1)
C-4	5980(3)	3942(3)	5333(1)	2.8(1)
C-5	7011(3)	5705(3)	5150(1)	3.0(1)
C-6	6456(3)	6898(2)	5918(1)	2.8(1)
C-7	9475(4)	3672(4)	7363(3)	7.5(3)

$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \vec{a}_i \vec{a}_j$.

TABLE II

FINAL ATOMIC CO-ORDINATES (× 10^4) AND ISOTROPIC THERMAL PARAMETERS (× 100) FOR NON-HYDROGEN ATOMS FOR **2**

Atom	*x*	*y*	*z*	U_{eq} (Å²)
O-4	7850(3)	2607(3)	7082(2)	4.1(1)
C-1	9590(4)	2423(4)	6393(2)	4.1(2)
O-1	10772(3)	1187(3)	6783(2)	4.8(1)
C-2	8549(4)	2209(5)	5020(2)	4.4(2)
O-2	7727(3)	3526(4)	4477(2)	6.2(2)
C-3	6586(4)	1281(0)	5184(2)	3.9(2)
O-3	7204(3)	−199(0)	5272(2)	4.6(1)
C-4	6089(4)	1742(4)	6515(2)	3.4(1)
C-5	5954(4)	300(4)	7181(2)	3.3(1)
O-5	6940(3)	282(3)	8484(1)	3.7(1)
C-6	7104(5)	−759(4)	6439(2)	3.9(2)
O-6	7783(4)	−1919(3)	6745(2)	5.7(2)
C-7	5779(4)	888(4)	9310(2)	3.5(1)
O-7	3967(3)	1306(3)	8992(2)	5.0(1)
C-8	7001(5)	991(4)	10655(2)	4.1(2)
C-9	5640(9)	326(10)	11561(4)	11.5(4)
C-10	9121(9)	261(11)	10808(4)	13.7(5)
C-11	7261(14)	2519(7)	10964(6)	13.8(7)

$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \bar{a}_j$.

Intensities were collected on an Enraf-Nonius CAD-4 diffractometer in the $\omega/2\theta$ mode with a graphite monochromator and Mo$K\alpha$ radiation in the $1.5<\theta<30°$ range. Dimensions of the crystals used in data collection were 0.57 × 0.60 × 0.20 mm (**1**), 0.30 × 0.40 × 0.27 mm (**2**), and 0.30 × 0.22 × 0.60 mm (**3**), and 1347 independent reflections of **1**, 1892 of **2**, and 2514 of **3** were measured. Of these, 1299 (**1**), 1760 (**2**), and 2497 (**3**) were treated as observed reflections [$I \geq 2\sigma(I)$].

The structures were solved by direct methods using the MULTAN-80 programme[6]. The values $|E| \geq 1.40$ for **1** (181 reflections), **2** (256 reflections), and **3** (264 reflections) were used. In the phase determination of the structure for **2**, the 0 0 5 reflection (estimated |E| = 3.03) biased the procedure and the solution was obtained after its exclusion. Difference Fourier syntheses were used to locate 2 carbon atoms of **2** and 9 atoms of **3**. All hydrogen atoms of **1** and **2** were located from difference syntheses. However, in the structure of **3**, difference synthesis revealed only those hydrogen atoms attached to the ring skeleton. High temperature movements* of the terminal methyl groups not allowed the location of the hydrogen atoms attached to these carbons. The structures were refined by a full-matrix least-squares procedure, minimising $\Sigma w.\Delta F^2$, w = 1. Scale factors, atomic

*Anisotropic thermal parameters, the co-ordinates of hydrogen atoms, and observed and calculated structure factors have been deposited with, and may 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/337/*Carbohydr. Res.*, 152 (1986) 21–32.

