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Crystal and molecular structures of D-*glycero*-D-*manno*-heptitol (α-sedoheptitol, volemitol) and D-*glycero*-D-*gluco*-heptitol (β-sedoheptitol)

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ABSTRACT

The molecular structures of the title heptitols were determined by X-ray crystallography, using direct methods, and refined to final residual parameters of $R = 0.037$ and 0.039, respectively. Each compound adopts a bent conformation. For α-sedoheptitol (**1**), this is not the expected conformation (with O-6 in the extended planar position). Instead, **1** adopts a conformation with a 1,3 parallel interaction between O-4 and C-7.

INTRODUCTION

Whereas the conformations in aqueous solution of alditols up to C_7 are known[1,2], this is not so for alditols in the crystalline state. Jeffrey and Kim[3] proposed that the conformations adopted by alditols would generally avoid 1,3 parallel interactions of carbon and oxygen atoms (C//C, C//O, and O//O). Thus, D-altritol, the structure of which in the solid state had not been determined at that time, would be predicted to have a sickle conformation which avoids the 1,3 parallel O//O interaction inherent in a planar zigzag conformation. However, D-altritol adopts a conformation that involves a C//O interaction[4], as was also found in D-*glycero*-D-*allo*-heptitol[2]. The conformation found for altritol is surprising, as a completely interaction-free sickle conformation is possible by rotation of the carbon chain at C-5.

In connection with the determination of the structure of D-*glycero*-D-*allo*-heptitol[2], some major questions that concerned the energies of various conformations were discussed in detail but some questions could not be answered without further data. We now report on the structure of D-*glycero*-D-*manno*-heptitol (**1**, α-sedoheptitol, volemi-

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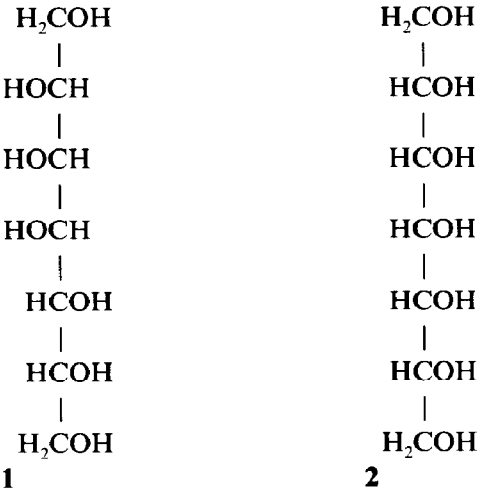
tol), obtained by reduction of D-*glycero*-D-*altro*-heptulose (sedoheptulose)[5], and D-*glycero*-D-*gluco*-heptitol[6] (**2**, β-sedoheptitol).

Of the ten possible heptitols, only the structures of *meso*-*glycero*-*gulo*-heptitol[7], D-*glycero*-D-*allo*-heptitol[2], D-*glycero*-D-*galacto*-heptitol (D-perseitol)[8], and D-*glycero*-L-*galacto*-heptitol[9] have been reported hitherto.



1 **2**

RESULTS AND DISCUSSION

Suitable single crystals of **1** and **2** were obtained from aqueous ethanol and the crystallographic data are given in Table I.

The molecular structures were determined in the usual way. The phase problem was solved by direct methods, using the program SHELXS-86[10]. The structures were refined by full-matrix least-squares procedures, using the program SHELX-76[11]. The final positional parameters (temperature factors U_{eq} included) of the carbon and oxygen atoms are listed in Tables II and III*. Tables IV and V give the observed bond lengths and bond angles in **1** and **2**. SCHAKAL representations[12] of **1** and **2** are shown in Figs. 1 and 2, respectively, together with the numbering scheme.

