

Hydrogen-Bonding Schemes of Galactonic Acid Hydrazide and its Hemihydrate

CHRISTOPH ANDRÉ,^{a*} PETER LUGER,^a JÜRGEN-HINRICH FUHRHOP^b AND FRIEDEMANN HAHN^c

^aInstitut für Kristallographie, Freie Universität Berlin, Takustrasse 6, 14195 Berlin, Germany, ^bInstitut für Organische Chemie, Freie Universität Berlin, Takustrasse 3, 14195 Berlin, Germany, and ^cStoe & Cie GmbH, Postfach 101302, 64213 Darmstadt, Germany. E-mail: andre@chemie.fu-berlin.de

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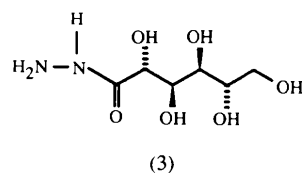
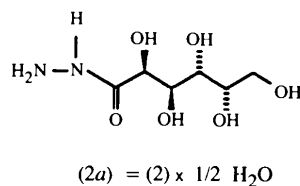
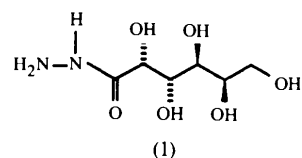
Abstract

The crystal structure of L-galactonic acid hemihydrate was determined using data obtained from an imaging plate detector (Stoe IPDS), whereas a conventional scintillation counter was used for the elucidation of the crystal structure of anhydrous D-galactonic acid. The H atom of the terminal hydroxyl group of the water-free sugar participates only in an intramolecular hydrogen bond with the preterminal O atom. This hydrogen bond is part of an antidromic hydrogen-bonding cycle. The hydrogen-bonding scheme of the hemihydrate is very intricate due to the occurrence of two independent molecules and the incorporated water, whose coordination shell can be described by a distorted tetrahedron. One of the hydrogen-bond chains observed in the structure of the hemihydrate is infinite, forming a spiral running in the *a* direction. The crystal packing of both compounds displays a herringbone arrangement. However, the tilt angle between molecules in different herringbone halves is by far smaller in the structure of the hydrated sugar than in the water-free compound (~60 versus 96°).

1. Introduction

Recently, considerable progress has been achieved in the systematization of the packing behaviour of carbohydrates by the discovery of a common packing motif occurring in the crystal structures of numerous acyclic sugar derivatives having different configuration (André, Luger, Fuhrhop & Rosengarten, 1993). The study of crystal structures of open-chain carbohydrate derivatives helps to elucidate the interplay between their conformation, hydrogen-bonding scheme and crystal packing. (André, Luger, Gutberlet, Vollhardt & Fuhrhop, 1995, and references therein). Such investigations therefore provide information on the molecular recognition of organic compounds in general.

Here the crystal structures of D-galactonic acid hydrazide (1) and the hemihydrate of its L-configured counterpart (2a) are reported and their hydrogen-bonding schemes discussed.



2. Experimental

2.1. Preparation and crystallization

Both D- and L-galactonic acid hydrazide, synthesized as previously described for the mannose derivative (André, Luger, Fuhrhop & Rosengarten, 1993), were kindly provided by B. Rosengarten (Freie Universität Berlin). Evaporation of the reaction solvent yielded single crystals of D-galactonic acid hydrazide.

Crystals of L-galactonic acid hydrazide hemihydrate were obtained during a series of experiments investigating the co-crystallization properties of different aldonic acid hydrazides (André, 1996): a 1:1 mixture of (2) and L-mannonic acid hydrazide (3) dissolved in boiling ethanol:H₂O (1:1) gave colourless single crystals by slow evaporation of the solvent at room temperature over 8 d. The concentration of each individual solute was ca 50 mmol l⁻¹.

2.2. Single crystal structure analysis

Crystal data, data collection and refinement parameters of (1) and (2a) are displayed in Table 1. Compound

