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Conformations and structure studies of sugar lactones in the solid state. Part I. The molecular structure of L-rhamnono- and L-mannono-1,4-lactones

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Abstract

The crystal structures of L-rhamnono-1,4-lactone (**1**) and L-mannono-1,4-lactone (**2**) have been determined by single-crystal X-ray diffraction. Pertinent crystal data are as follows: for **1**, orthorhombic, space group $P2_12_12_1$, $a=4.8829(2)$, $b=10.9088(8)$, $c=13.9758(9)$ Å, $V=744.4(1)$ Å^3, $D_c=1.447$ g cm^{-3}, $Z=4$, final $R=0.037$ and $R_w=0.035$ for 1226 reflections; for **2**, orthorhombic, space group $P2_12_12_1$, $a=4.8157(2)$, $b=11.0003(7)$, $c=13.8693(8)$ Å, $V=734.7(1)$ Å^3, $D_c=1.610$ g cm^{-3}, $Z=4$, $R=0.028$ and $R_w=0.035$ for 1586 reflections. The lactone ring of **1** adopts an envelope conformation, E_3, slightly distorted toward $^2T_3$, with $\varphi=103.1(7)°$ and $q=0.38(3)$ Å, whereas the lactone ring of **2** adopts a perfect envelope E_3 conformation, with $\varphi=106.6(4)°$ and $q=0.42(4)$ Å. Molecules of **1** and **2** are linked in their crystals through a three dimensional network of O–H···H hydrogen-bonding interactions that involves all hydroxyl groups as well as the carbonyl oxygen atom.

Keywords: L-Rhamno-1,4-lactone; L-Manno-1,4-lactone; X-ray crystal structure; Conformation

1. Introduction

Aldono-1,4-lactones are highly crystalline, easily manipulated and characterized substances that can be readily prepared in large amounts from inexpensive commercially available materials. Due to their potential as a source of chiral carbons, as well as absolute and relative stereochemistry, they have great potential in synthetic organic chemistry [1–4]. They provide several easy and short strategies for the preparation of novel, optically

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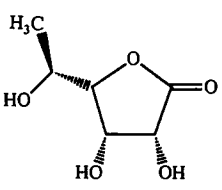
active furanones [5,6], natural products [7,8], and several chiral polyfunctionalized amino acids [9,10]. Such sugar lactones are also of significant biological interest. They are highly specific competitive inhibitors of several glycosidases and some β-galactosidases [11–13], and their importance as potential drugs for treatment of certain diseases and in metabolism is well documented [14]. L-Rhamnono-1,4-lactone (**1**), prepared by buffered bromine-water oxidation of L-rhamnose [15], has been considered an excellent intermediate for the synthesis of muscarine [16], one of the first substances known to reproduce responses induced by stimulation of the parasympathetic nervous system [17].

The conformations of aldono-1,4-lactones, having free or *O*-substituted hydroxyl groups, have been extensively studied in solution by NMR spectroscopy [18–20]. However, in the solid state their conformations and structural analyses have received little attention. Among the crystallographic studies on hexono-1,4-lactones, the crystal structures of D-galactono-1,4-lactone [21], D-gulono-1,4-lactone [22], and 2,3,4-tri-*O*-methyl-D-galactono-1,4-lactone [23] have been determined, and the results show that all of these lactones adopt envelope conformations having the OH-2 group quasiequatorially oriented.

In the present work, we report on the conformation and 3D molecular structures of L-rhamnono-1,4-lactone (**1**) and L-mannono-1,4-lactone (**2**) as determined by single-crystal X-ray crystallography. Our main objective in these studies is to provide information on the conformational properties of sugar lactones that might be helpful in detailed understanding of their chemical and biological behavior.