TABLE III

FINAL ATOMIC CO-ORDINATES ($\times 10^4$) AND ISOTROPIC THERMAL PARAMETERS ($\times 100$) FOR NON-HYDROGEN ATOMS FOR **3**

Atom	*x*	*y*	*z*	*U* (Å²)
O-4A	4139(5)	6017(0)	7423(4)	6.6(3)
C-1A	4954(7)	6059(0)	8571(7)	6.3(4)
C-2A	4361(8)	6711(10)	9147(7)	6.5(4)
C-3A	3498(7)	7607(10)	8271(6)	6.1(4)
C-4A	3237(6)	6922(10)	7147(6)	5.6(3)
O-3A	4089(5)	8812(7)	8290(5)	6.7(3)
C-5A	3297(7)	8042(10)	6456(6)	6.0(4)
C-6A	4073(8)	9046(11)	7319(8)	6.9(5)
O-6A	4599(7)	9911(8)	7198(6)	10.7(4)
O-1A	5876(5)	6869(8)	8739(5)	8.3(3)
C-7A	6492(10)	6423(18)	8142(11)	13.9(7)
O-2A	3769(6)	5691(7)	9369(5)	8.1(3)
C-8A	3329(10)	5957(13)	10042(9)	8.2(5)
O-7A	3434(7)	7011(9)	10483(6)	10.5(4)
C-9A	2687(11)	4869(15)	10181(10)	11.2(7)
O-5A	3755(4)	7768(7)	5717(4)	6.9(3)
C-10A	3083(8)	7095(9)	4789(6)	6.0(4)
O-8A	2148(5)	6781(10)	4582(5)	10.4(3)
C-11A	3639(7)	6824(11)	4063(7)	7.0(4)
C-12A	2898(15)	6093(26)	3097(13)	25(1)
C-13A	4680(21)	6082(35)	4727(13)	32(1)
C-14A	4118(29)	7974(19)	3841(24)	37(2)
O-4B	1914(4)	495(5)	7182(4)	5.0(2)
C-1B	2411(8)	1231(9)	8195(7)	6.0(4)
C-2B	1518(8)	1323(9)	8550(6)	6.4(4)
C-3B	423(8)	1393(9)	7456(7)	6.4(4)
C-4B	716(7)	677(7)	6628(6)	4.9(3)
O-3B	226(6)	2763(7)	7112(5)	8.2(3)
C-5B	288(6)	1626(8)	5645(6)	4.7(3)
C-6B	318(9)	2949(11)	6154(8)	7.8(5)
O-6B	322(8)	3967(7)	5796(7)	11.7(4)
O-1B	2657(6)	2519(7)	8015(5)	8.3(3)
C-7B	3437(9)	2631(12)	7583(9)	8.7(5)
O-2B	1534(6)	126(6)	9108(4)	7.4(3)
C-8B	924(10)	84(12)	9677(7)	8.7(5)
O-7B	409(8)	1015(8)	9724(6)	13.6(4)
C-9B	1040(12)	−1166(12)	10264(9)	11.1(6)
O-5B	937(4)	1595(5)	5074(4)	4.9(2)
C-10B	373(7)	1860(8)	3976(6)	5.5(3)
O-8B	−609(5)	2176(7)	3507(5)	7.7(3)
C-11B	1109(8)	1746(12)	3410(8)	8.4(5)
C-12B	1954(12)	644(15)	3904(13)	15.1(7)
C-13B	1600(21)	2976(15)	3472(25)	38(1)
C-14B	310(15)	1299(30)	2200(11)	22(1)

$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \vec{a}_i \vec{a}_j$.

co-ordinates of the non-hydrogen atoms and of those hydrogen atoms bonded to the ring skeleton in **1**, and the anisotropic thermal parameters of all non-hydrogen atoms were refined. Those hydrogen atoms which were not refined were included in the structure factor calculations only. For the hydrogen atoms, the isotropic thermal parameters were those of the bonded atoms enlarged for one unit (in Å^2). The final R values of 0.042 (**1**), 0.048 (**2**), and 0.093 (**3**) for observed reflections having $I \geq 2\sigma(I)$ were obtained [S = 1.13 (**1**), 0.87 (**2**), 0.94 (**3**); maximum value $\Delta/\sigma = 0.700$ (C-7 of **1**), 0.463 (O-5 of **2**), and 2.87 (C-1B of **3**)]. Data collection and structure determination of **3** were performed twice, resulting in the same accuracy.

