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The crystal and molecular structures of four heptitol heptaacetates

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ABSTRACT

The structures of the four 1,2,3,4,5,6,7-heptaacetates derived from D-*glycero*-D-*galacto*-heptitol and its racemate, D-*glycero*-D-*manno*-heptitol, and *meso*-*glycero*-*gulo*-heptitol have been determined by X-ray crystallography, using direct methods. The latter two substances are found in conformations that involve a 1,3-parallel O//O interaction.

INTRODUCTION

Only recently, it was realized that acyclic carbohydrates are not obliged, in the crystalline state, to avoid conformations that would involve 1,3-parallel interactions between heavy atoms, designated as C//O and O//O, respectively[1]. The acetylated alditols, especially, show great freedom in adopting unexpected conformations as was shown in the hexitol series[2–4] and to a lesser extent in the series of pentitol pentaacetates[2,5]. For this reason, we have extended our investigations to the acetates of higher alditols, including the heptitol heptaacetates. These compounds can occur as ten diastereomers, of which four are *meso* forms and the others are found as six enantiomeric pairs. Therefore, polymorphs not counted, sixteen solid-state structures (racemates included) have to be considered.

RESULTS AND DISCUSSION

The following four substances were investigated: 1,2,3,4,5,6,7-hepta-*O*-acetyl-D-*glycero*-D-*galacto*-heptitol[6] (perseitol heptaacetate) (D-**1**) and its racemate[7] (DL-**1**), 1,2,3,4,5,6,7-hepta-*O*-acetyl-D-*glycero*-D-*manno*-heptitol[8] (α-sedoheptitol heptaace-

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TABLE I

Crystallographic data [a,b] for the heptitol hepta-acetates D-**1**, DL-**1**, **2**, and **3** ($C_{21}H_{30}O_{14}$, mol wt 506.46)

Data	D-**1**	DL-**1**	**2**	**3**
Mp (degrees)	119	137–138	63–64	118
Crystal dimensions (mm)	0.4×0.3×0.3	0.2×0.2×0.1	0.3×0.1×0.1	0.2×0.2×0.1
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1$	*Pnma*
Cell parameters (pm, degrees)				
a	884.3(1)	1095.6(2)	906.2(1)	1452.7(2)
b	1211.3(1)	2761.6(3)	1244.8(2)	2038.5(3)
c	2373.2(2)	850.6(3)	1177.7(1)	856.0(1)
β		104.47(2)	99.67(1)	
Volume V ($pm^3 \times 10^{-6}$)	2542.1(4)	2492(1)	1309.6(3)	2534.9(6)
Z	4	4	2	8/2
$F(000)$	1072	1072	536	1072
Calculated density D_x ($g \times cm^{-3}$)	1.323	1.350	1.284	1.327
λ (Cu or Mo $K\alpha_1$) (pm)	154.051	154.051	154.051	70.9261
μ (cm^{-1})	9.3	9.5	9.0	1.1
$2\theta_{max}$ (deg)	153	153	153	50
Reflections measured	5854	5812	5956	2671
Reflections (symmetry independent)	5077	4711	5332	1908
Reflections with $F_0 > 3\sigma(F_0)$	4830	3870	4680	1083
Number of refined parameters	367	436	341	166
Ratio of valued reflections to parameters	13.2	8.9	13.7	6.5
Final residual factors				
R	0.053	0.069	0.043	0.065
R_w	0.053	0.063	0.039	0.060

[a] Enraf–Nonius CAD 4 diffractometer except for **3** for which a Syntex $P2_1$ was used. [b] Standard deviations in parentheses.

tate, volemitol heptaacetate) (**2**), and 1,2,3,4,5,6,7-hepta-*O*-acetyl-*meso-glycero-gulo*-heptitol[9] (**3**).

Suitable crystals for X-ray determinations were obtained from solutions in ethanol. For **2**, water was more appropriate. The structures were determined in the usual way by direct methods using the programs SHELXS-90[10] to solve the phase problem, and SHELX-76[11a] and SHELXTL PLUS[11b] (blocked matrix) for refinement. Table I covers the crystallographic properties of the compounds investigated and Table II contains the fractional positional parameters of the C and O atoms. The other basic data have been deposited *. No unusual bond

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* 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 from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/537/*Carbohydr. Res.*, 247 (1993) 111–118.