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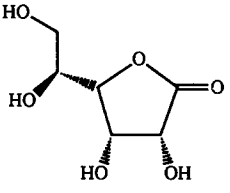

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2. Experimental

The samples of L-rhamnono-1,4-lactone (**1**) and L-mannono-1,4-lactone (**2**) were kindly provided by Professor H.S. El Khadem from the late Dr. H.S. Isbell's collection of rare sugars at The American University, Washington DC. Suitable crystals for structure determination were obtained from EtOAc (**1**) and 90% EtOH (**2**) as transparent needles with mp 149–151°C and 151–152°C, respectively.

Data collection and processing.—Diffraction data were collected on an Enraf–Nonius CAD4 diffractometer equipped with graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 23°C. Unit-cell parameters were obtained from setting angles of 25 reflections having $18 < 2\theta < 22°$ and $20 < 2\theta < 30°$ for **1** and **2**, respectively. The parameters utilized in intensity collections and refinements are summarized in Table 1 together with the crystallographic data. Crystal stability was monitored by recording three standard reflections every 10 000 s, and no significant variation was observed. The effects of absorption

Table 1
Data collection and crystallographic parameters for L-rhamnono-1,4-lactone (**1**) and L-mannono-1,4-lactone (**2**)

Compound	**1**	**2**
Molecular formula	$C_6H_{10}O_5$	$C_6H_{10}O_6$
Molecular weight	162.1	178.1
Melting point (°C)	149–151	151–152
Crystal dimensions (mm)	$0.10\times0.10\times0.55$	$0.28\times0.30\times0.45$
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
Cell dimensions (Å)		
a	4.8829(2)	4.8157(2)
b	10.9088(8)	11.0003(7)
c	13.9758(9)	13.8693(8)
Volume (Å^3)	744.4(1)	734.7(12)
Calculated density (g cm^{-3})	1.447	1.610
Z (molecules/cell)	4	4
μ (cm^{-1})	1.20	1.38
Radiation (graphite monochromator)	Mo$K\alpha$	Mo$K\alpha$
Data collection	CAD4	CAD4
Collection method	$\omega-2\theta$	$\omega-2\theta$
2θ range (°)	2, 70	2, 70
Scan rate (deg min^{-1})	0.46–3.30	0.66–3.30
No. of data collected	1929	3485
Unique reflections	1905	1884
$I>3\,\sigma(I)$	1226	1586
S (variables)	1.657(141)	1.568 (150)
Max shift	$<0.01\sigma$	$<0.01\sigma$
Max/min residual denisty (eÅ^{-3})	0.24/−0.11	0.29/−0.16
Extinction coefficient	$5(3)\times10^{-8}$	$2.5(3)\times10^{-6}$
Final residual factors		
R	0.037	0.028
R_w	0.035	0.035

for these compounds were very small, and were neglected in our calculations. Systematic absences uniquely specified that the crystals belong to orthorhombic space group $P2_12_12_1$ with $Z=4$.

Structure analysis.—Structures of **1** and **2** were solved by direct methods using the program MULTAN-80 [24] which revealed the positions of all nonhydrogen atoms. They were refined by full-matrix least squares based upon F with weights $w=4F_o^2\,[\sigma^2\,(I)+(0.02\,F_o^2)^2]^{-1}$ using the MolEN programs [25]. Nonhydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference maps and were refined isotropically. Atomic coordinates and equivalent isotropic thermal parameters, along with their esd's, are given in Table 2 [1]. All calculations were performed on a VAX 3600 computer. Atomic

[1] Lists of observed and calculated structure-amplitudes, anisotropic thermal parameters, hydrogen coordinates and isotropic thermal parameters, and trorsion angles for **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre and may be obtained on request from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Table 2
Atomic coordinates and isotropic [a] thermal parameters for L-rhamnono-1,4-lactone (**1**) and L-mannono-1,4-lactone (**2**)