D-*glycero*-D-*manno*-Heptitol (**1**) has a bent (sickle) conformation with C-1/6 in a planar (zigzag) arrangement, and C-7 is orientated by rotation around the C-5–C-6 bond so that it is 1,3 parallel to O-4. The O-4/C-7 distance is 291.2 pm. This is not the sickle conformation predicted by Mills[13] in which such a C//O parallel interaction would have been avoided. Thus, the structure of **1** resembles the conformation found in D-altritol[4] and D-*glycero*-L-*allo*-heptitol[2]. The observed twisting in the molecules seems

* Lists of observed and calculated structure amplitudes, atomic co-ordinates of the hydrogen atoms (calculated in a late stage of refinement), anisotropic thermal factors U_{ij} for C and O, and further information on structure determinations are deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. References should be made to No. BBA/DD/467/*Carbohydr. Res.*, 218 (1991) 55–62.

TABLE I

Crystallographic data for **1** and **2**[a]

Data	**1**	**2**
Formula	$C_7H_{16}O_7$	$C_7H_{16}O_7$
Mol. wt.	212.20	212.20
M.p. (degrees)	151	128–129
Crystal dimensions (mm)	0.7 × 0.5 × 0.4	0.8 ×0.6 × 0.5
Space group	$P2_12_12_1$	$P1$
Cell constants (pm, degrees)		
a	484.6(1)	498.6(1)
b	991.9(1)	561.0(1)
c	1908.6(1)	887.1(2)
α	(90)	77.30(1)
β	(90)	77.55(1)
γ	(90)	67.17(1)
Volume V (pm × 10^6)	917.4(1)	220.75(8)
Z	4	1
F(000)	456	114
Calculated density D_x (g cm^{-3})	1.536	1.596
λ (Cu-$K_{\alpha 1}$) (pm)	154.051	154.051
μ (cm^{-1})	11.6	12.0
2Θ range (degrees)	153	153
Reflections measured (symmetry independent)	1156	1037
Reflections with $F_o > 3\sigma(F_o)$	1152	1036
Number of refined parameters	192	189
Final residual factors		
R	0.037	0.039
R_w	0.050	0.059
Diffractometer	Enraf–Nonius (CAD-4)	Enraf–Nonius (CAD-4)

[a] Standard deviations in parentheses.

TABLE II

Fractional positional parameters (× 10^4) and temperature factors U_{eq} (× 10^3) of carbon and oxygen atoms in D-*glycero*-D-*manno*-heptitol (**1**)[a]

Atom	x	y	z	U_{eq}
O-1	6979(3)	155(1)	5294(1)	39(1)
O-2	1878(3)	−184(1)	6079(1)	40(1)
O-3	6937(3)	2178(1)	6726(1)	29(1)
O-4	1787(3)	2117(1)	7456(1)	25(1)
O-5	7100(3)	−260(1)	7983(1)	28(1)
O-6	1860(3)	−293(1)	8755(1)	25(1)
O-7	1404(3)	1968(1)	9705(1)	33(1)
C-1	5022(4)	1204(2)	5408(1)	35(1)
C-2	3419(4)	1037(1)	6081(1)	28(1)
C-3	5251(4)	998(1)	6733(1)	23(1)
C-4	3547(4)	961(1)	7410(1)	22(1)
C-5	5381(4)	900(1)	8065(1)	22(1)
C-6	3798(4)	788(1)	8765(1)	22(1)
C-7	2299(4)	2057(1)	8991(1)	27(1)

[a] Standard deviations in parentheses.

TABLE III

Fractional positional parameters (× 10^4) and temperature factors U_{eq} (× 10^3) of carbon and oxygen atoms in D-*glycero*-D-*gluco*-heptitol (**2**)[a]

Atom	x	y	z	U_{eq}
O-1	1480(4)	6113(3)	−595(2)	28(1)
O-2	6852(4)	1711(3)	−1352(2)	26(1)
O-3	7663(3)	−664(3)	1714(2)	24(1)
O-4	6646(3)	4469(3)	2773(2)	23(1)
O-5	1430(4)	1121(3)	4186(2)	26(1)
O-6	2476(4)	1873(3)	7096(2)	26(1)
O-7	−168(4)	7744(3)	6460(2)	29(1)
C-1	4371(4)	6019(4)	−582(3)	24(1)
C-2	6440(4)	3222(4)	−146(2)	20(1)
C-3	5323(4)	1813(3)	1391(2)	19(1)
C-4[b]	4469	3440	2717	18(1)
C-5	3743(4)	1926(3)	4311(2)	18(1)
C-6	2891(4)	3517(3)	5645(2)	18(1)
C-7	90(5)	5883(4)	5514(3)	24(1)

[a] Standard deviations in parentheses. [b] This atom was fixed in order to define the origin in *P*1.

