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1,3-Parallel O//O interactions in acyclic carbohydrates: the crystal and molecular structures of *meso*-D-*glycero*-L-*altro*-heptitol and the monohydrate, *meso*-D-*glycero*-L-*ido*-heptitol, and *meso*-D-*glycero*-L-*altro*-heptitol and D-*glycero*-L-*galacto*-heptitol heptaacetates

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Abstract

The molecular structures of the title compounds were determined by X-ray crystallography, using direct methods, and refined to final conventional residual parameters of $R =$ 0.042, 0.035, 0.060, 0.062, and 0.047, respectively. *meso*-D-*glycero*-L-*altro*-Heptitol crystallised usually as a monohydrate from moist ethanol with single molecules occurring in the crystal as a racemate of chiral conformers adopting a planar zigzag conformation. Thus, a 1,3-parallel O-3//O-5 interaction is tolerated with a distance of 265.0 pm. By thorough exclusion of water, an unhydrated morph was obtained from ethanol and investigated at 173 K. The conformations of single molecules parallel those observed in the hydrate. The O-3–O-5 distance is 267.6 pm. Molecules of the derived heptaacetate avoid this interaction by bending to a sickle, but tolerate, instead, an O-3//C-6 relationship with a distance of 295.0 pm. Also, in this case, chiral conformers are observed, which are matched by their enantiomers in the unit cell. *meso*-D-*glycero*-L-*ido*-Heptitol is found in a doubly bent chiral conformation which is free of 1,3-parallel interactions and resembles that found in iditol hexaacetate, but not in iditol itself. Again, a racemate of conformers is observed in the unit cell. The molecules of the heptaacetate of chiral D-*glycero*-L-*galacto*-heptitol are found in a

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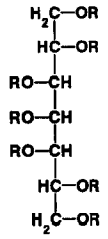
sickle conformation, free of 1,3-parallel interactions, a situation already observed for the parent alditol but which could not have been predicted from recent investigations of the solid state structures of other alditol acetates. The occurrence of 1,3-parallel O//O interactions in alditols and other acyclic carbohydrates is discussed comprehensively.

Key words: X-ray structures; Conformation; 1,3-Parallel interactions; Alditols; Heptitols

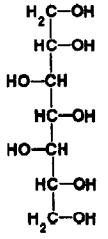
1. Introduction

Recently, we began a program to elucidate the solid state structures of alditols and alditol acetates which had not been investigated before, initiated by some very interesting findings on nitroalditols [1–18]. In a considerable number of cases, we have observed planar zigzag conformations involving 1,3-parallel O//O interactions or, in bent ("sickle") conformations, 1,3-parallel C//O interactions which could easily have been avoided. These findings were in most cases unexpected (cf. the Introduction of ref 10).

As part of our efforts to establish the data for all ten diastereomeric heptitols [4,5,8,18–21], we now report on the two remaining members. These are *meso*-D-*glycero*-L-*altro*-heptitol (**1a**), both anhydrous and as the monohydrate **1a** · H_2O, and meso-D-*glycero*-L-*ido*-heptitol (**2**). As far as derived heptaacetates are concerned [16,18], this study gives the data for two other isomers, namely *meso*-1,2,3,4,5,6,7-hepta-*O*-acetyl-D-*glycero*-L-*altro*-heptitol (**1b**) and 1,2,3,4,5,6,7-hepta-*O*-acetyl-D-*glycero*-L-*galacto*-heptitol (**3**). Although the heptaacetate of *meso*-D-*glycero*-L-*ido*-heptitol crystallises easily, as is well known, in our hands it resisted many attempts to grow individual crystals of acceptable size. The remaining three heptaacetates have so far not crystallised, so that this series is, for the moment, completed. We therefore decided to discuss the 1,3-parallel O//O interactions observed in some of these and related compounds in a more comprehensive manner. A similar account of C//O interactions will be given in another report [22].



1a R = H
1b R = Ac



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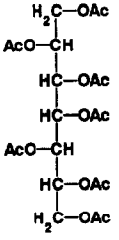

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2. Results and discussion

Suitable crystals of *meso*-D-*glycero*-L-*altro*-heptitol (**1a**) [23] were obtained by crystallisation from moist ethanol and were subsequently identified as the monohy-

drate **1a** · H_2O. Thorough exclusion of water yielded crystalline anhydrous **1a**. For the first time, **1a** is described as a crystalline compound. *meso*-D-*glycero*-L-*ido*-Heptitol (**2**) [24,25] and the heptaacetates **1b** [23] and **3** [1] [26] were crystallised from the same solvent. The relevant crystallographic data for **1a**, **1a** · H_2O, **1b**, **2**, and **3** are given in Table 1; **1a** was investigated at −100°C (173 K) in order to avoid hydration. The structures were solved by direct methods and refined with the help of the programs SHELXS-86 [27] (solution) and SHELXL-93 [28] (refinement). The refinement was done on F^2 for all reflections. The validated threshold $I > 2\sigma(I)$ was used for calculating R_{obsd} only.

All atoms, including hydrogens introduced at theoretical positions using the AFIX option [28], were refined. The final fractional coordinates of C and O with equivalent isotropic thermal parameters are listed in Table 2 for compounds **1a**, **1a** · H_2O, and **2**, and in Table 3 for **1b** and **3** [2]. Perspective views of all compounds investigated are presented in Figs. 1–5 (SCHAKAL-92 plots [29]) which show the atom numbering schemes as well. The molecules of **1a**, **1a** · H_2O, and **2** are held together in the crystal by complex patterns of hydrogen bonds, which are given in Table 4.