High thermal movements of the methyl groups in the pivaloyl residues (C-12,13,14 in molecule A, and C-13,14 in B, Table III) suggested a disordered arrangement of the terminal atoms of these bulky substituents. However, the values of the thermal parameters of the ring atoms in the structure **3** are in the same range as those in **1** and **2** (Tables I–III).

The difference Fourier map did not reveal any significant residual density ($-0.02 < \Delta\rho < 0.02$ eÅ^{-3}) around the atoms of the furanoid and the lactone rings. Thus, the conclusion about the conformations of furanose and lactone rings in **1**, **2**, and **3** given in the discussion (Table VI) are reliable.

Scattering factors given by Cromer and Mann[7], and (for H) Stewart *et al.*[8] were used. The calculations were performed on a Univac 1110 computer at the University Computing Centre in Zagreb with the XRAY system[9].

DISCUSSION

The structural formulae with the atom numbering are given for **1–3** in Fig. 1. Bond lengths and angles are listed in Table IV, the conformations in Tables V and VI, the molecular packing in Figs. 2–4, and the hydrogen-bond parameters in Table VII. The configuration and conformation are defined in accordance with the torsion angles for **1–3** (Table V). The Bijvoet pairs were not measured.

The values of bond lengths and angles of the chemically analogous bonds in **1** and **2** can be compared within 3σ (Table IV). The endocyclic C-4–O-4 bonds of the furanoid rings in **1–3** are symmetrical; valence angles at O-4 are in the range 109.2(2) (in **2**) to 112.5(6)° (in **3A**). Bond lengths of exocyclic C-1–O-1 bonds are not significantly different from the endocylic bonds. Bond angles at lactone O-3 are in the range 110.5(8) (in **3B**) to 112.4(2)° (in **2**). Furanoid and lactone rings are fused with dihedral angles 74.9(8) (**1**), 73.6(8) (**2**), 82(1) (**3A**), and 76(1)° (**3B**).

The furanose ring of **3A** is in the E_2 conformation, whereas other molecules adopt the $^1T_2$ conformation (Table VI). The values of puckering parameters[10] (φ) for lactone rings in **1**, **2**, and **3B** correspond to the intermediate conformations E and T. However, displacements of the atoms from the least-squares plane suggest the E conformation. Among the others, only the lactone ring of **3A** shows a T conformation with a strictly planar lactone group. The lactone groups in other molecules are close to the planarity. The least-squares planes were calculated