Fractional positional parameters ($\times 10^4$) of carbon and oxygen atoms [a] for D-**1** [b], DL-**1**, **2**, and **3**

Atom	D-**1** [b]			DL-**1**			**2**			**3**		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
O-1	−2143(2)	1343(1)	−2791(1)	3668(2)	2900(1)	938(3)	2484(2)	−1230(2)	5975(1)	8930(3)	4325(2)	−1958(5)
O-2	1058(2)	926(1)	−2639(1)	1730(2)	3400(1)	−1050(3)	2186(2)	−2739(1)	4193(1)	9879(3)	3600(2)	328(4)
O-3	2189(2)	2245(1)	−3506(1)	1321(2)	4118(1)	1183(3)	2653(1)	12 [c]	3415(1)	7470(3)	3234(2)	−125(4)
O-4	2039(2)	−688(1)	−3781(1)	−907(1)	3133(1)	245(2)	2588(1)	−1406(1)	1637(1)	8388(4)	2500 [c]	2124(6)
O-5	2915(3)	625(1)	−4685(1)	−1094(2)	3886(1)	2665(3)	567(1)	323(1)	1334(1)			
O-6	5759(2)	−364(1)	−3717(1)	−2978(2)	4017(1)	−1448(3)	−1814(1)	−1799(2)	2094(1)			
O-7	7054(4)	−636(3)	−4926(1)	−3183(2)	4687(1)	1045(3)	−2742(2)	−479(2)	137(1)			
O-11	−3859(3)	2364(2)	−3246(1)	5525(2)	3205(1)	2212(3)	3196(3)	−2707(3)	7002(2)	7739(3)	4952(3)	−2646(6)
O-21	−38(3)	−678(2)	−2403(1)	1349(3)	2631(1)	−1888(3)	4241(3)	−3737(2)	4199(2)	10144(3)	4160(3)	2542(6)
O-31	607(3)	3212(2)	−4063(1)	2263(3)	4078(1)	3842(3)	782(2)	900(2)	4033(2)	7311(3)	3306(3)	−2695(6)
O-41	3045(3)	−1367(2)	−2978(1)	−1596(3)	3123(1)	−2466(3)	1747(3)	−2884(2)	678(3)	9841(4)	2500 [c]	3066(7)
O-51	3321(3)	2435(2)	−4840(1)	−473(3)	4657(1)	3188(4)	889(3)	−69(2)	−468(1)			
O-61	5890(4)	−2183(2)	−3877(1)	−4590(3)	3495(1)	−1979(4)	−2598(6)	−1555(3)	3724(3)			
O-71	8834(6)	−192(6)	−4292(2)	−4233(5)	4871(1)	2815(7)	−4747(3)	550(2)	−406(2)			
C-1	−990(3)	1764(3)	−3171(1)	3035(3)	3277(1)	1604(4)	3654(3)	−1370(3)	5309(2)	8659(5)	4370(3)	−335(8)
C-2	289(3)	944(2)	−3178(1)	1702(3)	3273(1)	589(4)	3016(3)	−1764(3)	4117(2)	8905(4)	3729(3)	438(6)
C-3	1435(3)	1225(2)	−3631(1)	866(3)	3630(1)	1209(4)	1876(3)	−997(2)	3452(2)	8449(4)	3136(3)	−263(6)
C-4	2717(3)	380(2)	−3683(1)	−502(3)	3630(1)	225(3)	1320(3)	−1394(2)	2235(2)	8722(5)	2500 [c]	521(9)
C-5	3770(3)	647(2)	−4166(1)	−1324(3)	3969(1)	946(4)	73(3)	−753(2)	1498(2)			
C-6	5053(4)	−183(3)	−4257(1)	−2731(3)	3889(1)	245(4)	−1365(3)	−686(2)	2027(2)			
C-7	6080(5)	249(4)	−4724(2)	−3546(3)	4188(1)	1079(4)	−2590(3)	−53(3)	1282(2)			
C-11	−3559(3)	1743(3)	−2881(1)	4933(3)	2913(1)	1325(4)	2351(4)	−1974(3)	6778(3)	8390(5)	4636(3)	−2993(8)
C-12	−4631(3)	1251(3)	−2459(1)	5434(4)	2517(1)	467(5)	981(4)	−1781(4)	7319(3)	8733(5)	4533(4)	−4624(8)
C-21	803(3)	74(3)	−2293(1)	1667(3)	3033(1)	−2113(4)	2931(4)	−3675(3)	4242(3)	10424(5)	3822(3)	1502(8)
C-22	1716(5)	147(3)	−1768(1)	2073(4)	3198(1)	−3586(5)	1912(5)	−4598(3)	4341(4)	11385(5)	3584(4)	1309(8)
C-31	1713(4)	3177(3)	−3769(1)	2007(3)	4302(1)	2604(5)	1978(3)	899(3)	3735(2)	6972(5)	3329(3)	−1453(8)
C-32	2753(5)	4117(3)	−3646(1)	2376(5)	4815(1)	2411(6)	2937(4)	1870(3)	3671(3)	5978(5)	3476(4)	−1123(18)
C-41	2269(4)	−1489(3)	−3390(1)	−1350(3)	2910(1)	−1193(4)	2644(3)	−2176(3)	844(3)	9027(7)	2500 [c]	3279(10)
C-42	1381(5)	−2493(3)	−3530(1)	−1474(3)	2378(1)	−992(5)	3914(3)	−1991(3)	209(3)	8567(7)	2500 [c]	4840(10)
C-51	2762(4)	1578(3)	−4984(1)	−711(3)	4266(1)	3655(5)	1017(3)	538(3)	321(2)			
C-52	1768(5)	1405(4)	−5474(1)	−628(4)	4136(2)	5393(5)	1723(4)	1626(3)	346(3)			
C-61	6156(4)	−1419(3)	−3584(1)	−3964(3)	3791(1)	−2449(5)	−2367(4)	−2139(3)	3000(3)			
C-62	6901(4)	−1463(3)	−3028(1)	−4166(4)	3954(1)	−4159(5)	−2664(4)	−3310(3)	2952(3)			
C-71	8440(6)	−713(6)	−4687(3)	−3545(4)	4993(1)	2022(5)	−3850(3)	−79(3)	−657(3)			
C-72	9427(7)	−1542(6)	−4979(3)	−3021(4)	5482(1)	2025(6)	−3804(5)	−543(4)	−1794(3)			