Table 1. *Experimental details*

	(1)	(2a)
Crystal data		
Chemical formula	C ₆ H ₁₄ N ₂ O ₆	2C ₆ H ₁₄ N ₂ O ₆ ·H ₂ O
Chemical formula weight	210.19	438.40
Cell setting	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁
<i>a</i> (Å)	5.7444 (3)	4.7800 (10)
<i>b</i> (Å)	17.3140 (8)	13.603 (2)
<i>c</i> (Å)	4.6903 (4)	14.822 (3)
β (°)	106.770 (10)	98.830 (10)
<i>V</i> (Å ³)	446.65 (5)	952.3 (3)
<i>Z</i>	2	2
<i>D_x</i> (Mg m ⁻³)	1.563	1.529
Radiation type	Cu <i>K</i> α	Mo <i>K</i> α
Wavelength (Å)	1.54180	0.71069
No. of reflections for cell parameters	89	1561
θ range (°)	25–45	4.25–28.15
μ (mm ⁻¹)	1.217	0.138
Temperature (K)	293 (2)	293 (2)
Crystal form	Needle	Needle
Crystal size (mm)	0.50 × 0.18 × 0.11	0.32 × 0.12 × 0.04
Crystal colour	Colourless	Colourless
Data collection		
Diffractometer	Stoe four-circle	Stoe imaging plate diffraction system
Data collection method	ω -2 θ scans	ω scans
Absorption correction	None	None
No. of measured reflections	865	4399
No. of independent reflections	770	4254
No. of observed reflections	762	3214
Criterion for observed reflections	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)
<i>R_{int}</i>	0.0067	0.0270
θ_{\max} (°)	63.98	27.96
Range of <i>h, k, l</i>	-6 → <i>h</i> → 6 0 → <i>k</i> → 20 0 → <i>l</i> → 5	-6 → <i>h</i> → 6 -17 → <i>k</i> → 17 -19 → <i>l</i> → 19
No. of standard reflections	3	-
Frequency of standard reflections (min)	90	-
Refinement		
Refinement on	<i>F</i> ²	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0214	0.0441
<i>wR</i> (<i>F</i> ²)	0.0596	0.0981
<i>S</i>	1.118	1.123
No. of reflections used in refinement	769	4252
No. of parameters used	183	381
H-atom treatment	H atoms were refined unrestrained. Only the isotropic displacement parameter of H3 was linked up with the <i>U</i> _{eq} of C3 [<i>U</i> _{eq} (H3) = 1.1 <i>U</i> _{eq} (C3)]	It was found necessary only for H(O4), H(O6), H(O32) and H(O42), as well as the two water H atoms, to introduce a DFIX restraint of 0.90 Å (e.s.d. = 0.02). The isotropic displacement parameters of the two latter atoms had to be held fixed at an <i>U</i> value of 0.072 Å ² [= 1.2 <i>U</i> _{eq} (Ow)]
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0370P)^2 + 0.0848P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0142P)^2 + 0.7754P]$, where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) _{max}	0.002	0.005
$\Delta\rho_{\max}$ (e Å ⁻³)	0.135	0.213
$\Delta\rho_{\min}$ (e Å ⁻³)	-0.141	-0.227
Extinction method	<i>SHELXL93</i> (Sheldrick, 1993)	<i>SHELXL93</i> (Sheldrick, 1993)
Extinction coefficient	0.0210 (24)	0.0111 (21)
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration	Flack (1983)	Flack (1983)
Computer programs		
Structure solution	<i>SHELXS86</i> (Sheldrick, 1985)	<i>SHELXS86</i> (Sheldrick, 1985)
Structure refinement	<i>SHELXL93</i> (Sheldrick, 1993)	<i>SHELXL93</i> (Sheldrick, 1993)

(1) crystallizes with one molecule in the asymmetric unit, whereas the asymmetric unit of (2a) contains two sugar molecules and one water molecule as well.

2.2.1. *D-Galactonic acid hydrazide*. Two octants of independent reflections were measured on a Stoe four-

circle diffractometer. Three standard reflections measured every 90 min showed insignificant intensity variation during the data collection. Data were corrected for Lorentz–polarization effects, but not for absorption. Merging resulted in a unique data set of 770 reflections,

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (1)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.4858 (4)	0.20160 (14)	0.0785 (4)	0.0220 (5)
O1	0.3830 (3)	0.23233 (10)	0.2460 (4)	0.0326 (4)
C2	0.6656 (4)	0.24665 (13)	-0.0400 (5)	0.0217 (5)
O2	0.8149 (3)	0.19408 (9)	-0.1403 (4)	0.0266 (4)
C3	0.8159 (4)	0.30197 (13)	0.1956 (5)	0.0211 (4)
O3	0.9820 (3)	0.26002 (9)	0.4300 (3)	0.0247 (4)
C4	0.9480 (4)	0.36244 (13)	0.0611 (5)	0.0220 (5)
O4	0.7608 (3)	0.40332 (10)	-0.1528 (4)	0.0288 (4)
C5	1.0981 (4)	0.41791 (13)	0.2974 (5)	0.0249 (5)
O5	0.9443 (3)	0.46661 (10)	0.4126 (4)	0.0287 (4)
C6	1.2672 (5)	0.46771 (14)	0.1796 (6)	0.0298 (5)
O6	1.3843 (3)	0.52475 (11)	0.3919 (4)	0.0386 (5)
N1	0.4410 (4)	0.13004 (11)	-0.0224 (5)	0.0302 (5)
N2	0.2545 (4)	0.08392 (13)	0.0291 (5)	0.0320 (5)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (2a)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	-0.0742 (7)	0.5629 (2)	0.4784 (2)	0.0295 (7)
O1	-0.2300 (5)	0.4995 (2)	0.4370 (2)	0.0398 (6)
C2	0.1725 (6)	0.5320 (2)	0.5492 (2)	0.0271 (6)
O2	0.3613 (4)	0.6101 (2)	0.5778 (2)	0.0307 (5)
C3	0.0513 (6)	0.4842 (2)	0.6281 (2)	0.0250 (6)
O3	-0.1024 (5)	0.5556 (2)	0.6709 (2)	0.0299 (5)
C4	0.2778 (6)	0.4443 (2)	0.7023 (2)	0.0245 (6)
O4	0.4620 (4)	0.3796 (2)	0.66390 (15)	0.0302 (5)
C5	0.1573 (7)	0.3981 (2)	0.7810 (2)	0.0283 (6)
O5	-0.0120 (5)	0.3140 (2)	0.7524 (2)	0.0345 (5)
C6	0.3895 (7)	0.3676 (3)	0.8564 (2)	0.0315 (7)
O6	0.2788 (5)	0.3679 (2)	0.9400 (2)	0.0379 (6)
N1	-0.1188 (6)	0.6580 (2)	0.4650 (2)	0.0339 (6)
N2	-0.3633 (7)	0.6928 (2)	0.4073 (2)	0.0403 (7)
C12	-0.2162 (6)	0.2212 (2)	0.1122 (2)	0.0299 (7)
O12	-0.3886 (5)	0.2873 (2)	0.0846 (2)	0.0440 (7)
C22	-0.0412 (6)	0.1716 (2)	0.0493 (2)	0.0283 (7)
O22	0.1398 (5)	0.1024 (2)	0.0998 (2)	0.0357 (5)
C32	-0.2432 (6)	0.1226 (2)	-0.0274 (2)	0.0263 (6)
O32	-0.4216 (4)	0.0543 (2)	0.0092 (2)	0.0322 (5)
C42	-0.0946 (6)	0.0731 (2)	-0.0993 (2)	0.0267 (6)
O42	0.0838 (5)	0.1426 (2)	-0.1351 (2)	0.0321 (5)
C52	-0.3030 (7)	0.0262 (2)	-0.1748 (2)	0.0310 (7)
O52	-0.4727 (5)	0.0996 (2)	-0.2246 (2)	0.0367 (6)
C62	-0.1563 (8)	-0.0301 (3)	-0.2419 (3)	0.0412 (9)
O62	-0.3533 (6)	-0.0829 (2)	-0.3059 (2)	0.0461 (7)
N12	-0.1870 (6)	0.1894 (2)	0.1968 (2)	0.0348 (6)
N22	-0.3723 (8)	0.2179 (3)	0.2582 (2)	0.0439 (8)
Ow	0.0076 (7)	0.3176 (2)	0.4167 (2)	0.0603 (8)