Atom	Compound **1**				Atom	Compound **2**			
	x	y	z	B_{iso}(Å^2)		x	y	z	B_{iso}(Å^2)
O-1	0.8888(3)	0.4660(1)	0.58207(8)	3.37(2)	O-1	0.2970(2)	0.80541(7)	0.35080(6)	2.63(1)
O-2	0.5144(2)	0.30609(9)	0.4903(1)	3.75(3)	O-2	0.7149(2)	0.71168(9)	0.22164(5)	2.51(1)
O-3	0.6856(3)	0.4188(1)	0.32059(9)	3.49(2)	O-3	0.5004(3)	0.48704(8)	0.28353(6)	2.03(2)
O-4	0.7823(3)	0.60142(9)	0.46976(7)	2.52(2)	O-4	0.3875(2)	0.64495(7)	0.44451(5)	2.12(1)
O-5	0.5124(3)	0.69051(9)	0.23670(8)	3.64(3)	O-5	0.7245(2)	0.35578(7)	0.50153(6)	2.75(2)
C-1	0.7386(4)	0.4971(1)	0.5183(1)	2.34(2)	O-6	0.2855(2)	0.33615(7)	0.62958(6)	2.37(1)
C-2	0.4903(3)	0.4331(1)	0.4786(1)	2.50(3)	C-1	0.4421(3)	0.71969(9)	0.37025(7)	1.84(2)
C-3	0.4876(4)	0.4794(1)	0.3757(1)	2.62(3)	C-2	0.7033(3)	0.6701(9)	0.31907(7)	1.92(2)
C-4	0.5828(3)	0.6116(1)	0.3914(1)	2.27(3)	C-3	0.7018(3)	0.5426(1)	0.34256(7)	2.08(1)
C-5	0.7207(4)	0.6747(1)	0.3076(1)	2.70(3)	C-4	0.6015(2)	0.54913(9)	0.44696(7)	1.87(2)
C-6	0.8344(5)	0.7986(2)	0.3351(1)	3.58(4)	C-5	0.4880(3)	0.43162(9)	0.48871(7)	1.96(1)
H-2OH	0.379(4)	0.283(2)	0.501(2)	6.8(6)	C-6	0.3520(3)	0.4509(1)	0.58642(8)	2.28(2)
H-3OH	0.642(4)	0.350(2)	0.309(1)	4.3(4)	H-2OH	0.610(4)	0.676(1)	0.1986(9)	4.0(4)
H-5OH	0.540(4)	0.644(2)	0.194(1)	4.2(4)	H-3OH	0.566(6)	0.428(2)	0.265(1)	9.5(7)
H-2	0.339(3)	0.466(2)	0.514(1)	1.9(3)	H-5OH	0.724(4)	0.291(1)	0.463(1)	4.1(4)
H-3	0.310(4)	0.475(2)	0.349(1)	3.7(4)	H-6OH	0.431(4)	0.313(1)	0.6561(9)	3.3(3)
H-4	0.437(3)	0.658(1)	0.415(1)	2.3(3)	H-2	0.846(3)	0.717(1)	0.3526(8)	1.5(2)
H-5	0.864(3)	0.624(1)	0.284(1)	2.9(4)	H-3	0.872(4)	0.504(1)	0.3376(9)	2.9(3)
H-6a	0.915(4)	0.838(2)	0.281(2)	5.6(5)	H-4	0.751(3)	0.582(1)	0.4872(8)	2.6(3)
H-6b	0.956(4)	0.787(2)	0.383(1)	5.0(5)	H-5	0.353(3)	0.393(1)	0.4432(7)	1.7(3)
H-6c	0.688(4)	0.852(2)	0.356(1)	4.5(5)	H-6a	0.480(4)	0.499(1)	0.628(1)	3.2(3)
					H-6b	0.170(4)	0.494(1)	0.5809(9)	3.3(4)

[a] Equivalent isotropic thermal parameters are given for nonhydrogen atoms. The definition of this quantity is $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a^{i*} a^{j*} a^i a_j$