[a] Standard deviations in parentheses. [b] Coordinates for the atoms C-7n and O-7n are those of the molecule of disorder A. [c] These coordinates were fixed.

lengths and angles were observed. The crystal structures are represented as SCHAKAL-88 drawings[12] (Figs. 1–5) which also show the atom numbering schemes.

Perseitol heptaacetates.—1,2,3,4,5,6,7-Hepta-*O*-acetyl-D-*glycero*-D-*galacto*-heptitol[6] (D-**1**) and the racemate DL-**1**[7] adopt planar carbon-chain zigzag conformations that are free of any C//O and/or O//O interactions (cf. Figs. 1, 2, and 3). While O-1 and O-7 in D-**1** extend this zigzag arrangement, this is not the case for O-7 in DL-**1**. Nevertheless, in both cases, the oxygens at the termini are found in *gauche* (synclinal)[13] positions with respect to the oxygens attached to the neighbouring carbon atoms. The acetyl group at C-7 in D-**1** is disordered. Figs. 1 and 2 show the two positions (**A** with 60 and **B** with 40% site occupation) for modelling this disorder. Both represent the most favourable topology for an acetyl group, namely, that the carbonyl oxygen is orientated more or less parallel (synperiplanar)[13] to a hydrogen in the γ-position[14]. Recently, we encountered the same type of disorder in the structure determination of D-iditol hexaacetate[4].

Compared with the parent heptitols, D-**1** and DL-**1** are similar in the overall geometry of the central carbon chain. While D-perseitol[15] and its racemate[16] are bent at both ends of the chain, with a remarkable *trans* (antiperiplanar)[13] orientation of O-1 with respect to O-2, D-**1** shows the extended conformation at both ends and DL-**1** at one end.