of which 762 were observed based on the criterion of $F > 4\sigma$. The structure was solved with *SHELXS86* (Sheldrick, 1985). Full-matrix least-squares refinement of the atomic positional and displacement parameters, a scale factor and an extinction parameter was carried out with *SHELXL93* (Sheldrick, 1993), which suppressed one reflection. Floating origin restraints demanded by the polar space group were automatically generated by the program (Flack & Schwarzenbach, 1988). H atoms were located in difference-Fourier maps and refined without restraints in the isotropic mode. Only the isotropic displacement parameter of H3 had to be linked up

Table 4. Bond lengths (Å) and angles (°) of (1) and (2a)

	(1)	(2a)	
		Molecule 1	Molecule 2
C1—O1	1.232 (3)	1.239 (4)	1.246 (4)
C1—C2	1.522 (3)	1.513 (4)	1.504 (4)
C1—N1	1.325 (3)	1.320 (4)	1.313 (4)
C1—O2	1.421 (3)	1.417 (4)	1.413 (4)
C2—C3	1.527 (3)	1.528 (4)	1.527 (4)
C3—O3	1.429 (3)	1.424 (4)	1.423 (4)
C3—C4	1.532 (3)	1.520 (4)	1.525 (4)
C4—O4	1.429 (3)	1.424 (4)	1.428 (4)
C4—C5	1.531 (3)	1.515 (4)	1.520 (4)
C5—O5	1.435 (3)	1.427 (4)	1.419 (4)
C5—C6	1.517 (3)	1.507 (4)	1.511 (5)
C6—O6	1.426 (3)	1.421 (4)	1.424 (4)
N1—N2	1.412 (3)	1.420 (4)	1.418 (4)
O1—C1—C2	120.8 (2)	119.7 (3)	121.5 (3)
O1—C1—N1	123.5 (2)	122.5 (3)	121.2 (3)
C2—C1—N1	115.6 (2)	117.9 (3)	117.2 (3)
C1—C2—O2	109.3 (2)	113.1 (3)	108.9 (2)
C1—C2—C3	111.0 (2)	107.6 (3)	108.0 (2)
O2—C2—C3	111.9 (2)	112.9 (3)	111.7 (3)
C2—C3—O3	110.5 (2)	109.5 (2)	110.4 (2)
C2—C3—C4	112.0 (2)	113.2 (2)	113.8 (2)
O3—C3—C4	111.3 (2)	106.2 (2)	110.4 (2)
C3—C4—O4	105.4 (2)	110.3 (2)	109.7 (2)
C3—C4—C5	111.9 (2)	113.1 (3)	112.1 (2)
O4—C4—C5	110.5 (2)	112.5 (2)	111.4 (3)
C4—C5—O5	111.2 (2)	111.7 (3)	110.2 (3)
C4—C5—C6	112.3 (2)	111.2 (3)	112.3 (3)
O5—C5—C6	109.4 (2)	108.6 (3)	107.5 (3)
C5—C6—O6	111.2 (2)	108.4 (3)	111.6 (3)
C1—N1—N2	123.1 (2)	121.1 (3)	122.5 (3)

with the U_{eq} of C3 during the refinement [$U_{\text{iso}}(\text{H3}) = U_{\text{eq}}(\text{C3}) + 10\%$ of $U_{\text{eq}}(\text{C3})$].

2.2.2. *L-Galactonic acid hydrazide hemihydrate*. The data collection was performed on a Stoe imaging plate diffraction system (Stoe IPDS) using graphite-monochromated Mo $K\alpha$ radiation. The detector distance amounted to 60.0 mm.

93 reflection positions taken from four rotation exposures recorded at $\varphi = 0.0$ – 0.2 , 90.0 – 90.2 , 180.0 – 180.2 and 270.0 – 270.2° were used for the determination of preliminary unit-cell constants. The data collection took approximately 12 h and 100 exposures were taken starting at $\varphi = 0.0$ and ending at $\varphi = 200.0$, with a rotation angle of 2.0° and an irradiation time of 3 min per exposure. Identification and integration of the peaks, which resulted in 8839 reflections, was performed using the Stoe IPDS software. An analysis of the data showed the Laue and space groups to be $2/m$ and $P2_1$, respectively, and gave no evidence for the necessity of crystal decay correction. The reflections were merged by the IPDS software, leaving the Friedel pairs unmerged and resulting in 4399 reflections.

The structure solution with *SHELXS86* (Sheldrick, 1985) showed all non-H atoms of two hydrazide molecules as well as an additional major peak, which was interpreted as the O atom of a water molecule.