TABLE IV

BOND LENGTHS (Å) AND ANGLES (°) FOR **1–3**

	1	**2**	***3(A)***	***3(B)***
O-4–C-1	1.418(3)	1.420(4)	1.415(9)	1.43(1)
O-4–C-4	1.434(3)	1.429(4)	1.42(1)	1.42(1)
C-1–C-2	1.523(3)	1.518(4)	1.51(2)	1.48(2)
C-1–O-1	1.413(3)	1.400(5)	1.41(1)	1.41(1)
O-1–C-7	1.431(3)		1.47(2)	1.42(2)
C-2–C-3	1.531(3)	1.542(4)	1.51(1)	1.51(1)
C-2–O-2	1.423(3)	1.419(6)	1.43(1)	1.44(1)
C-3–C-4	1.532(3)	1.552(4)	1.56(1)	1.54(1)
C-3–O-3	1.461(3)	1.432(1)	1.46(1)	1.47(1)
O-3–C-6	1.358(3)	1.354(4)	1.33(1)	1.37(2)
C-4–C-5	1.527(3)	1.526(5)	1.51(1)	1.53(1)
C-5–C-6	1.507(3)	1.514(5)	1.54(1)	1.52(1)
C-5–O-5	1.408(3)	1.428(3)	1.43(1)	1.41(1)
O-5–C-7		1.349(4)		
O-5–C-10			1.34(1)	1.339(9)
C-6–O-6	1.196(3)	1.188(5)	1.19(2)	1.15(1)
C-7–C-8		1.520(4)		
C-7–O-7		1.208(4)		
C-8–O-2			1.32(2)	1.36(2)
C-8–O-7			1.21(2)	1.20(2)
C-8–C-9		1.514(7)	1.47(2)	1.48(2)
C-8–C-10		1.489(8)		
C-8–C-11		1.463(7)		
O-8–C-10			1.18(1)	1.20(1)
C-10–C-11			1.51(2)	1.51(2)
C-11–C-12			1.42(2)	1.51(2)
C-11–C-13			1.46(3)	1.41(2)
C-11–C-14			1.44(3)	1.54(2)
C-1–O-4–C-4	109.6(2)	109.2(2)	112.5(6)	109.4(7)
C-1–O-1–C-7	112.7(2)		113.4(9)	115.0(9)
C-2–O-2–C-8			117.5(9)	117.3(9)
C-3–O-3–C-6	111.0(2)	112.4(2)	112.3(7)	110.5(8)
O-4–C-1–O-1	112.4(2)	111.5(3)	110.6(7)	111.8(8)
O-4–C-1–C-2	104.6(2)	104.7(2)	105.3(7)	105.5(7)
O-1–C-1–C-2	108.0(2)	108.1(3)	106.5(6)	106.5(9)
O-2–C-2–C-1	109.7(2)	110.9(3)	105.0(8)	107.5(8)
O-2–C-2–C-3	107.1(2)	106.1(2)	108.8(8)	108.9(8)
C-1–C-2–C-3	101.6(2)	101.8(3)	104.8(8)	103.6(8)
O-3–C-3–C-2	108.3(2)	109.3(2)	107.4(6)	107.5(7)
O-3–C-3–C-4	106.5(2)	107.3(2)	105.7(8)	107.3(8)
C-2–C-3–C-4	104.1(2)	103.0(2)	103.0(8)	103.3(8)
O-4–C-4–C-3	106.4(2)	106.7(2)	105.6(6)	106.8(6)
O-4–C-4–C-5	113.1(2)	113.2(2)	112.1(8)	114.0(8)
C-3–C-4–C-5	103.6(2)	102.3(2)	101.9(8)	102.1(7)
C-5–O-5–C-7		115.1(2)		
C-5–O-5–C-10			116.2(8)	115.9(6)
O-5–C-5–C-4	116.0(2)	114.4(3)	116.7(8)	113.0(7)
O-5–C-5–C-6	109.7(2)	108.8(2)	108.0(9)	112.2(8)
C-4–C-5–C-6	104.2(2)	105.5(2)	104.9(7)	105.1(7)
O-3–C-6–O-6	121.4(2)	122.4(3)	122.5(9)	123(1)

TABLE IV *(continued)*

	1	2	3(A)	3(B)
O-3–C-6–C-5	109.6(2)	108.4(3)	109(1)	107.9(9)
O-6–C-6–C-5	128.9(2)	129.2(3)	129(1)	129(1)
O-5–C-7–O-7		122.6(2)		
O-5–C-7–C-8		112.9(2)		
O-7–C-7–C-8		124.6(3)		
O-2–C-8–O-7			122(1)	121(1)
O-2–C-8–C-9			114(1)	113(1)
O-7–C-8–C-9			124(1)	126(1)
C-7–C-8–C-9		108.3(3)		
C-7–C-8–C-10		113.2(3)		
C-7–C-8–C-11		107.2(3)		
C-9–C-8–C-10		109.3(4)		
C-9–C-8–C-11		108.2(5)		
C-10–C-8–C-11		110.5(5)		
O-5–C-10–O-8			122(1)	123(1)
O-5–C-10–C-11			112.8(9)	112.9(7)
O-8–C-10–C-11			125.5(8)	124.2(8)
C-10–C-11–C-12			111(1)	111(1)
C-10–C-11–C-13			108(1)	107(2)
C-10–C-11–C-14			113(2)	106(1)
C-12–C-11–C-13			109(2)	115(1)
C-12–C-11–C-14			115(2)	104(1)
C-13–C-11–C-14			100(2)	113(2)

through O-6, C-6, O-3, and C-5. Maximum displacement from the least-squares planes involves C-6 [0.010(3) in **1**, 0.012(6) in **2**, and 0.03(2) Å in **3B**).