TABLE IV

Bond distances (pm) between C and O atoms in **1** and **2**[a]

Distance	**1**	**2**	*Distance*	**1**	**2**
C-1–C-2	151.0(3)	152.5(3)	C-1–O-1	142.5(3)	142.4(3)
C-2–C-3	152.9(3)	152.8(3)	C-2–O-2	142.3(2)	144.0(3)
C-3–C-4	153.4(3)	153.4(2)	C-3–O-3	142.8(2)	144.4(2)
C-4–C-5	153.6(3)	153.0(2)	C-4–O-4	143.1(2)	142.7(1)
C-5–C-6	154.5(3)	152.7(2)	C-5–O-5	142.9(2)	142.4(3)
C-6–C-7	151.6(3)	151.3(3)	C-6–O-6	142.6(2)	143.6(2)
			C-7–O-7	143.3(2)	143.0(3)

[a] Standard deviations in parentheses.

TABLE V

Bond angles (degrees) between C and O atoms in **1** and **2**[a]

Angle	**1**	**2**	*Angle*	**1**	**2**
O-1–C-1–C-2	113.1(1)	111.3(1)	O-5–C-5–C-4	106.3(1)	106.7(1)
O-2–C-2–C-1	111.1(1)	109.7(1)	O-5–C-5–C-6	109.0(1)	111.4(1)
O-2–C-2–C-3	106.6(1)	107.5(1)	C-4–C-5–C-6	114.8(1)	113.2(1)
C-1–C-2–C-3	113.3(1)	113.7(1)	O-6–C-6–C-5	111.7(1)	108.9(1)
O-3–C-3–C-2	107.7(1)	106.4(1)	O-6–C-6–C-7	108.2(1)	108.1(1)
O-3–C-3–C-4	109.6(1)	111.4(1)	C-5–C-6–C-7	115.1(1)	113.3(1)
C-2–C-3–C-4	111.9(1)	111.4(1)	O-7–C-7–C-6	111.4(1)	111.8(2)
O-4–C-4–C-3	110.7(1)	112.6(1)			
O-4–C-4–C-5	109.1(1)	110.2(1)			
C-3–C-4–C-5	112.1(1)	112.5(1)			

[a] Standard deviations in parentheses.

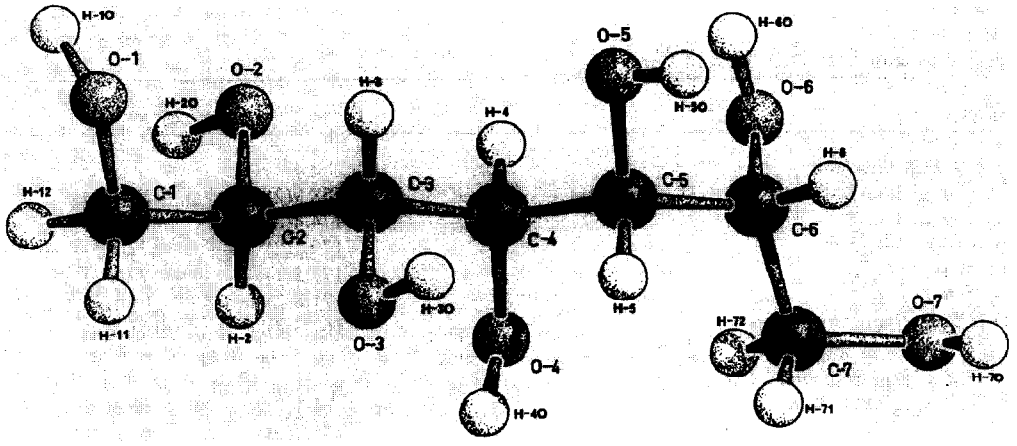


Fig. 1. SCHAKAL plot[12] of D-*glycero*-D-*manno*-heptitol (**1**), showing atom numbering.