Table 5. Relevant torsion angles of (1), (2a) and L-mannonic acid hydrazide

	(1)	(2a)		L-Mannonic acid hydrazide
		Molecule 1	Molecule 2	
C1—C2—C3—C4	-164.9 (2)	176.8 (3)	177.3 (2)	-175.3 (3)
C2—C3—C4—C5	179.9 (2)	179.3 (3)	-179.4 (3)	-179.3 (3)
C3—C4—C5—C6	168.8 (2)	-175.1 (3)	-175.2 (3)	-179.5 (4)
C4—C5—C6—O6	173.4 (3)	153.7 (3)	173.2 (3)	-57.8 (4)
N1—C1—C2—C3	-146.4 (2)	112.2 (3)	117.3 (3)	126.3 (3)
C2—C1—N1—N2	-170.6 (2)	-173.0 (3)	-169.0 (3)	172.5 (3)
O1—C1—C2—O2	160.7 (2)	168.6 (3)	178.2 (3)	62.5 (5)
O2—C2—C3—O3	-52.1 (2)	60.6 (3)	61.8 (3)	-170.4 (3)
O3—C3—C4—O4	-176.0 (2)	-173.9 (2)	-179.9 (2)	-60.0 (4)
O4—C4—C5—O5	48.9 (2)	-62.4 (3)	-58.4 (3)	179.5 (3)
O5—C5—C6—O6	49.4 (3)	-83.0 (3)	-65.4 (4)	61.6 (4)
C1—N1—N2—H(N21)	34 (2)	-50 (4)	39 (3)	11 (3)*
C1—N1—N2—H(N22)	-87 (3)	72 (4)	-86 (4)	118 (3)
H(N1)—N1—N2—H(N21)	-139 (3)	142 (5)	-131 (4)	-169 (4)†
H(N1)—N1—N2—H(N22)	100 (4)	-96 (5)	103 (5)	-61 (4)

* Actually, for C1—N1—N2—H(N21) the torsion angle of C1—N1—N2—H(N22) is given (and *vice versa*) in order to demonstrate the similarity with the values of (1) and (2a). † Actually, for H(N1)—N1—N2—H(N21) the torsion angle of H(N1)—N1—N2—H(N22) is given (and *vice versa*) in order to demonstrate the similarity with the values of (1) and (2a).

The data set with unmerged Friedel pairs was used for the refinement with *SHELXL93* (Sheldrick, 1993), giving 4254 unique reflections ($R_{\text{int}} = 0.0270$), of which two were suppressed by *SHELXL93*. Floating origin restraints necessary for the polar space group $P2_1$ were automatically generated by the program (Flack & Schwarzenbach, 1988). The extinction correction incorporated in *SHELXL93* was applied during the final refinement cycles.

All H atoms were located from difference-Fourier maps and refined isotropically. The hydroxyl O—H bonds exhibited some trend towards lengthened O—H distances (around 1 Å), but it was found necessary only for H(O4), H(O6), H(O32) and H(O42), as well as the two water H atoms, to introduce a DFIX restraint of 0.90 Å (e.s.d. = 0.02). The isotropic displacement parameters of the two latter atoms had to be held fixed at an U value of 0.072 [= $U_{\text{eq}}(\text{Ow}) + 20\%$ of $U_{\text{eq}}(\text{Ow})$].

3. Discussion

Atomic coordinates and equivalent isotropic displacement parameters of (1) and (2a) are given in Tables 2 and 3, respectively. Table 4 displays bond lengths and angles of both compounds. For comparison, relevant torsion angles of (1), (2a) and L-mannonic acid hydrazide (3) (André, Luger, Fuhrhop & Rosengarten, 1993) are shown in Table 5. The hydrogen-bond geometry of (1) and (2a) is given in Tables 6 and 7, respectively. Figs. 1 and 2 show the molecular conformations with atomic numbering for (1) and (2a). Fig. 3(a) displays the crystal packing of (1) exhibiting an antidromic hydrogen-bonding cycle; Fig. 3(b) shows the homodromic hydrogen-bond pattern observed in D-galactaric acid. The coordination shell of the water molecule of (2a) is displayed in Fig. 4. A schematic drawing of the

Table 6. Hydrogen-bonding geometry (Å, °) in (1)

Values obtained after O—H and N—H were normalized to 0.97 and 1.00 Å, respectively. The e.s.d.'s for X—H lie between 0.03 and 0.05. Values in squared brackets give the sum of the angles $D \cdots H \cdots A_1$, $D \cdots H \cdots A_2$ and $A_1 \cdots H \cdots A_2$.

$D \cdots H \cdots A$	H—A	$D \cdots A$	$D \cdots H \cdots A$	$A_1 \cdots H \cdots A_2$
N1—H(N1)···O2 ⁱ	2.23 (3)	2.614 (3)	101 (2)	
N1—H(N1)···O6 ⁱⁱ	1.95 (3)	2.887 (3)	156 (3)	102 (2) [359 (4)]
N2—H(N21)···O2 ⁱⁱⁱ	2.13 (5)	3.080 (5)	158 (3)	
N2—H(N22)···O4 ^{iv}	2.73 (5)	3.186 (3)	108 (3)	
N2—H(N22)···O6 ^v	2.14 (4)	3.079 (3)	155 (4)	85 (2) [348 (5)]
O2—H(O2)···O3 ^{vi}	1.75 (3)	2.721 (2)	176 (3)	
O3—H(O3)···O2 ^{vii}	2.61 (3)	2.810 (2)	92 (2)	
O3—H(O3)···O1 ^{viii}	1.77 (4)	2.725 (3)	166 (3)	96 (2) [354 (4)]
O4—H(O4)···O5 ^{ix}	1.81 (4)	2.776 (3)	178 (3)	
O5—H(O5)···N2 ^x	1.95 (4)	2.891 (3)	163 (3)	
O6—H(O6)···O5 ^{xi}	2.16 (5)	2.748 (3)	118 (4)	