In accordance with the Wallach "rule"[17], the molecules of DL-**1** are more densely packed than those of the pure enantiomer D-**1**, as can be deduced from the

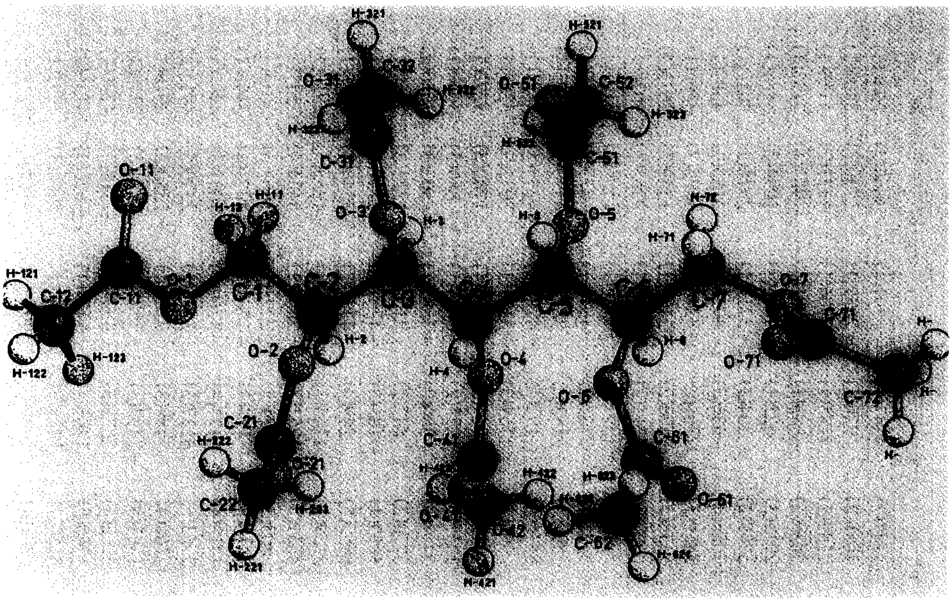

Fig. 1. SCHAKAL-88 plot[12] of a molecule of 1,2,3,4,5,6,7-hepta-*O*-acetyl-D-*glycero*-D-*galacto*-heptitol (D-**1**) with disordered conformation **A** at C-7, showing also the atom numbering scheme.

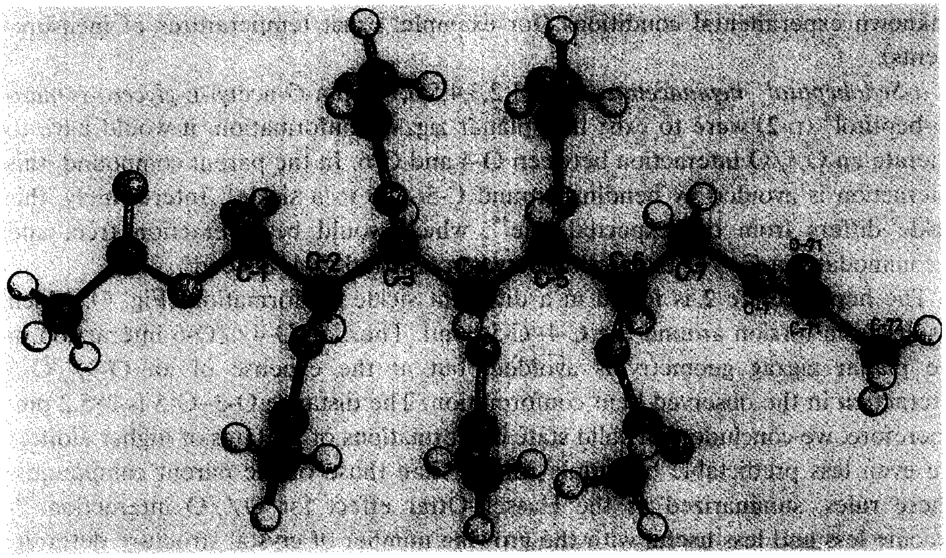

Fig. 2. SCHAKAL-88 plot[12] of a molecule of D-1 showing disordered conformation **B** at C-7.

entries for D_x in Table I. The implications of this "rule", for which many violations have been reported, are summarized in a recent account[18]. Nevertheless, it seems important to mention that these "violations" are mostly derived from crystal structure determinations performed at different places and times, and often with