Molecules in both **1a** and **1a** · H_2O adopt planar zigzag conformations, which are not symmetrical (compare Figs. 1 and 2). Therefore, these conformers are chiral, but are matched in the unit cell by the respective enantiomeric conformers. In both cases, O-3 and O-5 are found in a 1,3-parallel arrangement, and molecules do not bend to a sickle in order to avoid this interaction. The toleration of such O//O interactions is not as rare as was proposed until recently. In Table 5 are listed all those compounds which exhibit in the solid state such an interaction between secondary oxygens in a planar zigzag conformation [1,2,7,10,12,15,16,30–53]. In Table 6 are listed all those substances (in most cases acetates) where such an interaction is observed between secondary oxygens [13,16,54–56] in sickle conformations, and between primary and secondary oxygens in mostly planar conformations [7,10,13,15,50,51,57,58]. From the data of Table 5, it is evident that the establishment of O//O interactions in zigzag conformations is quite usual in those cases where the interacting oxygens are involved in a *xylo* sequence of three contiguous stereogenic centres (or *gluco* and *ido*, if a sequence of four stereogenic centres has to be considered). The examples listed in Table 5 are a considerable fraction (> 60%) of all those acyclic carbohydrate derivatives with an element of the aforementioned *xylo* configuration for which the structures were determined. For such compounds, the sickle conformation is almost the exception rather than the norm [15]. The whole sample given in Table 5 includes only one compound with an intrinsic *ribo* configuration; all others are of *xylo* configuration. Therefore,

[1] The L enantiomer is described in ref. 26.

[2] Lists of observed and calculated structure amplitudes, anisotropic thermal parameters, fractional coordinates of hydrogen atoms with isotropic thermal parameters, tables of bond distances and angles, and further information have been deposited with and can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1 EZ, United Kingdom.

Table 1
Crystallographic data [a] for **1a**, **1a**·H_2O, **2**, **1b**, and **3** [b]

Data	**1a**	**1a**·H_2O	**2**	**1b**	**3**
Formula	$C_7H_{16}O_7$	$C_7H_{16}O_7 \cdot H_2O$	$C_7H_{16}O_7$	$C_{21}H_{30}O_{14}$	$C_{21}H_{30}O_{14}$
Mol wt	212.20	212.20 + 18.01	212.20	506.46	506.46
Mp (°C)	113–115	68.5	111–112	83–85	107–108
Crystal dimensions (mm)	0.6×0.4×0.3	0.4×0.3×0.1	0.5×0.3×0.2	0.4×0.3×0.3	0.3×0.2×0.2
Space group	*Pbca*	*C*2/*c*	$P\bar{1}$	*Pbna*	$P2_12_12_1$
Cell parameters (pm, degrees)					
a [*α*]	1081.0(1)	2314.2(5)	531.7(1) [90.85(1)]	877.5(1)	1237.0(1)
b [*β*]	937.3(1)	478.9(1) [113.88(3)]	795.3(1) [94.74(1)]	1621.4(1)	1298.3(2)
c [*γ*]	1925.9(2)	2012.9(4)	1107.0(2) [100.49(1)]	3694.6(3)	1646.5(2)
Volume *V* (pm^3)	$1951.4(3)\times10^6$	$2039.9(7)\times10^6$	$458.5(1)\times10^6$	$5256.6(8)\times10^6$	$2644.3(6)\times10^6$
Z	8	8	2	8	4
F (000)	912	992	228	2144	1072
Calculated density, D_x ($g\ cm^{-3}$)	1.445	1.499	1.537	1.280	1.272
λ (Cu*Kα*) (pm)	154.178	154.178	154.178	154.178	154.178
μ (cm^{-1})	11.4	12.1	12.1	9.4	9.3
2*θ* range (degrees)	4.5–153	4.5–153	4.5–153	4.5–153	4.5–153
Reflections collected	4074	8406	2073	5541	5960
Symmetry independent reflections	2040	2120	1833	5484	5129
Observed reflections with $F > 2\sigma(F)$	1993	2068	1783	4287	3755

Number of refined parameters	151	168	151	326	354
Ratio of valued reflections to parameters	13.5	12.6	2.1	16.8	14.5
Final residual factors R^c					
$R1_{obsd}$	0.042	0.035	0.060	0.062	0.047
$\omega R2_{all}$	0.117	0.099	0.182	0.198	0.150
$\omega R2_{obsd}$	0.116	0.099	0.180	0.176	0.117
Goodness of fit S^d					
S_{all}	1.14	1.10	1.04	1.08	1.02
S_{obsd}	1.14	1.11	1.05	1.15	1.06
Largest difference peak ($e \times pm^{-3}$)	0.39×10^6	0.42×10^6	0.52×10^6	0.49×10^6	0.16×10^6
Largest difference hole ($e \times pm^{-3}$)	-0.25×10^6	-0.21×10^6	-0.37×10^6	-0.40×10^6	-0.15×10^6

[a] Standard deviations in parentheses.

[b] Diffractometer Enraf-Nonius CAD 4.

[c] Definitions of R:

$$R1 = \frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|}; \omega R2 = \sqrt{\frac{\Sigma\omega\left(F_o^2 - F_c^2\right)^2}{\Sigma\omega\left(F_o^2\right)^2}}$$

[d] Definition of S:

$$S = \sqrt{\frac{\Sigma\omega\left(F_o^2 - F_c^2\right)^2}{n-p}}.$$

Table 2
Fractional positional parameters of C and O atoms ($\times 10^4$) and temperature factors U_{eq} [a] ($\times 10^3$) for **1a**, **1a·H$_2$O**, and **2** [b]