Symmetry codes: (i) x, y, z ; (ii) $2 - x, y - \frac{1}{2}, -z$; (iii) $x - 1, y, z$; (iv) $1 - x, y - \frac{1}{2}, -z$; (v) $2 - x, y - \frac{1}{2}, 1 - z$; (vi) $x, y, z - 1$; (vii) $1 + x, y, z$; (viii) $1 - x, \frac{1}{2} + y, -z$; (ix) $\frac{1}{2} - x, \frac{1}{2} + y, -z$.

hydrogen-bond patterns of some carbohydrates is given in Fig. 5. The crystal packing of (2a) is shown in Fig. 6.*

3.1. Molecular structure

The C—C and the C—O(OH) bond lengths of both compounds are almost identical to their counterparts in the crystal structure of L-mannonic acid hydrazide and deserve no further discussion.

The two independent molecules of (2a) share a very similar overall geometry. Similar independent molecules (Sona & Gautham, 1992) are also observed in other acyclic sugar structures, e.g. *N*-(1-octyl)-D-

* Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: KA0031). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 7. Hydrogen-bonding geometry (Å, °) in (2a)

Values obtained after O—H, N—H and C—H were normalized to 0.97, 1.00 and 1.08 Å, respectively. The e.s.d.'s for D—H lie between 0.03 and 0.06 Å. Values in squared brackets give the sum of the angles $D-H \cdots A_1$, $D-H \cdots A_2$ and $A_1 \cdots H \cdots A_2$.

$D-H \cdots A$	H—A	$D \cdots A$	$D-H \cdots A$	$A_1 \cdots H \cdots A_2$
N1—H(N1)···O2 ⁱ	2.34 (5)	2.704 (4)	101 (3)	
N1—H(N1)···Ow ⁱⁱ	1.90 (4)	2.790 (4)	147 (4)	103 (2) [351 (5)]
N2—H(N21)···O1 ⁱ	2.50 (7)	2.725 (4)	92 (4)	
N2—H(N21)···O52 ⁱⁱⁱ	2.04 (6)	2.984 (4)	157 (5)	101 (3) [350 (7)]
N2—H(N22)···O2 ^{iv}	2.36 (6)	3.226 (4)	145 (5)	
O2—H(O2)···O3 ⁱ	2.36 (7)	2.882 (3)	113 (5)	
O2—H(O2)···N22 ⁱⁱ	1.99 (7)	2.832 (4)	144 (5)	95 (3) [352 (8)]
O3—H(O3)···O4 ^{iv}	2.87 (5)	3.164 (3)	99 (4)	
O3—H(O3)···O2 ^{iv}	1.88 (5)	2.818 (3)	163 (5)	89 (2) [351 (7)]
O4—H(O4)···O5 ⁱ	2.60 (4)	2.927 (3)	100 (3)	
O4—H(O4)···N2 ^v	1.89 (4)	2.764 (4)	148 (4)	104 (2) [352 (5)]
O5—H55···O4 ^{iv}	1.86 (7)	2.798 (3)	161 (6)	
O6—H(O6)···O12 ^{vi}	1.75 (5)	2.697 (3)	163 (5)	
N12—H(N12)···O22 ⁱ	2.16 (4)	2.568 (4)	102 (3)	
N12—H(N12)···O3 ^v	2.00 (4)	2.870 (4)	143 (3)	114 (2) [359 (5)]
N22—H(N221)···O22 ^{iv}	2.59 (6)	3.426 (4)	141 (4)	
N22—H(N222)···Ow ⁱ	2.28 (7)	3.057 (5)	133 (5)	
O22—H(O22)···O32 ⁱⁱⁱ	1.77 (5)	2.737 (3)	175 (4)	
O32—H(O32)···O22 ⁱ	2.71 (4)	2.886 (3)	91 (2)	
O32—H(O32)···O6 ^v	1.79 (3)	2.703 (3)	156 (4)	112 (2) [359 (5)]
O42—H(O42)···O52 ⁱ	2.50 (5)	2.845 (3)	101 (3)	
O42—H(O42)···O5 ^{viii}	2.02 (5)	2.862 (3)	144 (4)	110 (2) [355 (5)]
O52—H(O52)···O42 ^{iv}	1.76 (5)	2.731 (3)	175 (4)	
O62—H(O62)···O52 ⁱ	2.62 (6)	2.855 (4)	94 (4)	
O62—H(O62)···O1 ^{ix}	1.87 (6)	2.795 (4)	158 (5)	102 (2) [354 (7)]
Ow—Hw1···O1 ⁱ	1.79 (3)	2.758 (4)	174 (4)	
Ow—Hw2···O62 ^x	1.98 (5)	2.845 (4)	147 (4)	
C5—H5···O22 ⁱⁱ	2.64 (4)	3.693 (4)	165 (3)	
C22—H22···O6 ^x	2.52 (3)	3.585 (4)	172 (2)	

Symmetry codes: (i) x, y, z ; (ii) $-x, \frac{1}{2} + y, 1 - z$; (iii) $-1 - x, \frac{1}{2} + y, -z$; (iv) $x - 1, y, z$; (v) $-x, y - \frac{1}{2}, 1 - z$; (vi) $1 + x, y, 1 + z$; (vii) $1 + x, y, z$; (viii) $x, y, z - 1$; (ix) $-1 - x, y - \frac{1}{2}, -z$ (x) $-x, \frac{1}{2} + y, -z$.