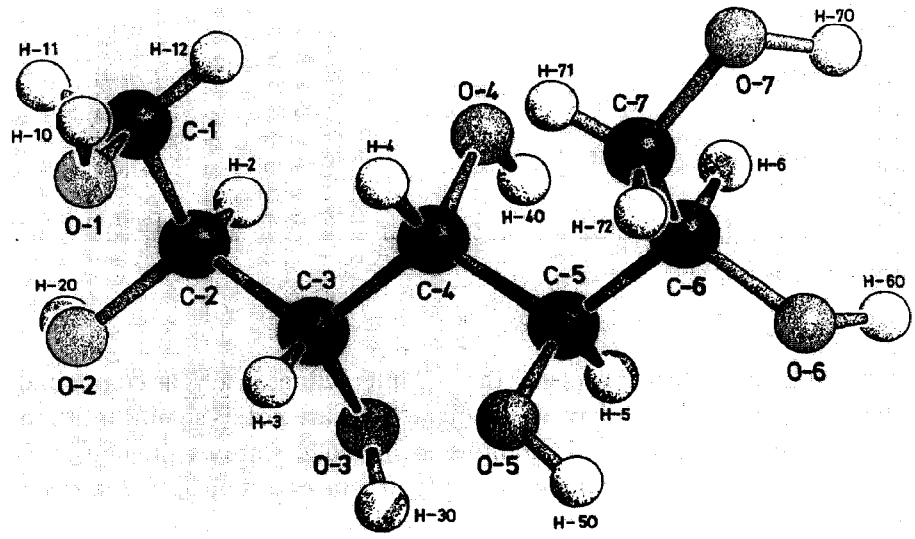


Fig. 2. SCHAKAL plot[12] of D-*glycero*-D-*gluco*-heptitol (**2**), showing atom numbering.

to be due to the sequence of three stereogenic centres of the same chirality. In Table VI, selected torsion angles are listed for **1**.

D-*glycero*-D-*gluco*-Heptitol (**2**) adopts a double sickle conformation with only C-2/6 in a planar arrangement (Fig. 2). This conformation is free from 1,3 parallel C//O interactions and corresponds to the conformation predicted by Mills[13]. There are three contiguous stereogenic centres of the same chirality but, in contrast to **1** and the other examples, **2** as well as allitol[14] does not adopt a conformation where C//O interactions are present.

TABLE VI

Selected torsion angles (degrees) in **1** and **2**[a]

Angle	**1**	**2**
(*a*) *Angles in the chain*		
O-1–C-1–C-2–C-3	58.9(2)	−54.1(2)
C-1–C-2–C-3–C-4	174.4(2)	−51.7(2)
C-2–C-3–C-4–C-5	179.1(2)	−172.2(1)
C-3–C-4–C-5–C-6	−177.1(1)	179.9(3)
C-4–C-5–C-6–C-7	−71.8(2)	64.1(2)
C-5–C-6–C-7–O-7	−167.3(2)	−161.8(2)
(*b*) *Angles between vicinal oxygen atoms*		
O-1–C-1–C-2–O-2	−61.1(2)	66.3(2)
O-2–C-2–C-3–O-3	176.7(1)	64.8(2)
O-3–C-3–C-4–O-4	60.5(2)	72.0(2)
O-4–C-4–C-5–O-5	−179.3(2)	176.2(1)
O-5–C-5–C-6–O-6	−67.0(2)	64.2(2)
O-6–C-6–C-7–O-7	66.9(2)	77.4(2)
(*c*) *Angles between vicinal hydrogen atoms*		
H-11–C-1–C-2–H-2	44.4(9)	70.8(5)
H-12–C-1–C-2–H-2	−60.6(10)	−51.8(5)
H-2–C-2–C-3–H-3	179.9(9)	−173.7(4)
H-3–C-3–C-4–H-4	−58.2(10)	−57.2(4)
H-4–C-4–C-5–H-5	−179.4(10)	−177.8(4)
H-5–C-5–C-6–H-6	−69.9(10)	61.0(4)
H-6–C-6–C-7–H-71	75.4(12)	78.4(5)
H-6–C-6–C-7–H-72	−167.0(11)	−156.1(5)

[a] Standard deviations in parentheses.