Atom	**1a**				**1a·H$_2$O**				**2**			
	x	*y*	*z*	U_{eq}	*x*	*y*	*z*	U_{eq}	*x*	*y*	*z*	U_{eq}
O-1	922(1)	2600(1)	3040(1)	22(1)	2261(1)	−553(2)	6064(1)	41(1)	5625(3)	−4555(2)	6584(2)	36(1)
O-2	2694(1)	1933(1)	4075(1)	18(1)	1377(1)	1674(2)	5651(1)	27(1)	2354(3)	−2753(2)	8090(1)	38(1)
O-3	3897(1)	4570(1)	4043(1)	17(1)	727(1)	−3506(2)	5111(1)	27(1)	−568(3)	−1854(2)	5933(1)	31(1)
O-4	5576(1)	1611(1)	3245(1)	17(1)	689(1)	1901(2)	3821(1)	26(1)	472(3)	1735(2)	6529(1)	29(1)
O-5	6142(1)	4219(1)	4604(1)	17(1)	−337(1)	−3808(2)	3924(1)	27(1)	5789(3)	2133(2)	7055(1)	31(1)
O-6	7318(1)	1501(1)	4717(1)	17(1)	−943(1)	1274(2)	3317(1)	27(1)	6209(3)	3353(2)	9494(1)	35(1)
O-7	9065(1)	3956(1)	3610(1)	24(1)	−1392(1)	−775(2)	1818(1)	34(1)	2157(4)	3204(2)	10773(1)	44(1)
C-1	2002(1)	3460(1)	3140(1)	19(1)	2092(1)	−2076(3)	5691(1)	34(1)	3609(4)	−3695(3)	6161(2)	32(1)
C-2	3050(1)	2571(1)	3431(1)	15(1)	1555(1)	−197(2)	5214(1)	24(1)	3464(4)	−2189(2)	7000(2)	27(1)
C-3	4205(1)	3471(1)	3560(1)	14(1)	995(1)	−1911(2)	4702(1)	22(1)	1923(4)	−960(2)	6392(2)	24(1)
C-4	5289(1)	2543(1)	3808(1)	13(1)	456(1)	−114(2)	4168(1)	20(1)	1552(4)	508(2)	7237(2)	23(1)
C-5	6448(1)	3399(1)	4001(1)	13(1)	−48(1)	−1946(2)	3597(1)	21(1)	4059(4)	1420(2)	7912(2)	24(1)
C-6	7556(1)	2425(1)	4146(1)	15(1)	−579(1)	−302(2)	3018(1)	22(1)	3755(4)	2777(2)	8855(2)	26(1)
C-7	8755(1)	3253(1)	4247(1)	18(1)	−1028(1)	−2284(2)	2463(1)	27(1)	1887(4)	2043(3)	9762(2)	31(1)
O–W [c]					−2245(1)	2823(2)	2373(1)	44(1)				

[a] $U_{eq} = 1/3\ \Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.
[b] Standard deviations in parentheses.
[c] In the deposited data, this atom is called O-9.

Table 3
Fractional positional parameters of C and O atoms ($\times 10^4$) and temperature factors U_{eq} [a] ($\times 10^3$) for **1b** and **3** [b]

Atom	**1b**				**3**			
	x	*y*	*z*	U_{eq}	*x*	*y*	*z*	U_{eq}
O-1	3932(2)	4266(1)	1007(1)	56(1)	69(2)	−769(2)	10165(2)	89(2)
O-2	3047(2)	5940(1)	799(1)	49(1)	1093(2)	1142(2)	10283(1)	66(1)
O-3	2324(2)	6566(1)	1491(1)	48(1)	2582(2)	867(1)	8960(1)	64(1)
O-4	−864(2)	5735(1)	1002(1)	48(1)	367(2)	2655(1)	8722(1)	61(1)
O-5	−1291(2)	6429(1)	1704(1)	55(1)	1840(2)	2175(2)	7377(1)	69(1)
O-6	−1532(2)	8156(1)	1697(1)	61(1)	2567(2)	4095(2)	7188(1)	70(1)
O-7	−555(2)	8404(1)	948(1)	61(1)	2101(2)	5636(2)	8335(1)	78(2)
O-11	5538(3)	3797(2)	1425(1)	93(2)	699(3)	−2354(2)	10052(2)	127(3)
O-21	1456(3)	5523(2)	358(1)	90(2)	−631(2)	1525(2)	10610(2)	88(2)
O-31	2548(3)	5812(1)	1996(1)	91(2)	2482(2)	−375(2)	8019(2)	102(2)
O-41	−1891(3)	6596(1)	594(1)	69(1)	440(2)	3521(2)	9906(1)	82(2)
O-51	−3697(3)	6247(2)	1508(1)	90(1)	3574(3)	1747(3)	7143(2)	113(2)
O-61	−234(4)	8323(4)	2189(1)	196(2)	1181(3)	4944(3)	6634(2)	116(2)
O-71	1255(3)	8017(2)	557(1)	93(2)	355(2)	5476(2)	8617(2)	113(2)
C-1	3514(3)	4922(2)	1251(1)	53(1)	826(3)	−436(2)	9547(2)	75(2)
C-2	2301(3)	5418(1)	1062(1)	45(1)	758(3)	725(2)	9513(2)	61(2)
C-3	1385(3)	5946(1)	1325(1)	43(1)	1464(2)	1156(2)	8845(1)	58(2)
C-4	65(3)	6399(1)	1141(1)	44(1)	1477(2)	2332(2)	8803(2)	55(2)
C-5	−929(3)	6921(1)	1389(1)	46(1)	2136(2)	2738(2)	8094(2)	58(2)
C-6	−257(3)	7729(1)	1529(1)	50(1)	1932(2)	3864(2)	7899(2)	58(2)
C-7	467(3)	8268(2)	1246(1)	59(1)	2269(3)	4586(2)	8575(2)	69(2)
C-11	4917(3)	3709(2)	1140(1)	61(1)	71(4)	−1770(3)	10348(3)	95(3)
C-12	5094(4)	2988(2)	893(1)	82(2)	−753(5)	−2013(4)	10978(4)	128(4)
C-21	2560(4)	5912(2)	452(1)	57(2)	312(3)	1497(2)	10790(2)	73(2)
C-22	3513(4)	6433(2)	214(1)	78(3)	788(4)	1869(4)	11563(2)	107(3)
C-31	2791(3)	6439(2)	1837(1)	58(2)	3003(3)	116(2)	8485(2)	78(2)
C-32	3594(4)	7176(2)	1984(1)	79(2)	4190(3)	16(3)	8629(3)	107(3)
C-41	−1785(3)	5920(2)	718(1)	54(1)	−60(3)	3245(2)	9334(2)	69(2)
C-42	−2623(4)	5173(2)	590(1)	81(2)	−1226(3)	3440(4)	9161(3)	97(2)
C-51	−2726(4)	6103(2)	1723(1)	67(2)	2651(4)	1719(3)	6942(2)	88(3)
C-52	−2858(6)	5536(3)	2039(1)	105(3)	2202(5)	1267(5)	6188(2)	135(4)
C-61	−1384(4)	8412(2)	2034(1)	74(2)	2090(3)	4612(3)	6587(2)	85(2)
C-62	−2788(4)	8774(2)	2187(1)	82(3)	2809(5)	4730(5)	5873(3)	127(4)
C-71	−7(4)	8279(2)	611(1)	63(2)	1085(4)	5993(3)	8380(2)	88(3)
C-72	−1139(5)	8482(2)	329(1)	80(3)	1018(4)	7079(3)	8072(3)	106(4)