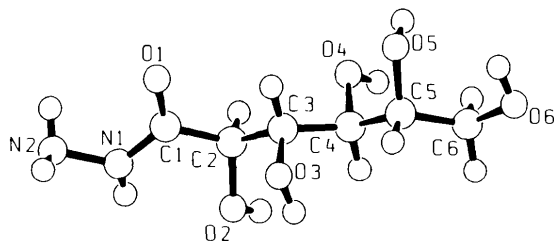


Fig. 1. Molecular conformation and atomic numbering scheme of (1).

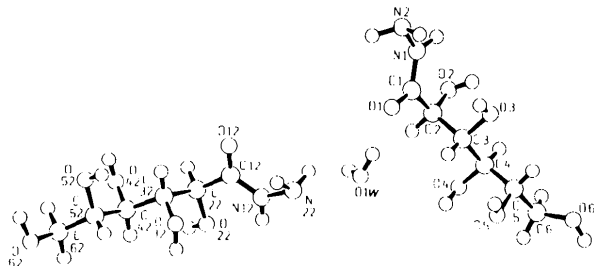
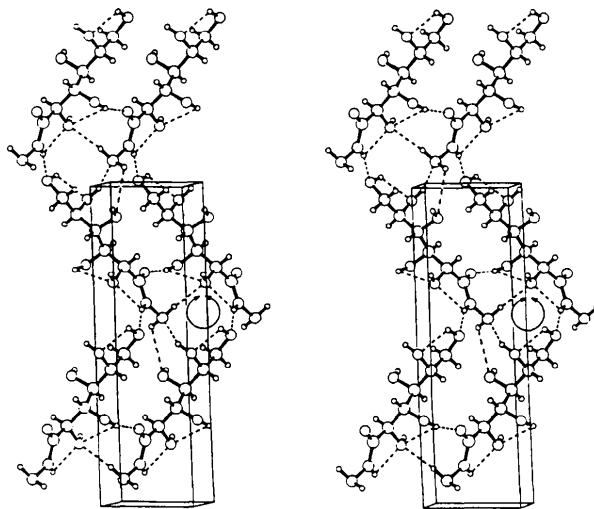


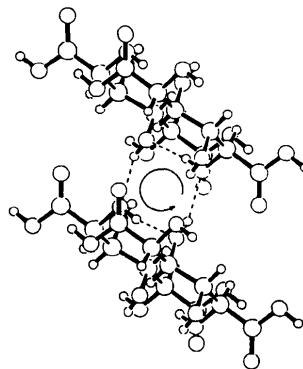
Fig. 2. Asymmetric unit and atomic numbering scheme of (2a).

talonamide (André, Luger, Svenson & Fuhrhop, 1993) or D-arabinitol (Kopf, Morf, Zimmer & Köll, 1991).

As expected (Jeffrey & Kim, 1970), the carbon chains of the title compounds exhibit an essentially linear conformation. The only non-extended sugar chains found so far for acyclic galacto-configured compounds are the dimorphs of 1,2:5,6-dianhydrogalactitol and the corresponding 3,4-diacetyl derivative (Czugler, Simon, Institoris, Vidra & Csöreg, 1982).



(a)



(b)

Fig. 3. (a) Crystal packing of (1) displaying an antidromic hydrogen-bonding cycle $\overline{O5^i} \rightarrow \overline{N2^{viii}} \rightarrow \overline{O2^{ix}} \leftarrow \overline{N1^{ix}} \rightarrow \overline{O6^i}$ formed by three molecules. The indices refer to the symmetry operations given in Table 6. (b) Homodromic quadrilateral hydrogen-bonding cycle found in the crystal structure of galactaric acid (Jeffrey & Wood, 1982). Homologous cycles are found in the crystal structures of further galacto- (André, 1996) ribo-, arabino-, manno-, gluco- and althro-configured acyclic carbohydrate derivatives (André, Luger, Fuhrhop & Rosengarten, 1993). The general connectivity of these cycles is $\overline{O(x)} \cdots \overline{O(x+2)} \cdots \overline{O(x+3)} \cdots \overline{O(x+1)}$; both the clockwise and the counterclockwise direction of the hydrogen bonds is realized.

The primary hydroxyl group of (1) and of both molecules of (2a) is a linear extension of the carbon chain. Galactitol (Berman & Rosenstein, 1968) and L-galacto-D-galactodecitol (Köll, Kopf, Morf, Zimmer & Brimacombe, 1992) also exhibit such a terminally extended conformation. In contrast to these, hexaacetyl-

galactitol (Kopf, Morf, Zimmer, Bischoff & Köll, 1992), 1-deoxy-1-nitro-D-galactohexitol (Kopf, Brandenburg, Seelhorst & Köll, 1990), 1,4-dimethyl-3-(D-galactopentitol-1-yl)-5-(p-tolyl)pyrazole (Estrada De Oya & Lopez-Castro, 1991) and a pentaacetyl-D-galactonic acid ester (Kopf, Abeln, Köll, Meisel & Peske, 1994) assume a synclinal conformation at the terminal OH group.

The conformational properties of the hydrazide moieties with respect to the non-H atoms are similar in all aldonic acid derivatives: the N1—C1—C2—C3 and the C2—C1—N1—N2 torsion angles are always in the *ac* and *ap* range, respectively. Differences lie in the absolute values of the N1—C1—C2—C3 torsion angles and their signs. The largest value (the only one with a negative sign) is found in (1) [$-146.4(2)^\circ$], whereas (2a) exhibits the smallest [$112.2(3)$ and $117.3(3)^\circ$] and the mannonic acid compound displays an intermediate value [$126.3(3)^\circ$]. Since the change of configuration involves the sign change of all torsion angles, the conformations of the oppositely configured title compounds are identical (neglecting the difference in the absolute values of the torsion angles).