These results provide further evidence that 1,3 interactions in acyclic compounds should not be overestimated[2,4]. Clearly, these interactions are not as significant in the determination of the conformations of alditols in the solid state as previously assumed[3,13]. This view is supported by findings on the structures of four nitroalditols, in which "unfavourable" O//O interactions are not avoided[15].

As in all carbohydrates with free hydroxyl groups, the molecules of **1** and **2** in the crystal are interconnected by a complex pattern of intermolecular hydrogen bonds, and "strong" bonds are given in Table VII. Whereas for **2**, all oxygens are involved as donors and acceptors, O-2 in **1** acts as a donor only. Furthermore, bifurcation of the hydrogen bonds at O-4 and O-6 occurs, with intramolecular hydrogen bonds to O-3 and O-5, respectively, which could be one of the reasons for stabilising the observed "unusual" conformation. In **2**, the hydrogen bond at O-1 is intermolecularly bifurcated.

The orientation of the terminal hydroxyl groups is g^-,g^+ at C-1 and g^+,t at C-7 in **1**, and g^+,g^- at C-1 and g^+,t at C-7 in **2**.

TABLE VII

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

Compound	*Distances* D–H···A	*Symmetry operation on A*	*Distance* $D \cdots A$	*Angle* D–$H \cdots A$	*Angle of bifurcation* $A \cdots H \cdots A$
1	O-1$^{94(1)}$H-10$^{198(1)}$O-7^{I}	$1/2-x, -y, 1/2+z-1$	289.5(2)	162(1)	
	O-2$^{99(1)}$H-20$^{185(1)}$O-1^{II}	$x-1, y, z$	282.7(2)	169(1)	
	O-3$^{94(1)}$H-30$^{182(1)}$O-4^{III}	$x+1, y, z$	273.3(2)	163(1)	
	O-4$^{94(1)}$H-40$^{253(1)}$O-3	(intramolecular)	285.9(2)	101(1)	93(1)
	O-4$^{94(1)}$H-40$^{191(1)}$O-5^{IV}	$-x+1, 1/2+y, 1/2-z+1$	278.6(2)	155(1)	
	O-5$^{85(2)}$H-50$^{195(1)}$O-6^{III}	$x+1, y, z$	273.7(2)	154(1)	
	O-6$^{91(1)}$H-60$^{259(1)}$O-5	(intramolecular)	293.6(2)	103(1)	92(1)
	O-6$^{91(1)}$H-60$^{187(1)}$O-3^{V}	$-x+1, 1/2+y-1, 1/2-z+1$	273.4(2)	160(1)	
	O-7$^{89(1)}$H-70$^{204(1)}$O-7^{VI}	$1/2+x, 1/2-y, -z+2$	287.2(2)	155(1)	
2	O-1$^{91(1)}$H-10$^{234(1)}$O-2^{I}	$x-1, x+1, z$	312.3(2)	144(1)	76(1)
	O-1$^{91(1)}$H-10$^{220(1)}$O-3^{I}	$x-1, x+1, z$	289.2(2)	133(1)	
	O-2$^{92(1)}$H-20$^{197(1)}$O-6^{II}	$x+1, y, z-1$	287.1(3)	163(1)	
	O-3$^{84(1)}$H-30$^{216(1)}$O-4^{III}	$x, y-1, z+1$	288.7(2)	144(1)	
	O-4$^{86(1)}$H-40$^{194(1)}$O-5^{IV}	$x+1, y, z$	275.1(3)	157(1)	
	O-5$^{90(1)}$H-50$^{179(1)}$O-7^{III}	$x, y-1, z+1$	266.3(3)	165(1)	
	O-6$^{95(1)}$H-60$^{188(1)}$O-2^{V}	$x, y, z+1$	278.4(3)	158(1)	
	O-7$^{96(1)}$H-70$^{182(1)}$O-1^{V}	$x, y, z+1$	276.2(3)	165(1)	

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

EXPERIMENTAL

Compounds **1** and **2** were prepared by known procedures[5,6]. Data on X-ray structure determinations are given in Table I or are deposited. Calculations of geometries were performed by using the PLATON program[16].

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