[a] $U_{eq} = 1/3\ \Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \boldsymbol{a}_j$.
[b] Standard deviations in parentheses.

it has to be concluded that the conformation of molecules in **1a** and **1a** · $\mathbf{H_2O}$ is very atypical. From the results of recent work [15,22] a bent conformation probably involving a C//O interaction would have been suggested, but it is the conformation which had been proposed by Mills [59]. The reason for the observed situation is almost certainly a special energetically very favourable homodromic pattern [60] of hydrogen bonds (O-2–O-3–O-5–O-6; Table 4) in both situations, involving O-3 and O-5 in an intramolecular hydrogen bond. The result is a very short distance

Fig. 1. SCHAKAL-92 [29] plot of a molecule of *meso*-D-*glycero*-L-*altro*-heptitol (**1a**), showing atom numbering.

between O-3 and O-5, which is not only considerably lower than the sum of the van der Waals radii of 303 pm, but is by far the shortest distance summarised in Table 5 for related situations.

Contrary to the situation observed for **1a**, molecules of the derived heptaacetate **1b** are bent into a sickle, with individual molecules also becoming chiral (compare Fig. 3). Again, chiral conformers are matched by their enantiomers in the unit cell. The observed sickle conformation should nowadays be considered as the expected one. It is not a sickle free of all 1,3-parallel interactions involving carbon and/or

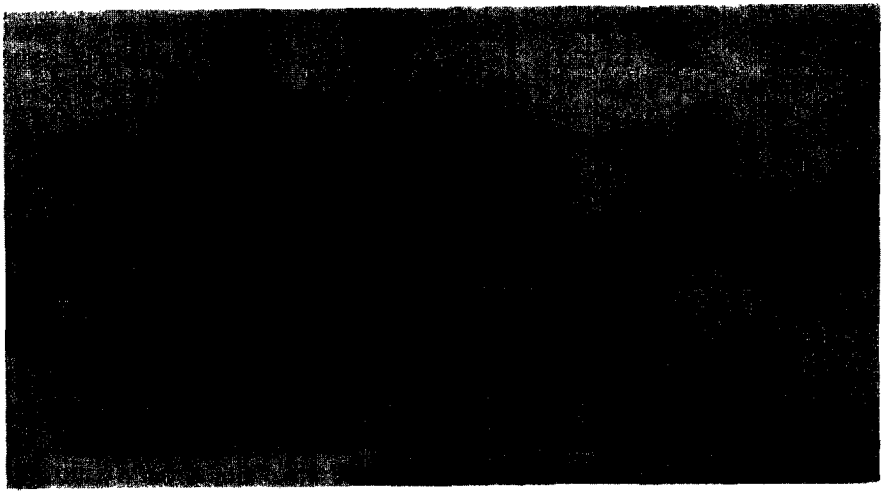

Fig. 2. SCHAKAL-92 [29] plot of a molecule of *meso*-D-*glycero*-L-*altro*-heptitol (**1a**) in the monohydrate **1a**·$\mathbf{H_2O}$, showing atom numbering.

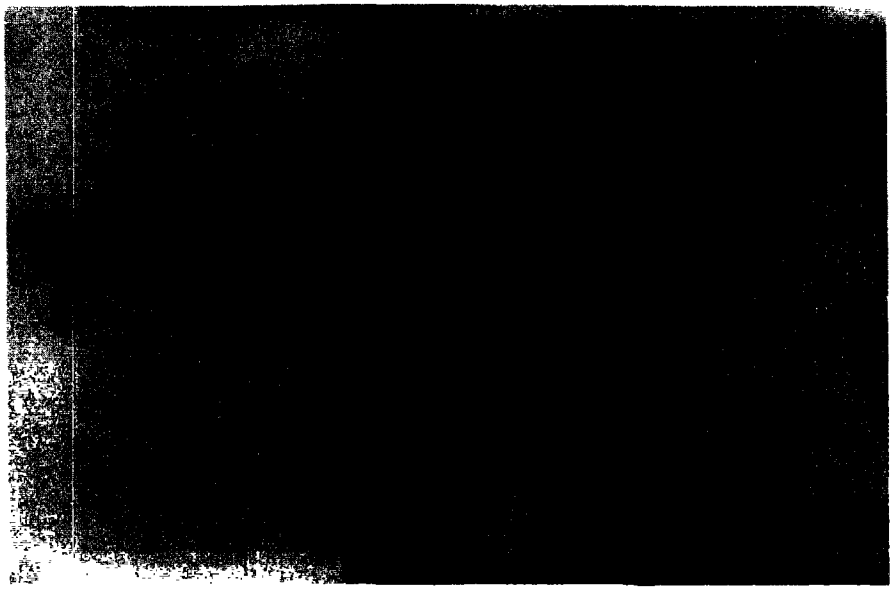

Fig. 3. SCHAKAL-92 [29] plot of a molecule of *meso*-D-*glycero*-L-*altro*-heptitol heptaacetate (**1b**), showing atom numbering.