The two galactohydrazide structures display almost identical *absolute* values for H(N1)—N1—N2—H(N21) and H(N1)—N1—N2—H(N22), which are in the *ac* range approximately 20° above and below 1120° , respectively.

The amine H atoms of (1) and (2a) are situated on the 'oxygen-side' of the amide bond. In contrast to these, the lone pair of each N2 atom is opposite the closest lone pair of the carbonyl O atom pointing towards the 'proton-side' of the amide bond. This *cis* configuration is more stable than its corresponding *trans* form, where

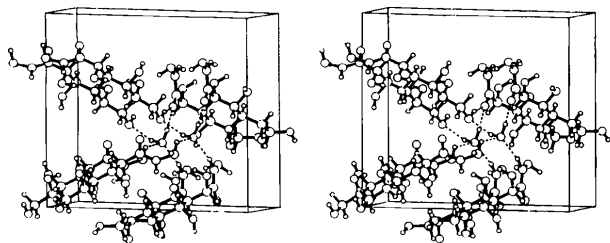


Fig. 4. Distorted tetrahedral coordination shells of two water molecules in (2a). Note the hydrogen bond between O62 of one tetrahedron to O1 of another.

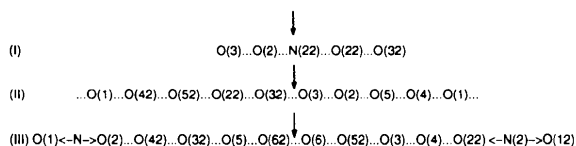


Fig. 5. Schematic drawing of the hydrogen-bonding schemes of (I) (2a), (II) D-arabinitol and (III) N-(1-octyl)-D-talonamide, which possess twofold symmetry if the direction of the hydrogen bond is neglected. For (2a) only the symmetrical part of the hydrogen-bonding scheme is given, whereas the complete schemes are given for (II) and (III). The position of the twofold axis is indicated by an arrow. All compounds exhibit two independent molecules in the asymmetric unit.

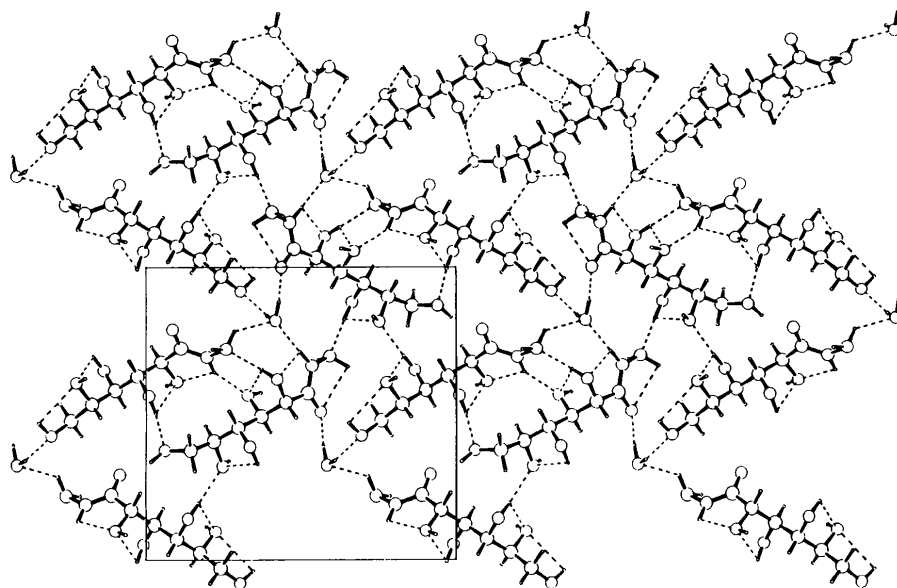


Fig. 6. Crystal packing of (2a), indicating the intricate hydrogen-bonding scheme.

the lone pair of N2 points to the closest carbonyl oxygen lone pair (Quaeyhaegens, Desseyn, Bracke & Lenstra, 1990). This is supported by the earlier observation that the less stable configuration is found only in two out of 14 structures (Quaeyhaegens, Desseyn, Bracke & Lenstra, 1990). Two further related structures, namely L-mannonic acid hydrazide and benzhydrazide (Kallel, Amor, Svoboda & Fuess, 1992), also display the more stable *cis* form. Accordingly, the conformation of a hydrazide moiety is basically an intrinsic molecular property, 'fine tuned' by intermolecular forces. A few less favoured *trans* configurations can be traced back to strong intermolecular hydrogen-bond effects.

3.2. Hydrogen-bonding scheme and crystal packing

3.2.1. *D-Galactonic acid hydrazide*. Molecules related by the screw axis along **b** are linked by a hydrogen bond N1—O6 (Table 6), which takes part in a hydrogen-bonding cycle formed by

$\overline{O5^i \rightarrow N2^{viii} \rightarrow O2^{ix} \leftarrow N1^{ix} \rightarrow O6^i}$ (Fig. 3a; for the symmetry codes see Table 6). Thus, three molecules are involved in this pattern, which is the predominant feature of the hydrogen-bonding scheme of (1). According to Saenger (1979) the cycle is of the antidromic type with two intracyclic hydrogen-bond chains running into opposite directions. The hydrogen bonds between N1 and O2 as well as between O6 and O5 are intramolecular.