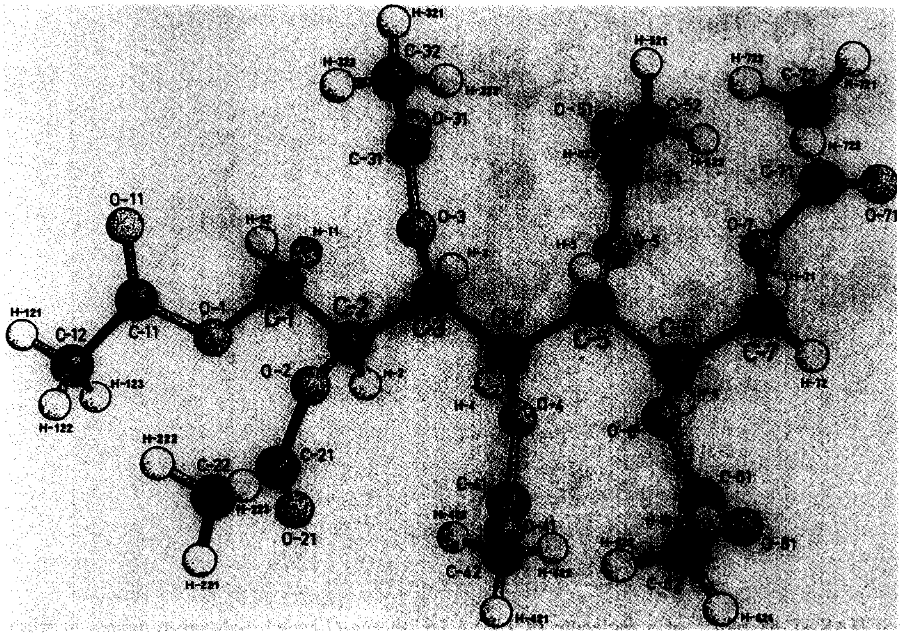

Fig. 3. SCHAKAL-88 plot[12] of a molecule of DL-1 (the D enantiomer) showing atom numbering.

unknown experimental conditions (for example, exact temperatures of measurements).

α-Sedoheptitol heptaacetate.—If 1,2,3,4,5,6,7-hepta-*O*-acetyl-D-*glycero*-D-*manno*-heptitol[8] (D-**2**) were to exist in a planar zigzag conformation, it would have to tolerate an O//O interaction between O-4 and O-6. In the parent compound, this interaction is avoided by bending around C-5–C-6 to a sickle[1]. Interestingly, this sickle differs from the expected one[19], which would be interaction free, and accommodates a C//O interaction between C-7 and O-4, instead[1].

The heptaacetate **2** is found in a different sickle conformation (Fig. 4), which results from torsion around the C-4–C-5 bond. Thus, an O-4//O-6 interaction in the planar zigzag geometry is avoided, but at the expense of an O-3//O-5 interaction in the observed bent conformation. The distance O-3–O-5 is 285.2 pm. Therefore, we conclude that solid state conformations of acetates of higher alditols are even less predictable by simple rules[20] than those of the parent compounds. These rules, summarized as the Hassel–Ottar effect for O//O interactions[20], become less and less useful with the growing number of crystal structure determinations of these compounds. With the present state of knowledge, only one assumption can be made without any doubt: acyclic polyhydroxy compounds are always found in planar zigzag conformations if no O//O interactions occur in this topology. Nevertheless, first attempts to systematize the occurrence of alditol