oxygen, but instead the one in which a C//O interaction is established between C-6 and O-3. The distance is 295.0 pm and the 1,3-dihedral angle 6.2°. This is the situation observed for most compounds involving an element of *ribo* (*allo*/*altro*)

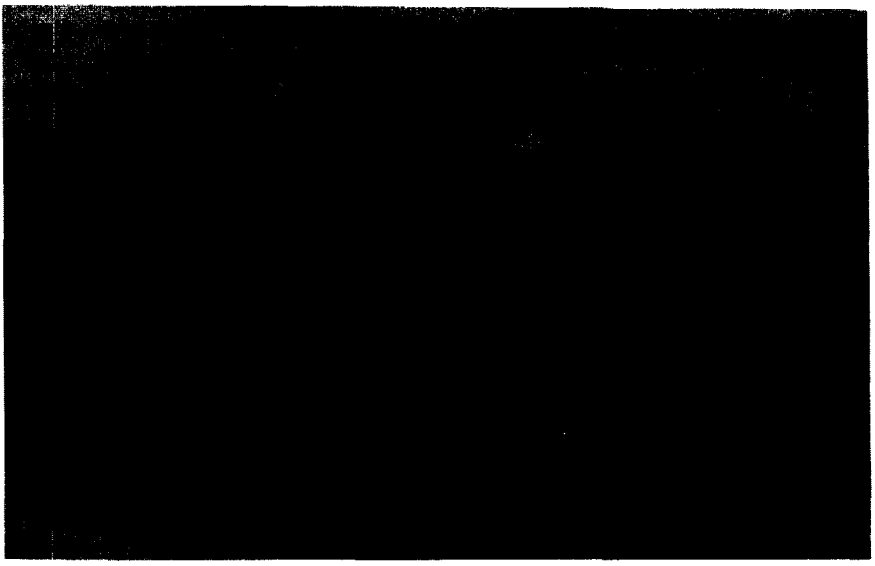

Fig. 4. SCHAKAL-92 [29] plot of a molecule of *meso*-D-*glycero*-L-*ido*-heptitol (**2**), showing atom numbering.

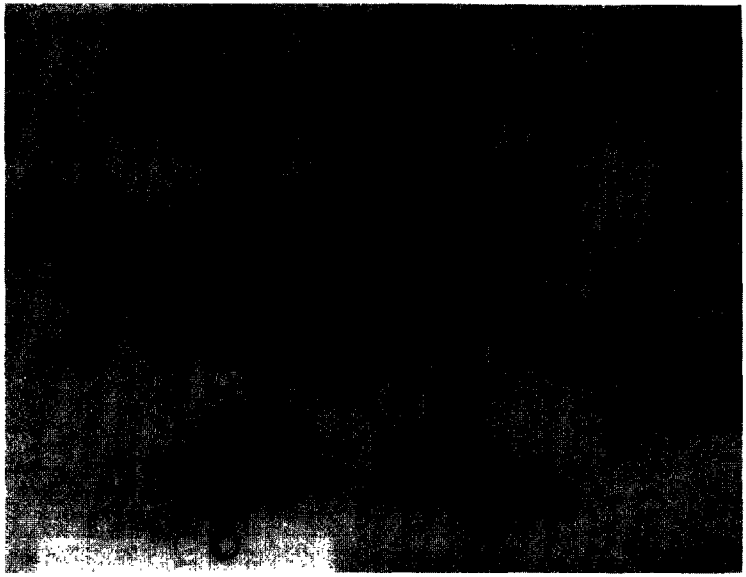

Fig. 5. SCHAKAL-92 [29] plot of a molecule of D-*glycero*-L-*galacto*-heptitol heptaacetate (**3**), showing atom numbering.

configuration in the solid state, as was discussed and realised only recently [15,22], with **1a** constituting another remarkable exception. Despite the fact that O-1 is situated in a *threo* (*arabino*) environment in a planar part of **1b** (compare Table 6), it is not found in a 1,3-parallel arrangement to O-3.

As is the case with the aforementioned compounds, *meso*-D-*glycero*-L-*ido*-heptitol (**2**) also loses the inherent symmetry by crystallisation. Individual molecules are found in a doubly bent chiral conformation, and are matched by the enantiomeric conformers in the unit cell (compare Fig. 4). The observed conformation compares with that observed in D- and DL-iditol hexaacetate [10], but not with the sickle found in D-iditol [61] and DL-iditol [9]. A planar conformation, involving two O//O interactions, which would be feasible considering the data of Table 5, is not observed. This could support evidence that in compounds of *ido* configuration, despite a very small data set, a higher tendency exists to adopt bent conformations compared to those of *gluco* configuration (see above).