The conformation of **3A** cannot be explained by the influence of molecular packing forces. The hydroxyl groups in **3** are protected and hydrogen bonding is not possible. Inspection of the van der Waals distances showed a short intermolecular contact O-3B · · · · O-8A of 3.072(9) Å [x, y, z; 2 − x, 1/2 + y, 1 − z]. This contact does not affect the ring conformation of **3A**, but, in the crystal lattice, there are two conformers (A and B) which differ in the conformations of the furanoid and lactone rings. Conformer **3B** has features identical to those of **1** and **2** which are only partly esterified. Thus, the conformations of these molecules are not influenced by bulky ring substituents or by hydrogen bonds.

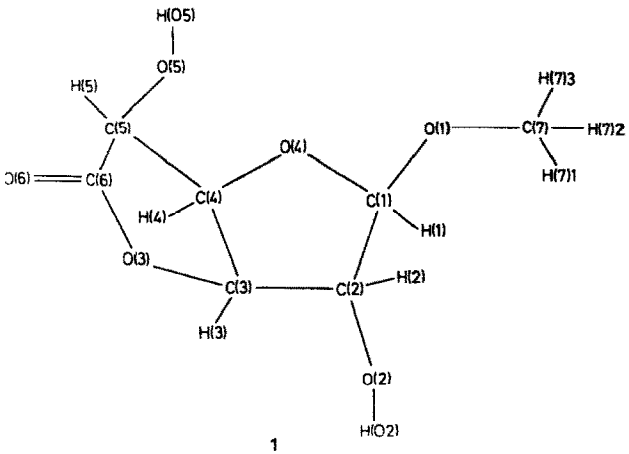
The results obtained from X-ray structure analysis of β-D-glucurono-6,3-lactone[11] confirm these findings where O-1 [HO-1 · · · · O-6, 2.730(5)] and O-2 [HO-2 · · · · O-1, 2.839(4) Å] are involved in the intermolecular hydrogen-bonds. The conformation of the furanose ring is $^1T_2$ [φ = 229.65(2)°, q_2 = 0.3500(1) Å]. The lactone ring exhibits an envelope conformation with C-5 shifted by −0.25 Å from the four-atom plane.

The molecular packing of **1** and **2** is through the hydrogen bonds (Table VII, Figs. 2 and 3); HO-2 of **1** acts as donor and acceptor and, together with O-5 and O-1, completes the three-dimensional hydrogen-bond system [HO-2 · · · · O-1,