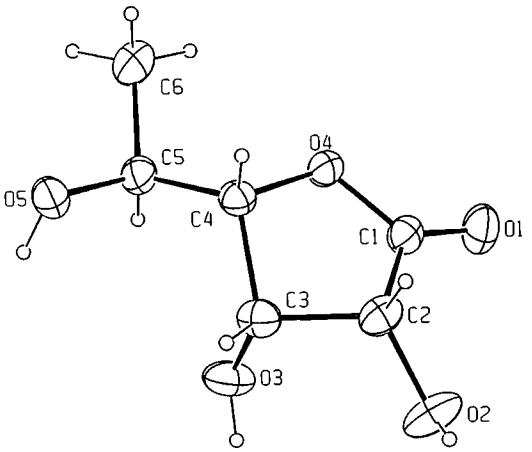

Fig. 1. Atom numbering and thermal ellipsoids (40%) of L-rhamnono-1,4-lactone (**1**).

scattering factors were obtained from the International Tables for X-ray Crystallography [26].

3. Results and discussion

A perspective view (ORTEP) [27] of the title compounds with the atomic numbering in the molecules is shown in Figs. 1 and 2. The bond lengths, bond angles and selected torsion angles in the molecules are listed in Table 3. The C–C bond distances for **1** and **2** are normal, ranging, respectively from 1.505(2) to 1.531(2) Å, and 1.515(2) to 1.528(1) Å as are the C–OH bonds, 1.400(2) to 1.431(2) Å, and 1.433(1) Å which are in good agreement with those values reported for other carbohydrates [28–30]. The C-O–C=O bond lengths show the characteristic lengthening and shortening of the formal C–O bonds because of contributions from the valence-bond resonance form C^{+}-O=C-O^{-}. In both

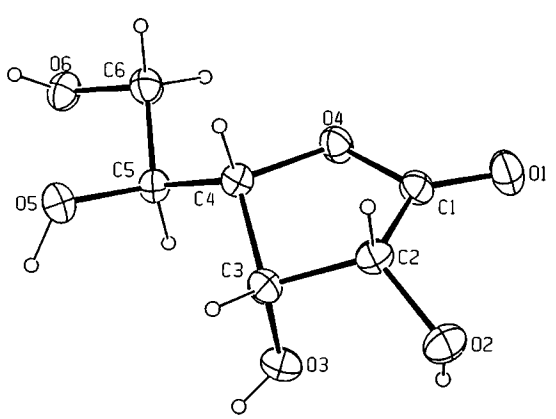

Fig. 2. Atom numbering and thermal ellipsoids (40%) of L-mannono-1,4-lactone (**2**).

Table 3
Bond lengths (Å), bond angles, and selected torsion angles (deg) in L-rhamnono-1,4-lactone (**1**) and L-mannono-1,4-lactone (**2**)

Atoms	Compound **1**	Compound **2**	Atoms	Compound **1**	Compound **2**
O-1–C-1	1.203(2)	1.204(1)	C-1–C-2	1.505(2)	1.515(1)
O-2–C-2	1.400(2)	1.402(1)	C-2–C-3	1.525(2)	1.525(2)
O-3–C-3	1.402(2)	1.409(2)	C-3–C-4	1.531(2)	1.528(1)
O-4–C-1	1.342(2)	1.344(1)	C-4–C-4	1.516(2)	1.518(1)
O-4–C-4	1.470(2)	1.474(1)	C-5–C-6	1.510(2)	1.520(2)
O-5–C-5	1.431(2)	1.423(2)			
C-1–O-4–C-4	109.6(1)	108.57(8)	O-3–C-3–C-4	108.3(1)	110.7(1)
O-1–C-1–O-4	121.1(1)	122.5(1)	C-2–C-3–C-4	100.0(1)	99.08(8)
O-1–C-1–C-2	129.3(1)	127.9(1)	O-4–C-4–C-3	103.7(1)	103.47(8)
O-4–C-1–C-2	109.6(1)	109.64(1)	O-4–C-4–C-5	108.4(1)	111.48(9)
O-2–C-2–C-1	110.4(1)	113.9(1)	C-3–C-4–C-5	116.9(1)	115.79(8)
O-2–C-2–C-3	116.0(1)	117.65(9)	O-5–C-5–C-4	105.9(1)	105.0(1)
C-1–C-2–C-3	101.6(1)	101.05(9)	O-5–C-5–C-6	109.3(1)	108.37(9)
O-3–C-3–C-2	110.9(1)	107.61(9)	C-4–C-5–C-6	112.0(1)	112.11(8)
C-4–O-4–C-1–C-2	−3.6(2)	−0.90(1)	C-1–C-2–C-3–C-4	−37.1(2)	39.21(1)
C-1–O-4–C-4–C-3	−21.1(2)	−25.30(1)	C-2–C-3–C-4–O-4	35.9(2)	39.88(1)
O-4–C-1–C-2–C-3	26.8(2)	26.56(1)	O-4–C-4–C-5–C-6	−56.7(2)	−53.06(2)
O-4–C-4–C-3–O-3	−80.1(1)	−73.0(1)	O-3–C-3–C-2–O-2	−42.8(2)	−48.6(2)
O-1–C-1–C-2–O-2	−28.5(2)	−26.2(2)	C-4–C-5–O-5–H-5	−107.7(14)	−113.6(11)
H-2–C-2–C-3–H-3	−44.8(14)	−49.3(12)	H-3–C-3–C-4–H-4	40.7(15)	50.3(13)