1,2,3,4,5,6,7-Hepta-*O*-acetyl-D-*glycero*-L-*galacto*-heptitol (**3**) is the only chiral isomer investigated in this paper. The overall sickle conformation of **3** in the crystal, as depicted in Fig. 5, was also observed for the parent heptitol [5], and is the "predicted" one [59]. In these cases, however, in the light of the entries in Table 5, a planar zigzag conformation should not have been excluded *prima facie*. The 7-deoxy-7-nitro derivative of the parent compound adopts such a planar conformation [2]. As in the case of **1b** (see above), O-1 extends the planar part of the molecules of **3** and is not using the option of the arrangement 1,3-parallel to O-3 (*cf.* the relevant entries in Table 6).

Table 4
Hydrogen-bond patterns [a] in **1a**, **1a**·H_2O, and **2** (bond lengths in pm, angles in degrees) [b]

Compound	Distances D–H···A	Symmetry operation on A	Distance D···A	Angle D–H···A	Angle of bifurcation A···H···A
1a	O-1 $\overset{84(1)}{\underline{\quad}}$ H-1O $^{185(1)}$ O-4	$1/2+x-1, y, 1/2-z$	266.9(2)	164(1)	
	O-2 $\overset{84(1)}{\underline{\quad}}$ H-2O $^{198(2)}$ O-3	$1/2-x, 1/2+y-1, z$	280.5(1)	167(1)	
	O-3 $\overset{84(1)}{\underline{\quad}}$ H-3O $^{193(1)}$ O-5	intramolecular	267.6(1)	148(2)	95(1)
	O-3 $\overset{84(1)}{\underline{\quad}}$ H-3O $^{245(2)}$ O-5	$-x+1, -y+1, -z+1$	284.3(1)	110(1)	[Σ = 353(1)]
	O-4 $\overset{84(1)}{\underline{\quad}}$ H-4O $^{178(1)}$ O-7	$1/2-x+1, 1/2+y-1, z$	261.4(1)	173(1)	
	O-5 $\overset{84(1)}{\underline{\quad}}$ H-5O $^{188(1)}$ O-6	$1/2-x+1, 1/2+y, z$	272.0(1)	179(1)	
	O-6 $\overset{84(1)}{\underline{\quad}}$ H-6O $^{194(1)}$ O-2	$1/2+x, 1/2-y, -z+1$	278.1(1)	174(2)	
	O-7 $\overset{84(1)}{\underline{\quad}}$ H-7O $^{179(2)}$ O-1	$x+1, y, z,$	261.8(1)	168(1)	
1a·H_2O	O-1 $\overset{85(1)}{\underline{\quad}}$ H-1O $^{206(1)}$ O-W	$1/2+x, 1/2-y, 1/2+z$	286.9(2)	160(1)	
	O-2 $\overset{85(2)}{\underline{\quad}}$ H-2O $^{253(1)}$ O-3	intramolecular	287.6(2)	106(1)	85(3)
	O-2 $\overset{85(2)}{\underline{\quad}}$ H-2O $^{217(1)}$ O-6	$-x, -y, -z+1$	300.2(1)	166(2)	[Σ = 357(2)]
	O-3 $\overset{85(1)}{\underline{\quad}}$ H-3O $^{188(1)}$ O-2	$x, y-1, z$	272.9(1)	176(1)	
	O-4 $\overset{85(1)}{\underline{\quad}}$ H-4O $^{192(1)}$ O-7	$-x, y, 1/2-z$	276.4(1)	176(1)	
	O-5 $\overset{85(1)}{\underline{\quad}}$ H-5O $^{190(1)}$ O-3	intramolecular	265.2(1)	147(1)	107(1)
	O-5 $\overset{85(1)}{\underline{\quad}}$ H-5O $^{245(1)}$ O-3	$-x, -y-1, -z+1$	277.0(1)	104(1)	[Σ = 358(1)]
	O-6 $\overset{85(1)}{\underline{\quad}}$ H-6O $^{191(1)}$ O-5	$x, y+1, z$	275.9(1)	173(1)	
	O-7 $\overset{85(1)}{\underline{\quad}}$ H-7O $^{190(1)}$ O-1	$1/2+x-1, 1/2-y-1, 1/2+z-1$	274.0(2)	170(1)	
	O-W $\overset{88(2)}{\underline{\quad}}$ H-W1 $^{207(2)}$ O-6	("intramolecular")	293.5(2)	165(2)	
	O-W $\overset{81(3)}{\underline{\quad}}$ H-W2 $^{201(2)}$ O-W	$1/2-x-1, 1/2+y, 1/2-z$	280.7(2)	168(2)	
2	O-1 $\overset{82(1)}{\underline{\quad}}$ H-1O $^{205(2)}$ O-3	$x+1, y, z$	281.7(2)	155(2)	
	O-2 $\overset{82(1)}{\underline{\quad}}$ H-2O $^{216(1)}$ O-6	$-x+1, -y, -z+2$	279.2(2)	135(1)	71(1)
	O-2 $\overset{82(1)}{\underline{\quad}}$ H-2O $^{241(1)}$ O-7	$-x+1, -y, -z+2$	316.5(3)	153(1)	[Σ = 359(1)]
	O-3 $\overset{82(1)}{\underline{\quad}}$ H-3O $^{192(1)}$ O-4	$-x, -y, -z+1$	273.3(2)	172(2)	
	O-4 $\overset{82(1)}{\underline{\quad}}$ H-4O $^{186(2)}$ O-5	$x-1, y, z$	267.6(2)	172(2)	
	O-5 $\overset{82(2)}{\underline{\quad}}$ H-5O $^{189(1)}$ O-1	$x, y+1, z$	270.8(2)	173(2)	
	O-6 $\overset{82(1)}{\underline{\quad}}$ H-6O $^{193(1)}$ O-7	$-x+1, -y+1, -z+2$	274.6(2)	177(2)	
	O-7 $\overset{82(1)}{\underline{\quad}}$ H-7O $^{195(2)}$ O-2	$-x, -y, -z+2$	276.8(3)	174(2)	

[a] A, Acceptor oxygen. D, Donor oxygen.
[b] Standard deviations in parentheses.