TABLE V

TORSION ANGLES (°) FOR **1–3**

	1	**2**	***3(A)***	***3(B)***
O-4–C-1–C-2–C-3	−37.0(2)	−38.5(3)	−29.1(8)	−34.2(9)
C-1–C-2–C-3–C-4	28.7(2)	28.7(3)	27.5(9)	27.2(9)
C-1–C-2–C-3–O-3	−84.3(2)	−85.1(3)	−83.7(9)	−86(1)
C-2–C-3–C-4–O-4	−11.1(2)	−9.9(3)	−17(1)	−11.2(9)
C-2–C-3–C-4–C-5	−130.6(2)	−129.0(2)	−133.9(8)	−131.1(7)
C-3–C-4–C-5–C-6	21.9(2)	19.4(3)	24.9(9)	25.3(9)
C-3–C-4–O-4–C-1	−12.8(2)	−14.7(3)	−1(1)	−10.2(9)
O-3–C-3–C-4–C-5	−16.3(2)	−13.7(3)	−21.3(8)	−17.6(8)
C-4–C-5–C-6–O-3	−21.0(2)	−19.5(3)	−21(1)	−25(1)
C-4–O-4–C-1–C-2	31.8(2)	33.9(3)	19.1(9)	28.1(9)
C-4–C-3–O-3–C-6	3.7(2)	2.1(3)	9(1)	2.5(9)
C-5–C-6–O-3–C-3	11.0(2)	10.9(3)	7(1)	14(1)
O-1–C-1–C-2–C-3	82.8(2)	80.4(3)	88.4(8)	84.7(8)
O-2–C-2–C-3–O-3	160.6(2)	158.8(2)	164.3(8)	159.7(9)
O-2–C-2–C-3–C-4	−86.4(2)	−87.4(3)	−84(1)	−87(1)
C-3–C-4–C-5–O-5	142.6(2)	138.9(2)	144.3(6)	148.0(7)
C-7–O-1–C-1–C-2	172.7(2)		−175.1(8)	−175.3(6)
C-4–C-5–O-5–C-7		78.2(3)		
C-5–O-5–C-7–O-7		6.0(5)		
C-5–O-5–C-7–C-8		−173.5(3)		
O-7–C-7–C-8–C-9		52.8(5)		
O-7–C-7–C-8–C-10		174.1(5)		
O-7–C-7–C-8–C-11		−63.7(5)		
O-4–C-1–C-2–O-2			85.5(5)	80.9(7)
C-1–C-2–O-2–C-8			168.8(7)	168.7(7)
C-2–O-2–C-8–O-7			−2(1)	−1(1)
C-4–C-5–O-5–C-10			74.1(9)	148.9(7)
C-5–O-5–C-10–C-11			−178.9(8)	−177.3(8)
O-5–C-10–C-11–C-12			179(1)	36(1)
O-5–C-10–C-11–C-13			59(2)	−90(1)
O-5–C-10–C-11–C-14			−50(1)	148(1)



1

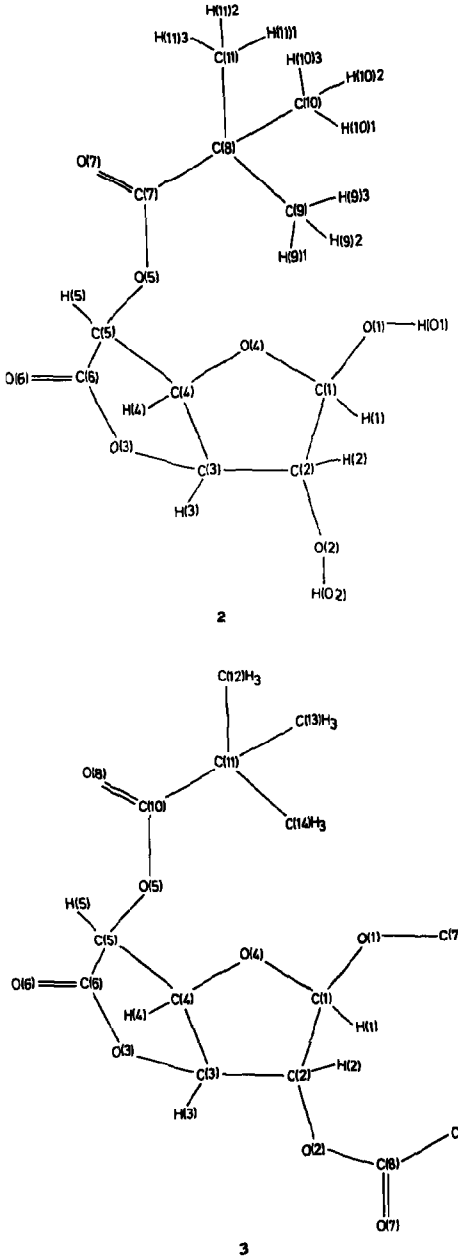


Fig. 1. Chemical formulae with the atom numbering of 1–3.