structures, the C=O bond length [1.203(2) Å (**1**) and 1.204(1) Å (**2**)] is within the range of expected values for the carbonyl group. The ring angles at the carbon atoms of the lactone ring range from 100.2(1) to 103.7(1)° in **1** and 99.08(8) to 103.47(8)° in **2** with the exception of that at the carbonyl atom, C-1, which is larger as would be expected from its sp^2 hybridization.

The lactone ring of **1** adopts an envelope conformation, E_3, slightly distorted toward $^2T_3$, with Cremer–Pople puckering parameters [31] $\varphi = 103.1(7)°$ and $q = 0.38(3)$ Å. These are similar to those observed in the lactone ring of 2,3,4-tri-*O*-methyl-D-galactono-1,4-lactone [23] ($\varphi = 104°$ and $q = 0.37$ Å). Displacement of the atoms from the least-squares plane suggest the E_3 conformation. Four atoms, C-4, O-4, C-1, and C-2 are coplanar within deviations of 0.01–0.02 Å. The flap atom, C-3, is displaced from this plane in the exo direction by 0.606(2) Å. The conformation of the methyl group is gauche–trans with respect to the lactone ring, the C-6–C-5–C-4–O-4 and C-6–C-5–C-4–C-3 torsion angles being 56.7(2) and −173.3(2), respectively. Similarly, the orientation of O-5–C-5 bond about the C-5–C-4 bond is gauche to C-4–C-3 and trans to C-4–O-4.

The lactone ring of **2** adopts an envelope conformation E_3 [$\varphi = 106.6(4)°$ and $q = 0.42(4)$ Å]. Four atoms, C-4, O-4, C-1, and C-2 are thus nearly coplanar within observed deviations of 0.03–0.05 Å. The flap atom, C-3, is displaced from this plane in the exo direction by 0.652(1) Å. The lactone ring is slightly more puckered as compared to that of L-rhamnono-1,4-lactone (**1**). This is presumably due to the small deviation from planarity of the C-O–C=O group in the latter as measured by the C-O–C=O torsion angle, 175.4(1)°. The side chain ($CHOHCH_2OH$) on C-4 favors an orientation in which 1,3-parallel interactions of