Table 5
Acyclic carbohydrate derivatives establishing 1,3-parallel O//O interactions between secondary oxygens in planar zigzag conformations, listed in the order of appearance in the literature

Compound	Code [a]	Configuration [b]	Interaction	Distance O//O (pm)	1,3-Dihedral angle (degrees)
(a) *Unsubstituted derivatives*					
Potassium D-gluconate [30] [c,d]	KGLUCO	*xylo (gluco)*	O-2//O-4	298.7	10.5
N-(2-Chloroethyl)-D-gluconamide [32] [d]	CEGLCA	*xylo (gluco)*	O-2//O-4	296.9	10.1
N-Cyclohexyl-D-gluconamide [33]	CIBWIT	*xylo (gluco)*	O-2//O-4	277.7	4.5
Sodium D-gluconate [34]	ZZZHGG	*xylo (gluco)*	O-2//O-4	279.8	5.1
N-Isopropyl-D-gluconamide [35]	DAYVUU	*xylo (gluco)*	O-2//O-4	280.2	5.5
Octyl D-gluconate [36]	DOJWII	*xylo (gluco)*	O-2//O-4	303.2	11.4
N-Octyl-D-gluconamide [37]	FAKFUS	*xylo (gluco)*	O-2//O-4	304.6	12.1
N-Benzyl-D-gluconamide [38]	FATXUT	*xylo (gluco)*	O-2//O-4	299.3	10.5
N-Heptyl-D-gluconamide [39]	FAKGAZ	*xylo (gluco)*	O-2//O-4	297.6	10.9
N-Decyl-D-gluconamide [39]	FAKGIH	*xylo (gluco)*	O-2//O-4	305.1	9.7
2-[(1*R*,2*R*,3*R*,4*R*)-(1-Benzamido-2,3,4,5-tetrahydroxy-pentyl)amino]thiazole-4-carboxamide [40]	GEFCOJ	*ribo*	O-2//O-4	284.2	30.5
1-Deoxy-1-(*N*-methyloctanamido)-D-glucitol [41]	KANTIC	*xylo (gluco)*	O-2//O-4	296.6	0.3
N-Undecyl-D-gluconamide [42]	JIJXEF	*xylo (gluco)*	O-2//O-4	298.1	9.9
1-Deoxy-1-nitro-L-*gluco*-hexitol [1]	JERHUJ	*xylo (gluco)*	O-2//O-4	283.4	19.8
1-Deoxy-1-nitro-D-*ido*-hexitol [1]	JERJAR	*xylo (ido)*	O-2//O-4	303.1	0.1
			O-3//O-5	296.7	2.8
7-Deoxy-7-nitro-D-*glycero*-L-*galacto*-heptitol [2]	JIGBEG	*xylo (gluco)*	O-4//O-6	283.9	19.9
1-Deoxy-1-nitro-D-*glycero*-D-*gulo*-heptitol [2]	JIGBUW	*xylo (gluco)*	O-3//O-5	301.8	4.4
N-(Tetradeca-6,8-diynyl)-D-gluconamide [43]	VOMCEF	*xylo (gluco)*	O-2//O-4	302.8	13.1

Lactitol [44] [e]	YADSOL	*xylo (gluco)*	O-2′//O-4′	305.1	1.3
Lactitol trihydrate [45] [e]	SUGBIF	*xylo (gluco)*	O-2′//O-4′	299.6	6.6
L-*galacto*-D-*galacto*-Decitol [12]	PELKOG	*xylo (gluco / ido)*	O-4//O-6 =		
		xylo (gluco / ido)	O-5//O-7	299.9	4.0
meso-D-*glycero*-L-*altro*-Heptitol (**1a**)		*ribo (altro)*	O-3//O-5	267.6	13.6
meso-D-*glycero*-L-*altro*-Heptitol mono hydrate (**1a** · H_2O)		*ribo (altro)*	O-3//O-5	265.0	6.6
N-[8-(D-Gluconamido)octyl]-D-gluconamide [48]		*xylo (gluco)*	O-2//O-4	286.4 (281.1)	2.1 (4.7)
			O-2′//O-4′	277.5 (285.7)	2.2 (1.9)
(b) *Acylated derivatives*					
Anamarine [49]	ANAMAR	*xylo (gluco)*	O-2//O-4	290.5	5.4
Hexa-*O*-acetyl-D-glucitol [7,50]	ZZZJJY	*xylo (gluco)*	O-2//O-4 [f]	289.3	3.7
Hexa-*O*-(*p*-chlorobenzoyl)-D-glucitol [51]	VUGHUA	*xylo (gluco)*	O-2//O-4 [f]	293.0	2.3
Penta-*O*-acetylxylitol (mp, 65°C) [50] [g]		*xylo*	O-2//O-4 [f]	292.7	5.5
Hexa-*O*-acetyl-DL-glucitol [10]	VUPXAF	*xylo (gluco)*	O-2//O-4 [f]	286.9	2.1
Hepta-*O*-acetyl-*meso-glycero-gulo*-heptitol [16]		*xylo (gluco)*	O-3//O-5	299.6	0.0 [h]
Octa-*O*-acetyl-L-*threo*-L-*galacto*-octitol [15]		*xylo (gluco / ido)*	O-4//O-6 [f]	274.0	3.4
		xylo (ido)	O-5//O-7 [f]	276.7	0.6
(1*S*)-2-*C*-[(*R*)-Acetoxy(phenyl)methyl]-					
-1,3,4,5,6-penta-*O*-acetyl-2-deoxy-1-*C*-phenyl-L-gulitol [52]		*xylo (ido)*	O-3//O-5	290.3	12.8
Penta-*O*-acetyl-D-glucose dimethyl acetal [53]		*xylo (gluco)*	O2//O4	281.3	17.2