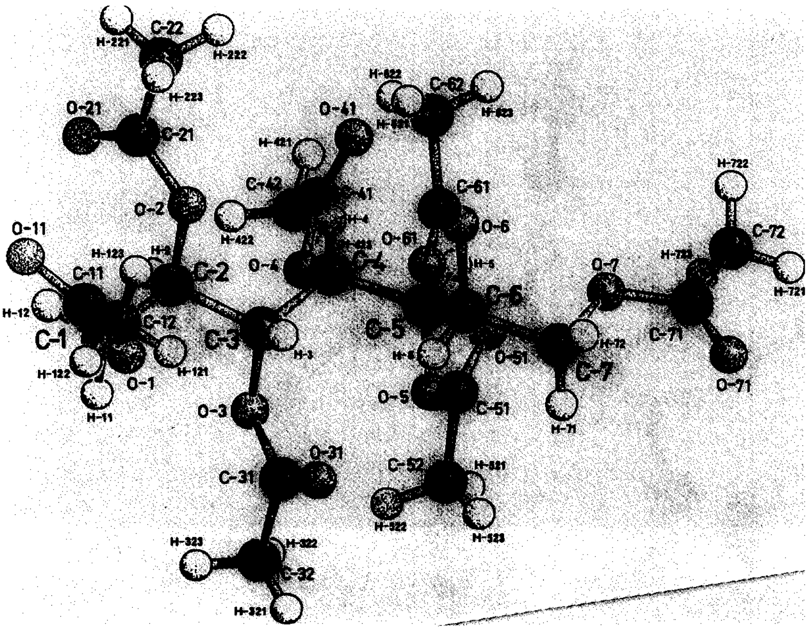

Fig. 4. SCHAKAL-88 plot[12] of a molecule of 1,2,3,4,5,6,7-hepta-*O*-acetyl-D-*glycero*-D-*manno*-heptitol (**2**) showing atom numbering.

conformations involving O//O and C//O interactions were made in connection with the structure determinations of two octitol octaacetates[21].

The orientations of the acetoxy groups at the termini in **2** are *gauche* to its neighbours as is the case in the parent heptitol[1].

meso-glycero-gulo-*Heptitol heptaacetate*.—The first crystal structure determination of a heptitol was performed on the parent compound of the heptaacetate **3**, *meso-glycero-gulo*-heptitol[22], which substantiated the early predictions of Mills[19] on conformations of higher alditols, because the parent compound is found in the predicted[19] sickle conformation which avoids an O-3//O-5 interaction that would occur in the planar zigzag conformation. In contrast to this, the heptaacetate **3** prefers just this alignment (Fig. 5).

The molecules of **3** possess a crystallographic mirror plane through the atoms H-4–C-4–O-4–C-41–O-41–C-42–H-421, which leaves O-3 and the symmetry-related O-5 in a 1,3-parallel position with an O-3–O-5 distance of 299.3 pm. While individual molecules in the parent compound (space group $P2_1/c$)[22] are chiral and aggregate as a pseudo racemate of pseudo enantiomers, the acetylated derivative **3** is found in highest (achiral) symmetry. Again, the acetoxy groups at the termini are oriented *gauche* to their neighbours, as in the parent compound[22].

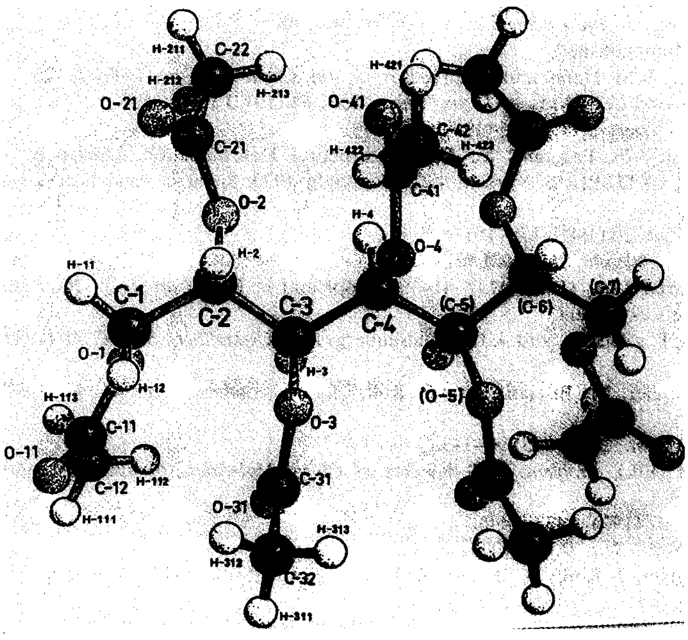

Fig. 5. SCHAKAL-88 plot[12] of a molecule of 1,2,3,4,5,6,7-hepta-*O*-acetyl-*meso-glycero-gulo*-heptitol (**3**) showing atom numbering, and depicted as the pseudo D configuration.

EXPERIMENTAL

The compounds investigated were prepared by the procedures cited. DL-**1** was prepared by acetylation[7] of racemic perseitol[16]. The X-ray structure determinations were performed at 20°C and the results are given in Table I or are deposited. All atoms were refined. The hydrogen atoms were introduced at theoretical positions and refined by using a riding model with the *AFIX* option of used programs[11b]. This probably results in standard deviations for hydrogen positions (see deposited material) which are underestimated. Calculations of geometries were executed by using the PLATON program[23].

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