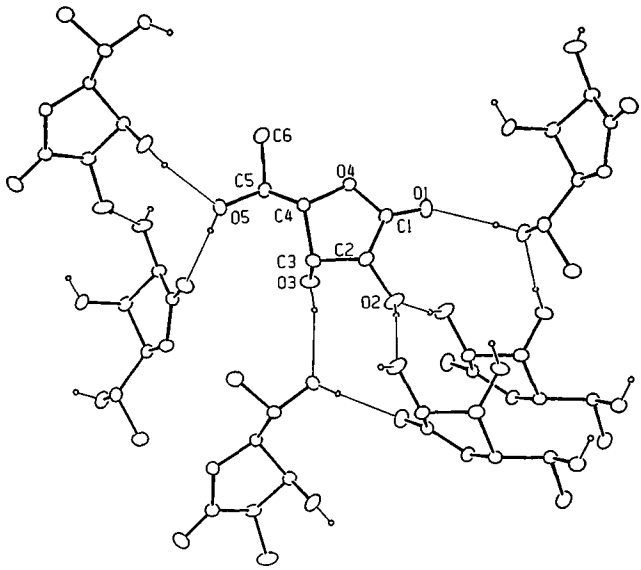

Fig. 3. The O–H· · ·O hydrogen bonding scheme in the crystal of L-rhamnono-1,4-lactone (**1**)

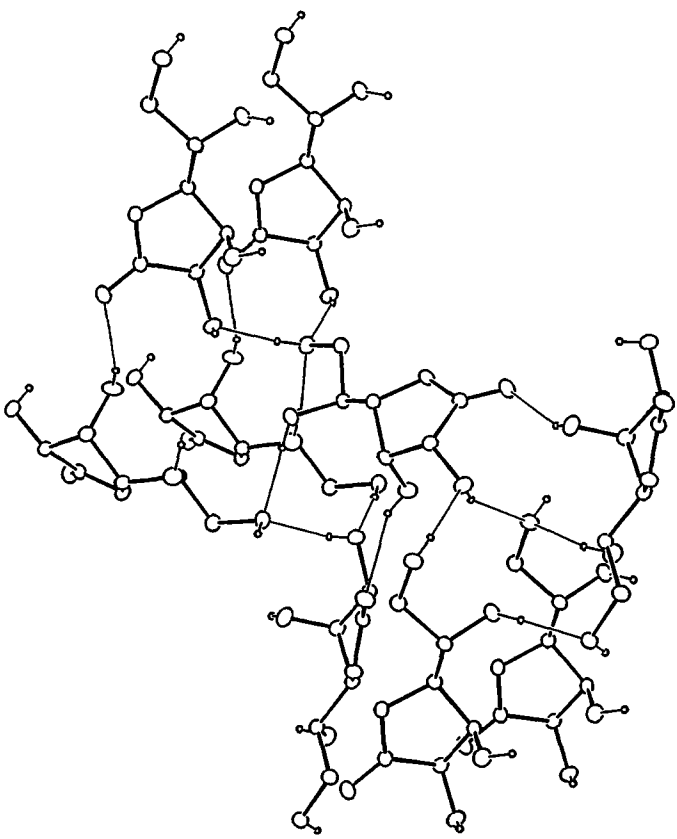

Fig. 4. The O–H· · · ·O hydrogen bonding scheme in the crystal of L-mannono-1,4-lactone (**2**).

Table 4
Geometry of the hydrogen bonds in L-rhamnono-1,4-lactone (**1**) [a]

Number	O···O (Å)	O–H (Å)	H···O (Å)	O–H···O (deg)
1. O-2–H-O2···O-2 [a]	2.744(2)	0.73(2)	2.03(2)	169(3)
2. O-3–H-O3···O-5 [b]	2.789(2)	0.80(2)	2.00(2)	170(2)
3. O-5–H-O5···O-1 [c]	2.796(2)	0.80(2)	2.00(2)	177(2)
	C···O (Å)	C–H (Å)	H···O (Å)	C–H···O (deg)
4. C-2–H-2···O-1 [d]	3.293(2)	0.96(2)	2.39(2)	156(1)
5. C-6–H-6a···O-3 [e]	3.456(3)	0.96(2)	2.57(2)	155(2)
6. C-6–H-6b···O-4 [f]	3.662(2)	0.91(2)	2.87(2)	147(2)
7. C-6–H-6c···O-1 [g]	3.560(2)	0.97(2)	2.62(2)	166(2)

[a] Symmetry operations: $a=x-0.5, 0.5-y, 1-z$; $b=1-x, y-0.5, 1.5-z$; $c=1.5-x, 1-y, z-0.5$; $d=x-1, y, z$; $e=2-x, 0.5+y, 0.5-z$; $f=1.5+x, 1.5-y, 1-z$; $g=x-0.5, 1.5-y, 1-z$.