[a] Code of the Cambridge Crystallographic Data File. [b] Configuration of the three (in brackets: four) contiguous stereogenic centres at which the interaction occurs. [c] The monohydrate (KDGLUM) is found in a sickle [31]. [d] The reported coordinates are incorrectly those of the L enantiomer. [e] In lactitol monohydrate (JEXZER), the glucitol moiety is found in a sickle conformation involving a C//O interaction [47], whereas a sickle free of all such 1,3 interactions is observed [46] in lactitol dihydrate (VIPKUA). [f] A second O//O interaction is established involving a primary oxygen (compare Table 6). [g] A modification, mp 50°C (SUHVEW), is found in a sickle, free of such interactions [10]. [h] This value is the result of the observed symmetry.

Table 6
Miscellaneous 1,3-parallel O//O interactions observed in acyclic carbohydrate derivatives, in the order of appearance in the literature

Compound	Code [a]	Configuration/ conformation [b]	Interaction	Distance O//O (pm)	1,3-Dihedral angle (degrees)
(a) *Between secondary oxygens in sickle conformations*					
(5*S*, 6*S*)-1,2,3,4,5-Penta-*O*-acetyl-1-*C*-(5-*exo*--nitrobicyclo[2.2.1]hept-2-en-6-*endo*-yl)-D-*manno*-pentitol [54]	VEGJIA	*arabino (manno)*/S	O-2//O-4	286.9	4.2
(5*S*, 6*S*)-1,2,3,4,5-Penta-*O*-acetyl-1-*C*-(5-*endo*--nitrobicyclo[2.2.1]hept-2-en-6-*exo*-yl)-D-*manno*-pentitol [54]	VEGJOG	*arabino (manno)*/S	O-2//O-4	281.8	1.8
(3*R*, 4*S*, 5*S*)-3,5-Dimethyl-3-nitro-4-(penta-*O*--acetyl-D-*manno*-pentitol-1-yl)-1-pyrazoline [55]	TAGZIK	*arabino (manno)*/S	O-2//O-4	280.6	12.0
(D)-Menthyl(2-deoxy-2-carboxy-D-menthyl)-3-*O*--trimethylsilyl-4,5,6,7-tetra-*O*-acetyl-D-*manno*--hepturonate [56]	VUSKUP	*arabino (manno)*/S	O-3//O-5	287.0	6.8
Deca-*O*-acetyl-L-*galacto*-L-*gulo*-decitol [13]	PEKKAR	*arabino (man / gal)*/S	O-5//O-7	277.4	1.7
Hepta-*O*-acetyl-D-*glycero*-D-*manno*-heptitol [16]		*arabino (man / alt)*/S	O-3//O-5	285.2	7.2
(b) *Between a primary and a secondary oxygen*					
Riboflavin hydrobromide monohydrate [57]	RBFLAV	*erythro (ribo)*/S	O-5//O-3	270.7	17.9
Hexa-*O*-(*p*-chlorobenzoyl)-D-glucitol [51]	VUGHUA	*threo (xylo)*/P	O-1//O-3	289.2	12.8
Hexa-*O*-acetyl-D-glucitol [7,50]	ZZZJJY	*threo (xylo)*/P	O-1//O-3	286.1	5.3
Hexa-*O*-acetyl-DL-glucitol [10]	VUPXAF	*threo (xylo)*/P	O-1//O-3	282.3	0.4
Hexa-*O*-acetylgalactitol [10]	VUPVOR	*threo (arabino)*/P	O-1//O-3 = O-4//O-6	281.7	2.7
Penta-*O*-acetylxylitol (mp, 65°C) [50] [c]		*threo (xylo)*/P	O-3//O-5	284.6	3.2
Octa-*O*-acetyl-L-*threo*-L-*galacto*-octitol [15]		*threo (arabino)*/P	O-1//O-3	278.6	0.4
		threo (xylo)/P	O-6//O-8	272.5	6.8
Deca-*O*-acetyl-L-*galacto*-L-*gulo*-decitol [13]	PEKKAR	*erythro (arabino)*/P	O-1//O-3	289.1	10.1
2,3,4,5,6-Penta-*O*-acetyl-D-galactonic acid (1-phenyl-2-carboxyethyl)vinyl ester [58]		*threo (arabino)*/P	O-4//O-6	288.4	12.5

[a] Code of the Cambridge Crystallographic Data File. [b] Configuration of the three(in brackets: four)-carbon chain involved in the mentioned interactions. Conformations at these sites: P, planar zigzag; S, sickle, [c] A modification; mp, 50°C (SUHVEW), is found in a sickle [10].

Summarising our results, we conclude that the conformational behaviour of acyclic carbohydrate derivatives in the crystalline state is more complex than was previously imagined [62]. Nevertheless, the general view, as presented in Tables 5 and 6 and in a complementary Table given in a preceding paper [22], covering the *ribo* (*allo/altro*) situation, could lead to new perceptions. For instance, and not mentioned before, we were very surprised in compiling the data for Table 6, to note that a considerable portion of the structures involving an acetylated region of *arabino* configuration occur in a sickle conformation. In these cases, the option of a planar conformation free of interactions is not used, but instead an O//O interaction is tolerated.

3. Experimental

The compounds investigated were prepared by conventional procedures. The X-ray structure determinations were performed at ~ 20°C, with the exception of **1a**, which was investigated at −100°C. The data file of the Cambridge Crystallographic Data Centre was extensively used. Calculations of geometrical parameters in Tables 5 and 6 were performed with the relevant options of the SCHAKAL-92 program [29].

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