A close inspection reveals that O6 accepting a hydrogen bond from N1 does not serve as an intermolecular hydrogen-bond donor; it solely donates an intramolecular hydrogen bond to O5. This is a rare finding since hydrogen-bonding patterns of carbohydrates tend to display a high degree of intermolecular cooperativity (Jeffrey, 1990). Actually, there are two potential intermolecular hydrogen-bond acceptors for O6ⁱ, namely N2^x and N2^{ix}, with contact distances of 3.079 (3) and 3.409 (3) Å, respectively [$(x) 2 - x, \frac{1}{2} + y, 1 - z$]. However, O6 only serves as an acceptor from these symmetry-related molecules, namely from H(N22) and H(N1). An additional hydrogen bond of O6ⁱ to N2^x would result in a cyclic dimer. Such a 'tandem hydrogen bond' (Jeffrey & Saenger, 1991) is unfavourable since it involves a very short non-bonding contact of the H atoms. In fact, an attempt to optimize interactively on a computer screen H(O6)^s distance to N2^x or N2^{ix} results in forbidden (Steiner & Saenger, 1991, 1992) H...H distances around 1.5 Å between H(O6)ⁱ and H(N22)^x or H(N1)^{ix}. Under these circumstances the intramolecular hydrogen bond of O6 to O5 is the only possible arrangement.

Acyclic galacto-configured compounds, whose unit cell shows two approximately 5 Å lattice constants, are able to form the same special hydrogen-bonding cycle (André, 1996) which is found in the crystal structures of many other open-chain sugar derivatives

(André, Luger, Fuhrhop & Rosengarten, 1993). In contrast to the antidromic hydrogen-bonding cycle which is observed in (1) and in which three molecules are involved (Fig. 3a), the former cycle which is built up by four molecules (Fig. 3b) is of the homodromic type, *i.e.* the hydrogen bonds are unidirectional. The finding that (1), exhibiting two 5 Å axes, does not show a quadrilateral homodromic arrangement agrees with our previous observation that larger deviations from rectangular lattices are incompatible with an occurrence of this pattern. In fact, the monoclinic angle observed in the crystal lattice of (1) is ~107°, whereas the monoclinic angles of those sugar derivatives exhibiting the homodromic quadrilateral cycle all are below 99° (André, Luger, Fuhrhop & Rosengarten, 1993).

The angle between the monoclinic axis and an axis passing through C1 and C5, giving the orientation of the molecule in the asymmetric unit, is 42°. Therefore, the molecule is substantially inclined against the *b* axis. Due to this tilt and the existence of a twofold screw axis, the molecules of (1) are arranged in a herringbone pattern (Fig. 3a). The tilt angle between molecules in different layers, *i.e.* between the two 'halves' of the herringbone, is 96°.

3.2.2. *L-Galactonic acid hydrazide hemihydrate*.

Due to the presence of two independent sugar molecules together with one water molecule, the hydrogen-bonding scheme of (2a) is more complicated than that of (1) (Table 7). For descriptive purposes, it is useful to formulate the hydrogen-bonding scheme of (2a) by neglecting intramolecular hydrogen bonds and considering only the major component of bifurcated bonds. It must, however, be kept in mind that this procedure is artificial to a certain extent, since it omits existing cooperative effects.

The water accepts and donates two hydrogen bonds. Its fourfold coordination shell (Fig. 4), formed by N1, N22, O1 and O62, can be approximated by a very distorted tetrahedron: its edges vary between 3.8 and 5.1 Å and the distance of the water O atom from the four faces is between ~0.5 and ~1.5 Å. The coordination shells of the neighbouring water units are connected by hydrogen bonds from O62 of one tetrahedron to O1 of another (Fig. 4).

The further hydrogen-bonding scheme of (2a) consists of a finite and an infinite chain, the latter forming a spiral running in the *a* direction: (I) N12→O3→O2→N22→O22→O32→O6→O12 and (II) N2→O52→O42→O5→O4→N2 *etc.* These chains are interconnected by several bifurcated bonds and by the only hydrogen bond formed by H(N22), namely to O2.

In addition to the 'conventional' X—H...Y bonds (X, Y = O, N), two almost linear C—H...O bonds are observed: they are formed between C5 and O22 as well as C22 and O6.

It is worth noting that one fragment of the above chain (I), namely O3...O2...N22, is connected to its

other fragment, namely N22...O22...O32, by a twofold axis running through N22 (Fig. 5). The direction of the hydrogen bonds within the chain has to be disregarded to fulfill this symmetry; therefore, the term 'symmetry' applies only to a limited extent. There exist further open-chain carbohydrate crystal structures with two independent molecules, where the complete hydrogen-bonding scheme possesses such a limited twofold symmetry. An endless chain is found in D-arabinitol (Kopf, Morf, Zimmer & Köll, 1991), whereas a finite pattern exists in *N*-(1-octyl)-D-talonamide [André, Luger, Svenson & Fuhrhop, 1993 (Fig. 5)]. There the twofold axis bisects the O3...O32 and the O6...O62 hydrogen bond, respectively.

The angles between the molecules of (2a) and the monoclinic axis are 63 and 58° for molecule (I) and (II), respectively. Therefore, the molecules of (2a) are more inclined against the *b*-axis than the molecules of the anhydrous hydrazide. Like (1), the crystal packing of (2a) displays a herringbone arrangement (Fig. 6).

In contrast to (1), where the layers are formed by only one conformer, the independent molecules of (2a) occur within an *ac* plane layer along the *c* axis in an alternating fashion. These alternating molecules are, unlike (1), not perfectly parallel, but have a tilt angle of 9°. The angles between molecules in different layers are 60° between the two independent molecules, 53° between molecule (I) and its screw-axis generated counterpart, and 64° between molecule (II) and its screw-axis related molecule. Thus, the mutual inclination of molecules of (2a) is by far steeper than of the molecules in (1), where the tilt angle between molecules in different layers amounts to 96°.

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