TABLE VI

CONFORMATION DESCRIBED BY ATOM DISPLACEMENTS (Å) FROM LEAST-SQUARES PLANES AND PUCKERING PARAMETERS[10] (q, φ)[a]

Furanose ring	**1**		**2**		**3A**		**3B**	
O-4	0*		0*		−0.01(1)*		0*	
C-3	0*		0*		0.00(2)*		0*	
C-4	0*		0*		0.01(2)*		0*	
C-1	0.297(3)		0.340(6)		0.00(2)*		0.24(2)	
C-2	−0.287(3)		−0.260(6)		−0.45(2)		−0.29(2)	
q (Å), φ (°)	0.353(2),	234.8(3)	0.366(4),	232.7(5)	0.29(1),	252(2)	0.32(1),	237(1)
Atom sequence	O-4, C-1, C-2, C-3,C-4							
Conformation	$^1T_2$		$^1T_2$		E_2		$^1T_2$	
Lactone ring	**1**		**2**		**3A**		**3B**	
O-3	0.021(2)*	0*	0.014(4)*	0*	0*		0.014(8)*	0*
C-3	−0.019(3)*	0*	−0.010(5)*	0*	0*		−0.01(1)*	0*
C-6	0.013(3)*	0*	−0.007(4)*	0*	0*		−0.01(1)*	0*
C-4	0.011(3)*	0.096(3)	0.006(3)*	0.054(3)	0.24(1)		0.01(1)*	0.06(1)
C-5	−0.349(3)	−0.270(3)	−0.317(3)	−0.272(3)	−0.18(1)		−0.41(1)	−0.36(1)
q (Å), φ (°)	0.220(2),	262.7(5)	0.199(3),	259.6(7)	0.25(1),	273(2)	0.26(1),	259(2)
Atom sequence	O-3, C-6, C-5, C-4, C-3							
Conformation	$E\text{⌙}T$		$E\text{⌙}T$		T		$E\text{⌙}T$	

[a]The values of puckering parameters[10] (for specified atom sequence) for the lactone rings of **1, 2**, and **3B** are in the range between T and E ($E\text{⌙}T$). Displacements from least-squares planes for both types are listed (* means that the corresponding atom is included in the least-squares plane calculations).

TABLE VII

HYDROGEN BONDS

X–H · · · *Y*	*X* · · · *Y*	X–H	H · · · *Y*	*X*–H–*Y*	Symmetry operation on *Y*
Compound **1**					
HO-2 · · · O-1	2.812(2) Å	0.82 Å	2.01 Å	165°	− x, 1/2 + y, 1/2 − z
HO-5 · · · O-2	2.898(3)	1.04(5)	1.95(5)	149(4)	x − 1/2, 1/2 − y + 1, − z
Compound **2**					
HO-1 · · · O-7	2.855(3)	0.99	1.90	161	x + 1, y, z

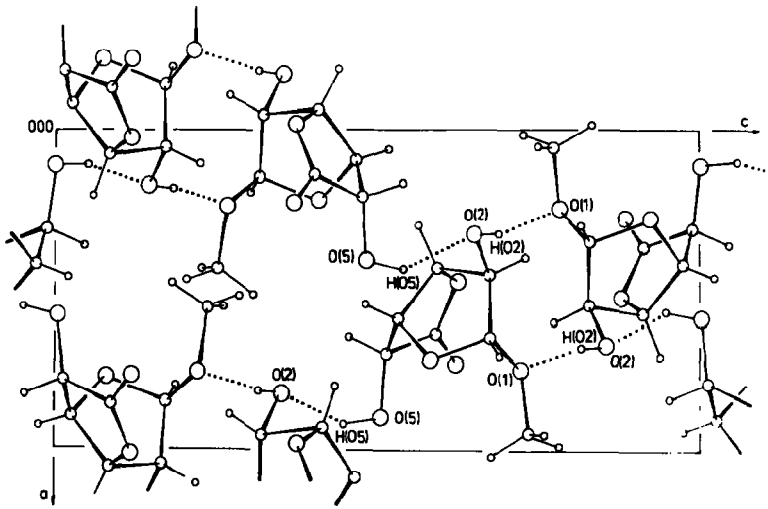


Fig. 2. A view of the crystal structure **1** down b̄. Hydrogen bonds (· · · ·) connect the molecules in a three-dimensional network.