OH groups are avoided. The hydroxyl group on C-5 adopts gauche–trans dispositions with respect to the hydroxy methyl group, OH-6 and the lactone ring atom, O-4; respectively; the O-6–C-6–C-5–O-5 and O-5–C-5–C-4–O-4 torsion angles being −55.92(1) and −170.53(1), respectively.

In the crystals of **1** and **2**, the molecules are associated by a three-dimensional intermolecular O–H···H hydrogen bonding network. The hydrogen-bond interactions are illustrated in Figs. 3 and 4 and the relevant hydrogen–oxygen and oxygen–oxygen distances are listed in Tables 4 and 5 together with angles about the H atoms. In the crystal of **1**, each molecule participates in six O–H···O hydrogen bonds. Two of the three hydroxyl groups, OH-2 and OH-5, participate both as hydrogen-bond donors and acceptors, while the third hydroxyl group, OH-3, acts as donor only and the carbonyl oxygen atom as acceptor. In addition, all three H atoms of methyl group C-6, as well as OH-2, are involved in intermolecular C–H···O interactions with C···O distances less than 3.7 Å (see Table 4). In the crystal of **2**, each molecule participates in eight O–H···O hydrogen bonds. Of the four hydroxyl groups, OH-6 participates in three hydrogen bonds, one as donor and two as

Table 5
Geometry of the hydrogen bonds in L-mannono-1,4-lactone (**2**) [a]

Number	O···O (Å)	O–H (Å)	H···O (Å)	O–H···O (deg)
1. O-2–H-O2···O-6 [a]	2.7776(13)	0.71(2)	2.14(2)	150(2)
2. O-3–H-O3···O-1 [b]	2.9009(12)	0.77(3)	2.20(2)	153(2)
3. O-5–H-O5···O-6 [c]	2.8020(11)	0.89(2)	1.92(2)	169(2)
4. O-6–H-O6···O-2 [d]	2.7739(13)	0.83(2)	1.95(2)	170(2)
	C···O (Å)	C–H (Å)	H···O (Å)	C–H···O (deg)
5. C-2–H-2···O-1 [e]	3.214(2)	0.94(2)	2.38(2)	149(1)
6. C-4–H-4···O-1 [f]	3.3637(13)	0.98(2)	2.57(2)	138(1)
7. C-5–H-5···O-4 [g]	3.4095(13)	1.00(2)	2.91(2)	112(1)
8. C-6–H-6a···O-1 [f]	3.541(2)	0.99(2)	2.66(2)	148(1)
9. C-6–H-6c···O-1 [h]	3.884(2)	1.00(2)	3.00(2)	148(1)

[a] Symmetry operations: $a=0.5-x, 1-y, z-0.5$; $b=1-x, y-0.5, 1.5-z$; $c=0.5+x, 0.5-y, 1-z$; $d=1.5-x, 1-y, 0.5+z$; $e=x+1, y, z$; $g=x-0.5, 0.5-y, 1-z$; $f=0.5+x, 1.5-y, 1-z$; $h=x-0.5, 1.5-y, 1-z$.

acceptor; OH-2 participates in two, one as donor and one as acceptor, while OH-3 and OH-5 participates as hydrogen-bond donors only. The carbonyl oxygen O-1 accepts one relatively long hydrogen bond. However, O-1 also accepts four intermolecular C–H$\cdots$O contacts, one of which is relatively short [32,33], with C$\cdots$O distance 3.214 (2) Å (Table 5). The extensive hydrogen bonding network accounts for the relatively high density of this compound.

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