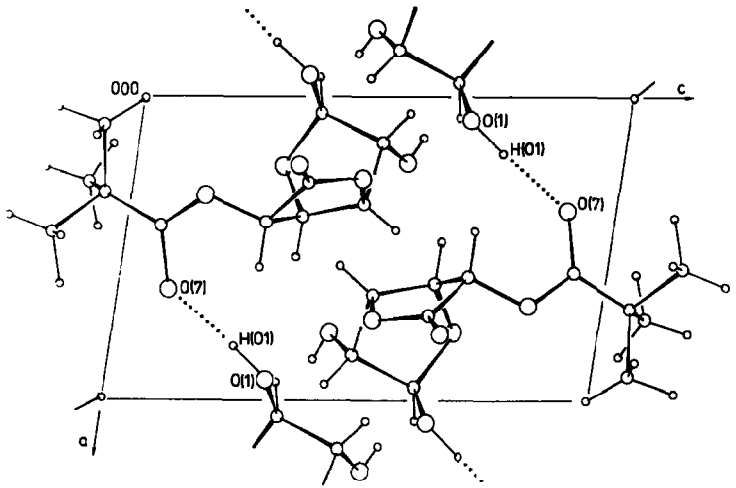


Fig. 3. A view of the crystal structure **2** down b̄. Hydrogen bonds connect molecules along ā.

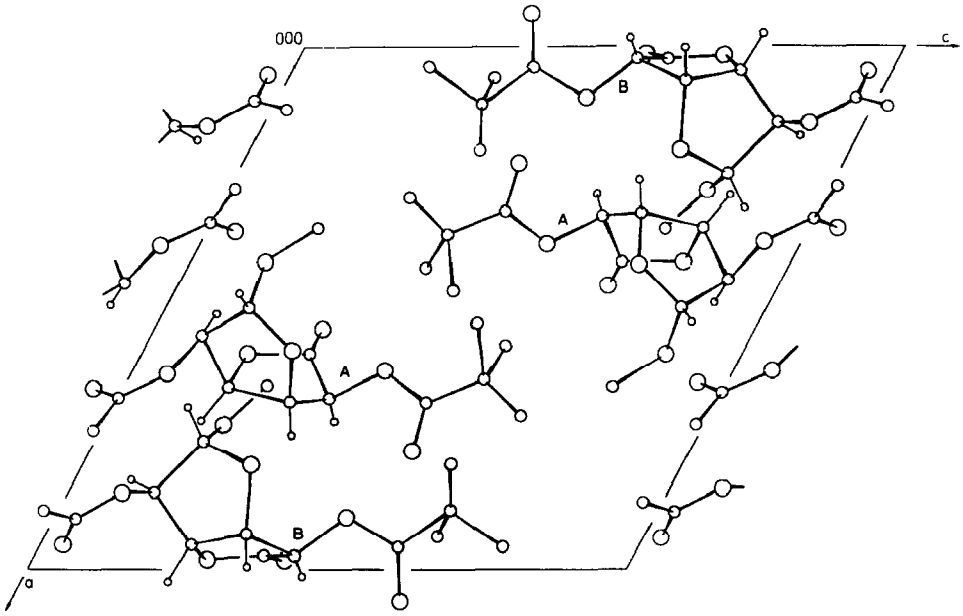


Fig. 4. A view of the crystal structure **3** down $\vec{b}$. Two conformers are denoted as A and B. Molecular packing is solely through the van der Waals interactions.

2.812(2) and HO-5 · · · · O-2, 2.898(3) Å]. In the crystal lattice of **2**, a hydrogen bond between a hydroxyl group and the pivaloyl carbonyl group [HO-1 · · · · O-7, 2.855(3) Å] connects the molecules. In **3**, the molecular packing is dictated solely by van der Waals interactions (Fig. 4).

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